Perspectives of disproportionation driven superconductivity in strongly correlated 3d compounds

A S Moskvin

Department of Theoretical Physics, Ural Federal University, 620083 Ekaterinburg, Russia

E-mail: alexandr.moskvin@usu.ru

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Abstract
Disproportionation in 3d compounds can give rise to an unconventional electron–hole Bose liquid with a very rich phase diagram, from a Bose metal, to a charge ordering insulator and an inhomogeneous Bose-superfluid. Optimal conditions for disproportionation driven high-$T_c$ superconductivity are shown to be realized only for several Jahn–Teller $d^n$ configurations that permit the formation of well defined local composite bosons. These are the high-spin $d^4$, low-spin $d^7$, and $d^9$ configurations given the octahedral crystal field, and the $d^1$, high-spin $d^6$ configurations given the tetrahedral crystal field. The disproportionation reaction has a peculiar ‘anti-Jahn–Teller’ character lifting the bare orbital degeneracy. Superconductivity in the $d^4$ and $d^6$ systems at variance with $d^1$, $d^7$, and $d^9$ systems implies unavoidable coexistence of the spin-triplet composite bosons and the magnetic lattice. We argue that unconventional high-$T_c$ superconductivity, observed in quasi-2d cuprates with tetragonally distorted CuO$_6$ octahedra and iron-based layered pnictides/chalcogenides with tetrahedrally coordinated Fe$^{2+}$ ions presents a key argument to support the fact that the disproportionation scenario is at work in these compounds.

(Some figures may appear in colour only in the online journal)

1. Introduction

The origin of high-$T_c$ superconductivity [1] remains a matter of great controversy. Copper oxides start out life as insulators, in contrast with BCS superconductors, which are conventional metals. The unconventional behavior of these materials under charge doping, in particular, a remarkable interplay of charge, lattice, orbital, and spin degrees of freedom, differs strongly from that of ordinary metals and merely resembles that of a doped semiconductor. Novel non-copper based layered high-$T_c$ materials such as iron oxyarsenide LaOFeAs [2] reveal normal and superconducting state properties very different from those of standard electron–phonon coupled ‘conventional’ superconductors.

We believe that the unconventional behavior of high-$T_c$ superconductors can be consistently explained in the frame of a so-called dielectric scenario [3–5] that implies an instability of the respective parent compound with regard to d–d charge-transfer (CT) fluctuations with the formation of local composite bosons. This implies the realization of Ogg–Schafroth’s real-space pairing model for the Bose–Einstein superconducting condensation [6, 7]. At first sight the d–d disproportionation

$$3d^n + 3d^n \rightarrow 3d^{n+1} + 3d^{n-1} \quad (1)$$

whose energy is usually estimated to be $U$ ($U_{dd}$), the mean intra-atomic electron–electron (Mott–Hubbard) repulsion energy, is quite uncommon and a priori much more expensive in narrow-band 3d transition-metal compounds as compared with compounds containing broad-band 6s$^1$ ions such as Bi$^{4+}$, Pb$^{3+}$ or Tl$^{2+}$, due to their strong tendency to form 6s$^0$ and 6s$^2$ closed shells [8]. Experimental values of the minimal energies of the d–d CT, or Mott–Hubbard transitions in different 3d oxides as usually derived from the optical gap measurements, $\Delta_{dd}^\text{opt} \sim 2–4$ eV (see, e.g., [9] and references therein) yield effective values of $U$ which are much less...
than the typical $U_{\text{dd}} \sim 5$–$10$ eV, but far, however, from the so-called ‘negative-\(U\)’ regime [8]. Yet, \(\Delta_{\text{dd}}^{\text{opt}}\) is a minimal energy cost of the optically excited d–d disproportionation or electron–hole formation due to a direct Franck–Condon (FC) CT transition. The question arises, what is the energy cost for the thermal excitation of such a local d–d disproportionation? The answer first of all implies knowledge of the relaxation energy, or the energy gain due to the lattice polarization by the localized charges that can exceed 1 eV [10]. For instance, in insulating cuprates such as La$_2$CuO$_4$ the true (thermal) d–d charge-transfer gap appears to be as small as 0.4–0.5 eV, rather than 1.5–2.0 eV as derived from the optical gap measurements [5]. In other words, parent cuprates should be addressed as d–d CT- unstable systems.

At present, the CT instability with regard to the d–d disproportionation and the formation of ‘negative-\(U\)’ centers [8] is believed to be a rather typical property for a number of perovskite 3d transition-metal oxides such as CaFeO$_3$, SrFeO$_3$, RNiO$_3$ [11, 12]; furthermore, in solid state chemistry one considers tens of disproportionated systems [13].

Classical disproportionation seems to be observed in the perovskite ferrate CaFeO$_3$, where the average formal valence of the iron ion is Fe$^{4+}$ (3$d^4$) and is known to show a gradual charge disproportionation $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$ below 290 K, with antiferromagnetism below 115 K, according to Mössbauer studies [14]. The single magnetic hyperfine pattern for isostructural ferrate SrFeO$_3$ at 4 K, on the other hand, indicates a seemingly rapid electron exchange between Fe$^{3+}$ and Fe$^{5+}$ ions, and the hyperfine field coincides approximately with the average value of the corresponding parameters for CaFeO$_3$. In this 3$d^4$ oxide, we most likely meet with a manifestation of quantum effects and the formation of a quantum dimerized phase such as a ‘valence bond solid’ composed of S- or P-type neutral dimers described by wavefunctions:

$$\frac{1}{\sqrt{2}} \left[ \Psi_1(3d^{n+1}) \Psi_2(3d^{n-1}) \pm \Psi_1(3d^{n-1}) \Psi_2(3d^{n+1}) \right],$$

respectively. The $^{57}$Fe Mössbauer measurements point to a charge disproportionation in Sr$_2$FeO$_4$, which has a double-layered perovskite structure [15].

Rare earth nickelates RNiO$_3$ (\(R\) is a trivalent rare earth ion) exhibit a first-order metal–insulator phase transition (MIT) upon cooling, with distinct signatures of the charge disproportionation [12, 16]. At $T_N \lesssim T_{\text{MIT}}$ these exhibit a further transition to a long-range antiferromagnetic ordered state with a nonzero magnetic moment for one of the two nonequivalent Ni sites [17]. A clear fingerprint of charge disproportionation is the breathing-type distortion of metal–oxygen octahedra, since the different charge states of the transition-metal ion have different ionic radii (see, e.g., [12]).

However, a large body of 3d materials do not manifest the charge instability as clearly as (Ca, Sr)FeO$_3$ or RNiO$_3$. For instance, the perovskite manganites RMnO$_3$ with the same 3$d^4$ configuration of Mn$^{3+}$ ions as in ferrates reveal a ‘hidden’ CT instability [18, 19]. At first glance the disproportionation in manganese compounds is hardly possible since the manganese atom does not manifest a ‘valence-skipping’ phenomenon such as, for example, the bismuth atom, which can be found as Bi$^{3+}$ or Bi$^{5+}$, but not Bi$^{4+}$, with a generic bismuth oxide BaBiO$_3$ being a well known example of a charge-disproportionated system (see, e.g., [20] and references therein). However, strictly speaking, sometimes manganese reveals a valence preference, e.g., while both Mn$^{2+}$ and Mn$^{4+}$ are observed in MgO:Mn and CaO:Mn, the Mn$^{3+}$ center is missing [21].

The reason for valence-skipping or valence preference observed for many elements still remains a mystery. Recently, Harrison [22] argued that traditional lattice relaxation effects, rather than any intra-atomic mechanisms [8] (specific behavior of ionization energies, stability of closed shells, strong screening of the high-charged states) are most likely a driving force for disproportionation with the formation of ‘negative-\(U\)’ centers.

Earlier it was argued that the disproportionated system can form an unconventional electron–hole Bose liquid whose phase diagram incorporates different phase states from classical (or chemical disproportionated) states to quantum states—in particular, to the unconventional Bose-superfluid (superconducting) state [4]. Regrettably, physicists have paid remarkably little attention to the problem of valence disproportionation and negative-\(U\) approaches (the ‘chemical’ route!), which are surely being grossly neglected in all present formal theoretical treatments of HTSC. On the subject of a close relation between disproportionation and superconductivity it is worth noting the textbook example of the BaBiO$_3$ system, where we unexpectedly deal with the disproportionated Ba$^{3+}$ + Ba$^{5+}$ ground state instead of the conventional lattice of Ba$^{4+}$ cations [8]. The bismuthate can be converted to a superconductor by a non-isovalent substitution such as in Ba$_2$K$_2$BiO$_3$. At present, this system seems to be the only one where the unconventional superconductivity is related in some way to the disproportionation reaction.

In this paper we concern ourselves with the main points of a so-called ‘disproportionation’ scenario in 3d compounds which has been addressed earlier by many authors; however, it has still not been properly developed, as its consistent description in terms of conventional Hubbard-type models is complicated. Our final goal is to ascertain the criteria for a motivated search of the 3d systems, which are the most promising as high-temperature superconductors. The paper is organized as follows. In section 2, addressing a simple model of the CT-unstable 2d system, we demonstrate the potential of disproportionation as a driving force for superconductivity. In section 3 we analyze the features of the disproportionation reaction for different 3d$^n$ pairs and find 3d$^n$ configurations optimal for the disproportionation driven superconductivity. In sections 4 and 5 we address the electron structure of familiar 3d compounds with the optimal 3d$^n$ configurations and indicate the high-$T_c$ superconductivity observed in quasi-2d cuprates and iron pnictides/chalcogenides to be the result of the d–d disproportionation. A short conclusion is made in section 6.
2. Simple toy model of the mixed-valence system and the disproportionation driven superconductivity

2.1. Pseudospin description of the model mixed-valence system

Valent electronic states in strongly correlated 3d oxides manifest both significant correlations and p–d covalency, with a distinct trend towards the localization of many-electron configurations formed by antibonding Me 3d–O 2p hybridized molecular orbitals. The localization effects are particularly clearly featured in the crystal field d–d transitions, whose spectra vary slightly from diluted to concentrated 3d oxides. An optimal way to describe valent electronic states in strongly correlated 3d oxides is provided by quantum-chemical techniques such as the ligand field theory [23], which implies a crystal composed of a system of small 3d-cation–anion clusters. Naturally, such an approach has a number of shortcomings, but nevertheless provides a clear physical picture of the complex electronic structure and the energy spectrum, as well as the possibility of quantitative modeling.

In a certain sense the cluster calculations might provide a better description of the overall electronic structure of insulating 3d oxides than different band structure calculations, mainly due to a better account of correlation effects and electron–lattice coupling.

In the 3d oxides with the disproportionation instability (1) we should consider as a minimum three different many-electron configurations, or different valent states, with different types of charge transfer. One strategy to deal with such a mixed-valence system is to create model pseudospin Hamiltonians which can reasonably well reproduce both the ground state and important low-energy excitations of the full problem. Standard pseudospin formalism represents a variant of the equivalent operators technique widely known in different physical problems from classical and quantum lattice gases, binary alloys, (anti)ferroelectrics, and neural networks. The formalism starts with a finite basis set for a lattice site (tripllet of \( M^0, M^\pm \) centers in our model, see below).

Such an approach differs from well known pseudospin-particle transformations, akin to the Jordan–Wigner [24] or Holstein–Primakoff [25] transformation, which establish a strict linkage between pseudospin operators and the creation/annihilation operators of the Fermi or Bose type. The pseudospin formalism for electron systems generally proceeds with a truncated basis and does not imply a strict relation to fermion operators that obey the fermionic anti-commutation rules.

To demonstrate the perspectives of the disproportionation in driving the superconductivity we address hereafter a simplified toy model of a mixed-valence system with three possible stable valence states of a cation–anion cluster (CuO\(_4\), MnO\(_6\), FeAs\(_4\), . . .), hereafter \( M; M^0, M^\pm \), forming the charge (isospin) tripllet, and neglect all other degrees of freedom, apart from the quantum charge. Similarly to the neutral-to-ionic electronic–structural transformation in organic charge-transfer crystals (see, e.g., the paper by T. Luty in [26]) the system of charge triplets can be described in the frame of the \( S = 1 \) pseudospin formalism [4]. To this end we associate the three different valence charge states of the \( M \)-center: \( M^0, M^\pm \) with three components of the \( S = 1 \) pseudospin (isospin) triplet with \( M_S = 0, +1, -1 \), respectively. Bearing in mind quasi-2d cuprates, we associate \( M^0, M^\pm \) centers with three charge states of the CuO\(_4\) plaquette: a bare center \( M^0 = \text{CuO}_4^{2-} \), a hole center \( M^+ = \text{CuO}_4^{5-} \), and an electron center \( M^- = \text{CuO}_4^{7-} \), respectively.

However, the physically simple toy mixed-valence system should be described by a rather complex effective pseudospin Hamiltonian as follows [4]

\[
\hat{H} = \sum_i (\Delta_i S^z_i - h_i S^z_i) + \sum_{i<j} V_{ij} S^z_i S^z_j + \sum_{i<j} D^{(1)}_{ij} (S^+_{i} S^-_{j} + S^-_{i} S^+_{j}) + D^{(2)}_{ij} (T^+_{i} T^-_{j} + T^-_{i} T^+_{j}) + \sum_{i<j} t_{ij} (S^2_i S^2_j + S^2_i S^2_j),
\]

with a charge density constraint: \( \frac{1}{N} \sum_i \langle S^z_i \rangle = \Delta n \), where \( \Delta n \) is the deviation from a half-filling (\( N^+_M = N^-_M \)). Two first single-site terms describe the effects of a bare pseudospin splitting, or the local energy of \( M^{0,\pm} \) centers. The second term may be related to a pseudo-magnetic field \( h_i \parallel Z \), in particular, a real electric field which acts as a chemical potential. The third term describes the effects of the short- and long-range intersite density–density interactions including screened Coulomb and covalent couplings. The last three kinetic energy terms in (2) describe one- and two-particle hopping, respectively (\( T_{\pm} = [S^z, S^\pm] \)). All the parameters have a clear physical meaning. The energy \( \Delta_{\text{CT}} \) for the creation of uncoupled electron and hole centers, or the effective parameter \( U_{\text{dd}} \), is given by \( \Delta_{\text{CT}} = 2\Delta \), while the energy \( \Delta_{\text{EH}} \) for the creation of coupled electron and hole centers, or the EH-dimer, is given by \( \Delta_{\text{EH}} = 2\Delta - V_{nn} \).

One should note that, despite many simplifications, the effective pseudospin Hamiltonian (2) is rather complex, and represents one of the most general forms of the anisotropic \( S = 1 \) non-Heisenberg Hamiltonians. Its real spin counterpart corresponds to an anisotropic \( S = 1 \) magnet with a single-ion (on-site) and two-ion (bilinear and biquadratic) anisotropy in an external magnetic field. The spin Hamiltonian (2) describes an interplay of the Zeeman, single-ion and two-ion anisotropic terms giving rise to competition of an (anti)ferromagnetic order along the Z-axis with an in-plane XY magnetic order. Simplified versions of anisotropic \( S = 1 \) non-Heisenberg Hamiltonians have been investigated rather extensively in recent years [27, 28].

Our system is characterized by several order parameters. These are two classical (diagonal) order parameters: \( \langle S^z \rangle \) being a valence, or charge density, with an electro-neutrality constraint, and \( \langle S^{2}_i \rangle \) being the density of polar centers \( M^\pm \), or ‘ionicity’. In addition, there are two unconventional off-diagonal order parameters \( \langle S^+_i \rangle \) and \( \langle T^+_i \rangle \) related to two different types of correlated single-particle transport, and one order parameter \( \langle S^+_i \rangle \) related to two-particle transport. It is
worth noting that the $\tilde{S}_z^2$ operator creates an on-site hole pair, or composite boson, with a kinematic constraint $(\tilde{S}_z^2)^2 = 0$, which underlines its ‘hard-core’ nature. For real $S = 1$ spin systems we deal with conventional ‘linear’ magnetic order parameters $\langle S_z \rangle$ and $\langle S_+ \rangle$ related to diagonal $(Z)$- and off-diagonal $(XY)$-orderings and several spin-quadrupole order parameters: $\langle S_z^2 \rangle$, $\langle S_+ \rangle$, and $\langle S_2^2 \rangle$. Recently, the spin-quadrupole (spin-nematic) order $\langle S_2^2 \rangle$ has been investigated in [28].

The last three terms in (2) representing the one- and two-particle hopping, respectively, are of primary importance for the transport properties, and deserve special attention. Two types of one-particle hopping are governed by two transfer integrals $D_{ij}^{(1,2)}$, respectively. The transfer integral $t_{ij} = (D_{ij}^{(1)} + D_{ij}^{(2)})$ specifies the probability amplitude for a local disproportionation, or the EH-pair creation:

$$M^0 + M^0 \rightarrow M^0 + M^\mp,$$

and the inverse process of the EH-pair recombination:

$$M^\pm + M^\mp \rightarrow M^0 + M^0,$$

while the transfer integral $t_{ij}' = (D_{ij}^{(1)} - D_{ij}^{(2)})$ specifies the probability amplitude for a polar center transfer:

$$M^\pm + M^0 \rightarrow M^0 + M^\pm,$$

or the motion of the electron (hole) center in the lattice of $M^\pm$-centers or motion of the $M^0$-center in the lattice of $M^\mp$-centers. It should be noted that, if $t_{ij}' = 0$ but $t_{ij} \neq 0$, the EH-pair is locked in a two-site configuration. The two-electron (hole) hopping is governed by the transfer integral $t_{ij}$ that defines a probability amplitude for the exchange reaction:

$$M^\pm + M^\mp \rightarrow M^\mp + M^\pm,$$

or the motion of the electron (hole) center in the lattice of the hole (electron) centers. It is worth noting that in the conventional Hubbard-like models all types of one-electron (hole) transport are governed by the same transfer integral: $t_{ij}' = t_{ij}'$, while our model implies independent parameters for the disproportionation/recombination process and a simple quasiparticle motion on the lattice of $M^\pm$-centers. In other words, we deal with a ‘correlated’ single-particle transport.

2.2. Electron–hole Bose liquid, hard-core composite bosons and superconductivity in disproportionated systems

A classical (or chemical) description of the mixed-valence systems implies fully neglecting the off-diagonal purely quantum CT effects: $D_{ij}^{(1,2)} = 0$, hence the valence of any site remains definite: $0, \pm 1$, and we deal with a system of localized polar centers. A quantum description implies taking account of the CT effects so that we arrive at quantum superpositions of different valence states, resulting in an indefinite on-site valence and ionicity whose effective, or mean values $\langle S_z \rangle$ and $\langle S_2^2 \rangle$ can vary from $-1$ to $+1$ and 0 to $+1$, respectively.

Simple uniform mean-field phases of the mixed-valence system include an insulating monovalent $M^0$-phase (parent phase), mixed-valence binary (disproportionated) $M^\mp$-phase, and mixed-valence ternary (‘under-disproportionated’) $M^{0,\pm}$-phase [4].

The insulating monovalent $M^0$-phase with $\langle S_z^2 \rangle = 0$ is a rather conventional ground state phase for various Mott–Hubbard insulators such as 3d oxides with a large enough positive magnitude of $\Delta > \Delta_{cr}$ parameter $(U > 0)$. All the centers have the same bare $M^0$ valence state. The mixed-valence binary (disproportionated) $M^\mp$-phase with $\langle S_z^2 \rangle = 1$ implies an overall disproportionation $M^0 + M^0 \rightarrow M^\mp + M^\mp$. It is a rather unconventional phase for insulators. All the centers have the ‘ionized’ valence state, one half the $M^\mp$ state, and the other half the $M^0$ state, though one may commonly conceive of a deviation from the half-filling. A simplified ‘chemical’ approach to the $M^\pm$-phase as a classical disproportionated phase is widespread in solid state chemistry [13]. The typical ground state of such a classical phase corresponds to a checkerboard charge order, or longitudinal antiferromagnetic (staggered) pseudospin Ising-like Z-ordering. In systems with a short-range density–density coupling $V_{nn}$ the disproportionation phase transition $M^0 \rightarrow M^\pm$, or pseudospin reorientation occurs, if $\Delta < \Delta_{cr} = \sqrt{4V_{nn}}$, where $z$ is the number of nearest neighbors. In other words, the charge-transfer instability of the parent $M^0$-phase implies not only negative but also small enough positive $\Delta_{CT} = U_{dd}$.

The mixed valence $M^{\pm}$ phase as a system of strongly correlated electron and hole centers appears to be equivalent to a Bose-liquid, in contrast with the electron–hole Fermi-liquid in conventional semiconductors, hence it can be termed as an electron–hole Bose liquid (EHBL) [4, 5, 19]. Indeed, one may address the electron $M^\pm$ center to be a system of a local composite boson ($e^2$) localized on the hole $M^\mp$ center: $M^\mp = M^\mp + e^2$.

The three well known molecular-field uniform phase states of the $M^{\pm}$ binary mixture, or EHBL phase, can be specified as follows:

(i) a charge ordered (CO) insulating state with $\langle S_z \rangle = \pm 1$ and zero modulus of bosonic off-diagonal order parameter $\langle |S_2^2| \rangle = 0$;

(ii) a Bose-superfluid (BS) superconducting state with $\langle S_z \rangle = 0$, $\langle S_2^2 \rangle = e^{2i\phi}$;

(iii) a mixed Bose-superfluid–charge ordering (BS + CO) superconducting state (supersolid) with $0 < |\langle S_z \rangle| < 1$, $\langle S_2^2 \rangle \neq 0$.

In addition, we should mention the high-temperature non-ordered (NO) Bose-metallic phase with $\langle S_z \rangle >> 0$. Disproportionation in such oxides as (Ca, Sr)FeO$_3$, RNIo$_3$ yields an electron–hole Bose system with a 50% concentration of the composite bosons, or half-filling. At variance with the parent quasi-2d cuprates, the disproportionated 3d oxides from the very beginning can be addressed as being ‘negative-U’, or $M^\pm$ systems, with $\Delta < \Delta_{cr}$, where the superconductivity can be driven by a deviation from the half-filling.

How can a typical insulating parent 3d $M^0$-system, such as La$_2$CuO$_4$, be driven to the disproportionated $M^{\pm}$?
or the EHBL phase? The simplest way is hole/electron doping due to a nonsovalent substitution (NIS), which solves two problems at once. First, it creates impurity centers for a local condensation of the EH dimers, or pairs of $M^\pm$-centers, thus shifting the system to the ‘negative-$U$’ regime. Second, the doping in cuprates such as La$_{2-x}$Sr$_x$CuO$_4$ and Nd$_{2-x}$Ce$_x$CuO$_4$ gradually shifts the $M^\pm$-phase away from half-filling, making the concentration of the local $S$-bosons either $n_B = 0.5 - 1/2$ (LSCO) or $n_B = 0.5 + 1/2$ (NCCO), thus promoting the superconductivity. In both the hole- and electron-doped cuprates we deal with composite $S$-bosons moving on the lattice of the hole centers CuO$_2$, which makes the unconventional properties of the hole centers [29, 30] common for both types of cuprates. It is clear that the disproportionation scenario makes doped cuprates objects of bosonic physics. Obviously, the appearance of an inhomogeneous impurity potential under non-sovalent substitution deforms the phase diagram typical for uniform systems; in particular, in the ‘underdoped’ regime where the system transforms from the parent phase $M^0$ into the disproportionated phase $M^\pm$.

In the limit $\Delta \to -\infty$, the EHBL phase is equivalent to the lattice hard-core Bose system with an intersite repulsion whose Hamiltonian can be written in a standard form as follows (see [31, 32] and references therein):

$$H_{h.c.} = -\sum_{i<j} t_{ij} \{ \hat{B}^\dagger_i \hat{B}_j + \hat{B}^\dagger_j \hat{B}_i \} \hat{P} + \sum_{i<j} V_{ij} N_i N_j - \mu \sum_i N_i,$$

(3)

where $\hat{P}$ is the projection operator which removes double occupancy of any site. Here $\hat{B}^\dagger \{ \hat{B} \}$ are the Pauli creation (annihilation) operators, which are Bose-like commuting for different sites $[\hat{B}_i, \hat{B}_j] = 0$, if $i \neq j$, $[\hat{B}_i, \hat{B}_j] = 1 - 2N_i, N_i = \hat{B}^\dagger_i \hat{B}_i; N$ is the full number of sites. $\mu$ is the chemical potential determined from the condition of a fixed full number of bosons $N = \sum_{i=1}^N N_i$ or concentration $n = N_i/N \in [0, 1]$. The $t_{ij}$ denote effective transfer integrals; $V_{ij}$ denote intersite interactions between the bosons. It is worth noting that near half-filling ($n \approx 1/2$) one might introduce the renormalization $N_i \to (N_i - 1/2)$, or neutralizing background, that immediately provides the particle–hole symmetry.

The model of hard-core bosons with an intersite repulsion as a minimal model of the EH Bose liquid can be mapped to a system of pseudospins $s = 1/2$ exposed to an external magnetic field in the $Z$-direction (Matsubara–Matsuda transformation [33]). For the system with a neutralizing background we arrive at an effective pseudospin Hamiltonian

$$H_{h.c.} = \sum_{i<j} J_{ij} (\hat{S}^+_i \hat{S}^-_j + \hat{S}^+_j \hat{S}^-_i) + \sum_{i<j} J_{ij} \hat{S}^+_i \hat{S}^+_j - \mu \sum_i \hat{S}^z_i,$$

(4)

where $J_{ij} = 2t_{ij}J_{ij}^* = V_{ij} \sqrt{2} \hat{S}^+ = -\frac{1}{\sqrt{2}}\hat{B}^\dagger \hat{B}, \hat{S}^\pm = -\frac{1}{2} + \hat{B}^\dagger \hat{B}, \hat{S}^z = \frac{1}{2}(\hat{S}^+ + i\hat{S}^-)$.

In terms of the $s = 1/2$ pseudospins the non-ordered NO, or liquid phase, corresponds to a paramagnetic phase, the Bose-superfluid BS order corresponds to a magnetic order in the $XY$ plane, while the charge density order CO corresponds to a magnetic order in the $Z$ direction.

In figure 1 we present the phase diagram of the square lattice hard-core boson Hubbard model with the nearest neighbor ($nn$) transfer integral $t_{nn} = t$ (the Josephson coupling) and repulsion $V_{nn} = 3t$, derived from the quantum Monte-Carlo (QMC) calculations by Schmid et al [34] (see also [31]). Different shading represents the CO phase, BS phase, and phase-separated supersolid BS + CO phase. The AB line $T_{KT}(x)$ represents the 2d Kosterlitz–Thouless phase transition; the C–B–D–C’ line represents the first-order phase transition; the D–E line $T_{CO}(\Delta n)$, which can be termed as the pseudogap onset temperature $T^*_\sigma(\Delta n)$, represents the second-order Ising kind, melting the phase transition CO–NO into a non-ordered, or normal fluid phase. At half-filling ($n_B = 0.5, \Delta n = 0$) the system obviously prefers a checkerboard charge order (Néel antiferromagnetic order in the $Z$-direction below $T_{CO} = 0.567 V_{nn}$ given $t = 0$).

It is worth noting that the phase diagram in figure 1 greatly resembles that typical for doped quasi-2d cuprates [35], truly reproducing many important aspects of the normal and superconducting state, in particular, the pseudogap-like effects of the charge ordering and various signatures of the local superconductivity that explain the anomalous Nernst and local diamagnetism signals [37].

2.3. Topological phase separation in the 2d hard-core Bose system

It is worth noting that all the lines in the phase diagram of the 2d hard-core Bose system in figure 1 point only to long-range orders and do not concern the intricate intrinsic inhomogeneity. However, the CO state was shown [32] to be unstable with regard to a so-called CO + BS topological phase separation under doping, or deviation from the half-filling. The boson addition or removal in the half-filled hard-core...
boson system is assumed to be a driving force for the nucleation of a multi-center skyrmion-like self-organized collective mode, which resembles a system of CO bubble domains with a Bose-superfluid and extra bosons both confined in domain walls. The antiphase domain wall in the CO bubble domain appears to be a very efficient ring-shaped potential well for the localization of a single extra boson (or bosonic hole), thus forming a novel type of a topological defect with a neutral or single-charged ($q = \pm e$) domain wall. Such a topological CO + BS phase separation, more than likely being the dynamical one, rather than an uniform mixed CO + BS supersolid phase predicted by the mean-field approximation [31], is believed to describe the evolution of the hard-core BH model away from half-filling.

Figure 2 presents a schematic view of the smallest neutral skyrmion-like bubble domain in a checkerboard CO phase for a 2d square lattice with an effective size of three lattice spacings ($\approx 12 \, \text{Å}$) [32]. The domain wall is believed to include, as a minimum, eight sites forming a ring-shaped system of four dimers, each composed of two sites. There are two types of domains, which differ by a rotation of $\pm \pi/2$. Such a charged topological defect can be addressed as an extended ($q = \pm 2e$) skyrmion-like mobile quasiparticle. On the other hand, the bubble seems to be a peculiar quantum of a ‘local superconductivity’.

The bubble domain may be addressed as well isolated only if its close surroundings do not contain another domain(s) which could be involved in a ‘dangerous’ frustrating overlap. Each domain in figure 2 has $z = 12$ such neighbors. Hence the concentration of well isolated domains can be written as follows: $P_0(\Delta n) = |\Delta n|(1 - |\Delta n|)^2$, where $z$ is the number of ‘dangerous’ neighbors and $\Delta n$ is the doped boson concentration. The $P_0(\Delta n)$ maximum is reached at $\Delta n_0 = \frac{1}{2z}$. In our case $\Delta n_0 = 1/13$, or $\approx 0.077$. With increasing doping the deviation of $P_0(\Delta n)$ from the linear law rises. On the other hand, knowing the effective domain area $S_d \approx 9a^2$, we can roughly estimate the limiting concentration of the single-domain model description to be $\Delta n_{\text{max}} \approx 1/9 \approx 0.11$.

The bubble’s system is believed to reveal many properties typical for granular superconductors, CDW materials, Wigner crystals, and multi-skyrmion systems akin to a quantum Hall ferromagnetic state of a 2d electron gas [32]. The concept of a static or dynamic bubble system introduces a large body of novelties into the physics of the EHBL, related to a complex intra-bubble structure, bubble transport, bubble-bubble coupling, novel excitation modes, pinning of the bubble system etc. From the viewpoint of the novel charge order effects we point to an evolution of the bubble system upon lowering the temperature, which implies a sequence of the isotropic liquid phase, the liquid-crystal phase, and the incommensurate bubble crystal phase with a quantum melting effect near the ‘magic’ doping level, e.g. $\Delta n_g = 1/16$, where the bubble lattice undergoes the structural phase transition. It is worth noting that the bubble crystallization is accompanied by different (pseudo)gap effects. From the viewpoint of the off-diagonal BS order we should point to a step-by-step formation of the local BS condensate, starting with an intra-EH-dimer order at $kT \sim t_{nn}$, an intra-bubble order at $kT \sim t_{bb}$, a short-range bubble order at $kT \sim t_{bb}$ ($t_{bb}$ is a bubble transfer integral) and the formation of extended quasi-1d clusters which can undergo a transition to a phase-coherent state (filamentary or gossamer superconductivity [38]). Finally, upon the increase in the number of such clusters, the prerequisites for percolative 2d and bulk 3d superconductivity are created. Attractively high temperatures for the emergence of the nonzero local BS condensate density engender different reasonable speculations as regards its practical realization.

The topologically inhomogeneous phase of the hard-core BH system away from half-filling can exhibit the signatures of s-,d-, and p-symmetry of the off-diagonal order [32]. The model allows us to study subtle microscopic details of the order parameter distribution, including its symmetry in a real rather than momentum space, though the problem of the structure and stability of nanoscale domain configurations remains to be solved.

It is worth noting that the bubble model predicts the optimal conditions for 2d and 3d superconductivity in the doped cuprates at $x_{\text{opt}} \approx 2\Delta n_0 \approx 0.154$ and a suppression of superconductivity at $x > 2\Delta n_{\text{max}} \approx 0.22$. On the other hand, the bubble model predicts a so-called ‘self-doping’ (SD) mechanism of superconductivity in ‘negative-U’, or $M^\pm$ systems. Such a mechanism is realized when the CO phase in the system appears to be unstable with regard to a nucleation of positively and negatively charged bubbles preserving a charge neutrality. Such ‘self-doping’ most likely explains the superconductivity in YBa$_2$Cu$_3$O$_y$ [39] and LiFeAs [40].

It should be noted that the bubble system can manifest two types of dispersive features, which reflect a dominance...
of the kinetic energy (the bubble transfer) or the potential energy (the bubble–bubble coupling), respectively. Indeed, a single mobile bubble has energy $\varepsilon(q)$, while different static bubble crystal configurations (Wigner electronic crystals) can be specified by the quasimomentum $q$ and corresponding energy $E(q)$.

3. Disproportionation and local composite bosons in 3d$^n$ systems

3.1. Local composite bosons in 3d$^n$ systems

As we have seen above the disproportionation

$$3d^n + 3d^n \rightarrow 3d^{n+1} + 3d^{n-1}$$

is addressed as being a candidate mechanism driving the superconductivity in nominally insulating 3d compounds. A simple view of the disproportionated system implies the electron (hole) center $3d^{n+1}$ ($3d^{n-1}$) to be composed of a hole (electron) center plus an electron (hole) coupled pair $3d^2$ ($3d^2$) that seems to constitute a composite electron (hole) local boson. In other words, the disproportionated system is anticipated to be a system of local bosons moving in a lattice formed by electron (hole) centers. The disproportionation scenario implies the composite local boson to be somehow an integral part of a stable many-electron atomic configuration, $3d^{n+1}$ or $3d^{n-1}$. The microscopic nature of the attractive force which could overcome the natural Coulomb repulsion between two electrons which constitute a Bose pair [41] evolves both from the main intra-atomic correlations and electron–lattice polarization effects [22] providing the stability of $3d^{n\pm1}$ configurations.

However, for the representation of local composite bosons to be justified we should take into account some rather strict limitations imposed by the orbital structure of the 3d states and the genealogy of many-electron 3d$^{n\pm1}$ states. First of all, the effective two-particle–two-site transfer integrals

$$\langle 3d_1^{n+1} 3d_2^{n-1} | \hat{H} | 3d_1^{n-1} 3d_2^{n+1} \rangle,$$

that describe the exchange reaction

$$3d^{n+1} + 3d^{n-1} \rightarrow 3d^{n-1} + 3d^{n+1}$$

reduce to a simple form

$$\langle 3d_1^{n+1} 3d_2^{n-1} | \hat{H} | 3d_1^{n-1} 3d_2^{n+1} \rangle = \langle 3d_1^n | \hat{H} | 3d_2^n \rangle = t_{12}$$

which we need to introduce the local boson representation directly. The two-particle transfer integral $t_{12}$ is a key parameter that governs both the transport and superconducting perspectives of the disproportionated system. It can be written as follows:

$$t_{12} = \langle 20 | V_{ee} | 02 \rangle - \sum_{11} \frac{\langle 20 | \hat{h} | 11 \rangle \langle 11 | \hat{h} | 02 \rangle}{\Delta_{dd}},$$

where the first term describes a simultaneous tunnel transfer of the electron pair due to the Coulomb coupling $V_{ee}$, which may be called a ‘potential’ contribution, whereas the second describes a two-step (20-11-02) electron–pair transfer via successive one-electron transfer due to the one-electron Hamiltonian $\hat{h}$, which may be called a ‘kinetic’ contribution. The value of the composite boson transfer integral is closely related to that of the exchange integral, i.e. $t_{12} \approx J_{12}$.

Justification of the local composite boson implies a specific genealogy of the many-electron states $\Psi(3d^{n+1})$ and $\Psi(3d^{n-1})$; the wavefunctions should have a simple structure

$$\Psi(3d^{n+1}) = \Psi(3d^2)\Psi(3d^{n-1}),$$

$$\Psi(3d^{n-1}) = \Psi(3d^2)\Psi(3d^{n+1})$$

in the electron, or hole representation, respectively. To gain more insight into the main features of the disproportionation reaction hereafter, we analyze the d–d CT transition $3d^n + 3d^n \rightarrow 3d^{n+1} + 3d^{n-1}$ in strongly correlated 3d systems with a high (octahedral, tetrahedral, and cubic) local symmetry. For crystal field configurations such as $t_{2g}e_g^2$, the optimal disproportionation scheme (5) implies single configurations both for $\Psi(3d^{n+1})$ and $\Psi(3d^{n-1})$. It is easy to see that the optimal conditions for the superconductivity are expected for parent 3d$^n$ systems with 3d$^{n\pm1}$ configurations which correspond to either empty, or filled and half-filled $t_{2g}$ and $e_g$ orbitals. Second, to minimize the reduction effect of the electron–lattice interaction and avoid the localization, we need the S-type ($A_{1g}, A_{2g}$) orbital symmetry of the local boson, which provides the conservation of the orbital degeneracy when it moves on the lattice. Third, to minimize the reduction effect of the spin degrees of freedom, we need spin–singlet local bosons. Fourth, to maximize the transfer integral we need a participation of the strongest $\sigma$ bonds. In other words, we should point to a specific role of the one-electron orbitals forming the two-electron boson state. Furthermore, the optimized ground state of the local boson should be well isolated; that is, separated from excited states by a gap on the order of 1 eV. In any case, along with the electron–lattice polarization effects which stabilize the 3d$^{n\pm1}$ configurations and minimize the CT energy, the many-electron configuration, intra-atomic correlations, force and symmetry of the crystal field seem to be the most important factors of the disproportionation scenario. All the above constraints strongly restrict the number of 3d$^n$ systems which are candidates for the high-$T_c$ superconducting materials in the frame of the disproportionation scenario.

3.2. Optimal disproportionation schemes for different 3d$^n$ ions in a high-symmetry crystal field

Below we address the optimal disproportionation schemes for different 3d$^n$ ions in a high-symmetry crystal field. It is worth noting that for an octahedral or tetrahedral (cubic) crystal field the electron filling starts with the $t_{2g}$ or $e_g$ orbitals, respectively. Depending on the relation between the crystal field and intra-atomic correlation energies we will consider either high-spin (HS) or low-spin (LS) complexes, such as MeO$_6$ or MeO$_4$ in 3d oxides.

3d$^1$ ions ($T_{1g^3}, V^{4+}$). Disproportionation $3d^1 + 3d^1 \rightarrow 3d^0 + 3d^2$ gives rise to a system of local composite bosons, or electron pairs 3d$^2$, moving in a lattice formed by the 3d$^0$ centers. The simplest electronic configuration $3d^1$ is
realized as the $t_{2g}^2$ configuration for the octahedral or the $e_g^1$ configuration for a cubic or tetrahedral crystal field. For the $t_{2g}^2$ configuration we arrive at an orbital and spin-triplet ground state $3^{T_1g}$ with seemingly no optimistic expectations as regards the superconductivity. Some perspectives may be related to a spin–orbital coupling $V_{SO}$ that stabilizes a singlet state with a net momentum $J = 0$, though the electron–lattice interaction can destroy spin–orbital coupling, giving rise to an Jahn–Teller polaron. More attractive expectations are related to the $e_g^2$ configuration in a tetrahedral crystal field when we arrive at an $S$-like though spin–triplet ground state $3^{A_2g}$.

In other words, there appears to be an opportunity to realize an unconventional system of spin–triplet local $S$-like bosons moving on the electronically ‘inactive’ lattice (see figure 1).

3d$^2$ ions ($V^{3+}$, $Cr^{3+}$). The two-electron configuration 3d$^2$ is realized as the $t_{2g}^2$ configuration for the octahedral or the $e_g^2$ configuration for a cubic or tetrahedral crystal field. Disproportionation 3d$^2 + 3d^2 \rightarrow 3d^1 + 3d^3$ seems to give rise to a system of electron pairs 3d$^2$, or local composite bosons, moving in a lattice formed by the 3d$^1$ centers. However, the genealogy of the low-spin $e_g^1, 2E_g$ configuration does not permit the insertion of a well defined composite boson. Indeed, the genealogical link of the $e_g^3$ and $e_g^4$ configurations reads as follows:

$$|e_g^3, 2E_g⟩ = \frac{1}{\sqrt{6}}(|e_g^1⟩ A_{1g}; e_g^1, 2E_g⟩)$$

and implies a participation of not one but three different terms of the $e_g^3$ configuration. The genealogy of the high-spin $t_{2g}^1, 4A_{2g}$ configuration obeys the master condition (see expression (2)) that permits the formation of a well defined composite boson with the HS-configuration $t_{2g}^2, 3^{T_1g}$. It means that the disproportionation reaction

$$t_{2g}^2 + t_{2g}^2 \rightarrow t_{2g}^1 + t_{2g}^1$$

gives rise to a system of local electron-type bosons ($t_{2g}^2$) on a lattice with the on-site $t_{2g}^2$ configuration or hole-type bosons ($t_{2g}^1$) on a lattice with the on-site HS-$t_{2g}^1, 4A_{2g}$ configuration. However, in any case such a composite boson should be charged by both spin- and orbital degrees of freedom; in addition, this is prone to move on the lattice with a spin or spin-and-orbital degeneracy that strongly restricts ‘superconducting perspectives’. Some hopes may be related to a spin–orbital coupling $V_{SO}$ that stabilizes a singlet state with a net momentum $J = 0$, though the electron–lattice interaction will compete with the spin–orbital coupling, giving rise to an Jahn–Teller polaron.

3d$^3$ ions ($V^{2+}$, $Cr^{4+}$, $Mn^{4+}$). The three-electron configuration 3d$^3$ is realized as the $t_{2g}^3$ configuration for the octahedral, and the $e_g^3$ or $e_g^2 t_{2g}^1$ configuration for strong or weak tetrahedral or cubic crystal fields, respectively, however, the local boson representation can be introduced only for the tetrahedral/cubic high-spin configuration:

$$e_g^2 t_{2g}^2 + e_g^2 t_{2g}^2 \rightarrow e_g^2 + e_g^2 t_{2g}^2$$

when the disproportionated system can be addressed as being a system of $t_{2g}^2, 3^{T_1g}$ local composite bosons on a lattice with the on-site $e_g^2, 3^{A_2g}$ 3d-configuration. Obviously, we arrive at illusive perspectives for the high-$T_c$ superconductivity.

3d$^4$ ions ($Mn^{3+}$, $Cr^{2+}$, $Fe^{4+}$). The electron configuration near the half-filling, 3d$^4$, is particularly interesting given the octahedral crystal field. Then, the high-spin (Hund) 3d$^4$ configuration disproportionsates as follows:

$$(t_{2g}^3 e_g^1, 5E_g) + (t_{2g}^1 e_g^1, 5E_g) \rightarrow (t_{2g}^3, 4A_{2g}) + (t_{2g}^1 e_g^2, 6A_{1g}),$$

where $(t_{2g}^1 e_g^2, 6A_{1g}) = (t_{2g}^3, 4A_{2g}) \times (e_g^2), 3^{A_2g}$. In other words, the disproportionated system can be viewed as a system of spin–triplet composite electron bosons $(e_g^2), 3^{A_2g}$ moving in a lattice composed of the localized hole spin-3/2 S-type $(t_{2g}^3, 4A_{2g})$ centers (see figure 1). Interestingly, we can address the system in another way as being a system of spin–triplet composite hole bosons $(e_g^2), 3^{A_2g}$ moving in a lattice composed of the localized electron spin-5/2 S-type $(t_{2g}^3 e_g^2, 6A_{1g})$ centers. It is worth noting that the electron-type boson obeys a conventional (ferromagnetic) Hund rule on lattice sites while the hole-type boson obeys an unconventional (antiferromagnetic) ‘anti–Hund rule on lattice sites. Local composite bosons can be formed also for the low-spin octahedral or high-spin tetrahedral d$^4$ systems, however, we arrive at a composite boson with a $t_{2g}^2, 3^{T_1g}$ or $t_{2g}^3, 3^{T_1g}$ configuration and a spin-3/2 or 5/2 lattice.

3d$^5$ ions ($Fe^{3+}$, $Mn^{2+}$). The low-spin 3d$^5$ configuration appears to be near filling both in octahedral and tetrahedral crystal fields, when it disproportionsates as follows:

$$(t_{2g}^5) + (t_{2g}^5) \rightarrow (t_{2g}^4, 3^{T_1g}) + (t_{2g}^1, 1A_{1g})$$

or

$$(e_g^4 t_{2g}^1) \rightarrow (e_g^4, 1A_{1g}) + (e_g^4 t_{2g}^1, 3^{T_1g})$$

where $(t_{2g}^4, 3^{T_1g}) = (t_{2g}^2, 3^{T_1g}) \times (t_{2g}^0, 1A_{1g})$. In other words, the disproportionated system given the octahedral crystal field can be viewed as a system of spin and orbital triplet composite hole bosons $(t_{2g}^2, 3^{T_1g})$ moving in a lattice composed of the spinless S-type $(t_{2g}^0, 1A_{1g})$ centers. Given a tetrahedral crystal field we arrive at a system of spin and orbital triplet composite electron bosons $(t_{2g}^1, 3^{T_1g})$ moving in a lattice composed of the spinless S-type $(e_g^4, 1A_{1g})$ centers. Orbital degeneracy of the local bosons can give rise to the formation of JT polaron by their localization.

3d$^6$ ions ($Fe^{2+}$, $Co^{3+}$). In this case the specific genealogy (5) of polar 3d$^{6\pm 1}$ centers can be realized only for the high-spin (Hund) configuration. In tetrahedral or cubic crystal fields the 3d$^6$ system disproportionsates as follows:

$$(e_g^3 t_{2g}^1, 5E_g) + (e_g^3 t_{2g}^1, 5E_g)$$

$$(e_g^3 t_{2g}^1, 6A_{1g}) + (e_g^4 t_{2g}^1, 4A_{2g}),$$
where \((e_g^{4}t_{2g}^{5}A_{2g}) = (e_g^{4}t_{2g}^{5}A_{2g}) \times (e_g^{2})^3A_{2g}\). In other words, the disproportionated system can be viewed as a system of spin–triplet composite hole bosons \((e_g^{2})^3A_{2g}\) moving in a lattice composed of the electron \(S = 3/2\) \((e_g^{4}t_{2g}^{5}A_{2g})\) centers. We can address the system in another way as being a system of spin–triplet composite electron bosons \((e_g^{2})^3A_{2g}\) moving in a lattice composed of the localized hole spin-\(5/2\) S-type \((e_g^{4}t_{2g}^{5}A_{2g})\) centers (see figure 1). The situation resembles that of the Hund 3d energy electron configuration given an octahedral crystal field.

In an octahedral crystal field the HS-3d\(^6\) system disproportionates as follows:

\[
(t_{2g}^{4}e_{g}^{2}; 5T_{2g}) + (t_{2g}^{4}e_{g}^{2}; 5T_{2g})
\rightarrow (t_{2g}^{4}e_{g}^{2}; 6A_{1g}) + (t_{2g}^{6}e_{g}^{2}; 4T_{1g}).
\]

The disproportionated system can be viewed as a system of spin–triplet composite electron-type bosons \((t_{2g}^{4}e_{g}^{2}; 5T_{2g})\) moving in a lattice composed of the electron spin-\(3\) \(S\)-type centers. The disproportionated system can be viewed as a system of spin–triplet composite electron-type bosons \((e_g^{2})^3A_{2g}\) moving in a lattice composed of the electron spin-\(5/2\) \(S\)-type centers.

3d\(^7\) ions \((\text{Ni}^{3+}, \text{Co}^{2+})\). For the low-spin (non-Hund) configuration in an octahedral crystal field the 3d\(^7\) system disproportionates as follows:

\[
(t_{2g}^{5}e_{g}^{1}; 2E_{g}) + (t_{2g}^{6}e_{g}^{3}; 2E_{g})
\rightarrow (t_{2g}^{5}e_{g}^{1}; 1A_{1g}) + (t_{2g}^{6}e_{g}^{3}; 3A_{2g}).
\]

where \((t_{2g}^{5}e_{g}^{1}; 1A_{1g}) = (t_{2g}^{5}e_{g}^{1}; 1A_{1g}) \times (e_g^{2})^3A_{2g}\). In other words, the disproportionated system can be viewed as a system of spin–triplet composite electron bosons \((t_{2g}^{5}e_{g}^{1}; 1A_{1g})\) moving in a lattice composed of the hole \(S = 0\) \((t_{2g}^{5}e_{g}^{1}; 1A_{1g})\) centers (see figure 1).

For the high-spin (Hund) configuration in an octahedral crystal field the 3d\(^7\) system disproportionates as follows:

\[
(t_{2g}^{5}e_{g}^{2}; 4T_{1g}) + (t_{2g}^{5}e_{g}^{2}; 5T_{2g})
\rightarrow (t_{2g}^{5}e_{g}^{2}; 5T_{2g}) + (t_{2g}^{6}e_{g}^{2}; 3A_{2g}).
\]

The disproportionated system can be viewed as a system of spin–triplet composite hole bosons \((t_{2g}^{5}e_{g}^{2}; 5T_{2g})\) moving on a lattice composed of the electron \(S = 1\) \((t_{2g}^{5}e_{g}^{2}; 3A_{2g})\) centers.

3d\(^8\) ions \((\text{Ni}^{2+}, \text{Cu}^{3+})\). For the ground state configuration in an octahedral crystal field the 3d\(^8\) system disproportionates as follows:

\[
(t_{2g}^{6}e_{g}^{3}; 3A_{2g}) + (t_{2g}^{6}e_{g}^{3}; 3A_{2g})
\rightarrow (t_{2g}^{6}e_{g}^{3}; 3A_{2g}) + (t_{2g}^{6}e_{g}^{3}; 2E_{g}).
\]

with the formation of the two Jahn–Teller centers which are prone to a vibronic localization. However, the genealogy of the \(e_g^{2}; 2E_g\) configuration does not permit the insertion of the well defined composite boson (see expression (6)). The 3d\(^8\) system given a tetrahedral crystal field disproportionates as follows:

\[
(e_g^{4}t_{2g}^{5}; 3T_{1g}) + (e_g^{4}t_{2g}^{5}; 3T_{1g})
\rightarrow (e_g^{4}t_{2g}^{5}; 4A_{2g}) + (e_g^{3}t_{2g}^{5}; 2T_{2g}).
\]

In other words, such a disproportionated system can be viewed as a system of spin–triplet composite electron-type JT bosons \((t_{2g}^{5}e_{g}^{2}; 5T_{1g})\) moving on a lattice composed of the hole spin-\(3/2\) \((t_{2g}^{5}e_{g}^{2}; 3A_{2g})\) S-type centers.

3d\(^9\) ions \((\text{Cu}^{2+})\). In an octahedral crystal field the 3d\(^9\) system disproportionates as follows:

\[
(t_{2g}^{6}e_{g}^{3}; 2E_{g}) + (t_{2g}^{6}e_{g}^{3}; 2E_{g})
\rightarrow (t_{2g}^{6}e_{g}^{3}; 3A_{2g}) + (t_{2g}^{6}e_{g}^{3}; 1E_{g}).
\]

where \((t_{2g}^{6}e_{g}^{3}; 3A_{2g}) = (t_{2g}^{6}e_{g}^{3}; 1A_{1g}) \times (e_g^{2})^3A_{2g}\). In other words, the disproportionated system can be viewed as a system of spin–triplet composite hole bosons \((t_{2g}^{6}e_{g}^{3}; 3A_{2g})\) moving in a lattice composed of the electron spin-0 \((t_{2g}^{6}e_{g}^{3}; 1A_{1g})\) centers (see figure 1).

In a tetrahedral or cubic crystal field the 3d\(^9\) system disproportionates as follows:

\[
(e_g^{4}t_{2g}^{5}; 2T_{2g}) + (e_g^{4}t_{2g}^{5}; 2T_{2g})
\rightarrow (e_g^{4}t_{2g}^{5}; 3T_{1g}) + (e_g^{6}t_{2g}^{2}; 1A_{1g}).
\]

where \((e_g^{4}t_{2g}^{5}; 3T_{1g}) = (e_g^{6}t_{2g}^{2}; 1A_{1g}) \times (t_{2g}^{5}e_{g}^{2}; 3T_{1g})\). In other words, the disproportionated system can be viewed as a system of spin–triplet composite hole bosons \((t_{2g}^{5}e_{g}^{2}; 3T_{1g})\) moving in a lattice composed of the electron spinless \((e_g^{6}t_{2g}^{2}; 1A_{1g})\) centers.

### 3.3 Summary

Let us summarize our findings.

(i) The most effective \(e_g^{2}\) configuration of the local composite boson providing maximal values of the boson transfer integral, without strong reduction effects of the electron–lattice coupling, is realized only for several optimal \(d^n\) configurations. These are HS-\(d^4\), LS-\(d^3\), \(d^0\) configurations given an octahedral crystal field, and \(d^1\), HS-\(d^6\) configurations given a tetrahedral crystal field [42].

(ii) All these bare systems are characterized by E-type orbital degeneracy, i.e. these are prone to a strong Jahn–Teller effect. In all the instances the disproportionation reaction lifts the bare orbital degeneracy; that is, it has a peculiar ‘anti-Jahn–Teller’ character [43].

(iii) All these bare systems are characterized by a strong suppression due to a vibronic reduction of the one-particle (electron or hole) transport, while after disproportionation these are characterized by an effective two-particle (local boson) transport.

(iv) An undesirable spin–triplet structure of the local composite bosons appears to be a common feature of all the above-mentioned disproportionated systems with a high-symmetry crystal field.
disproportionation, or charge-transfer instability, in systems of ions in the s rule) [8]. The approach explains the missing oxidation states as excitation effects or those of half-filled configurations, such as

![Diagram of electronic configurations]

**Figure 3.** Disproportionation schemes for the high-symmetry crystal field which are believed to provide optimal conditions for the disproportionation driven superconductivity.

### Table 1. 3dⁿ JT-systems optimal for the disproportionation driven superconductivity (see text for detail).

| Electron configuration | Symm. | LS/HS | Local boson | Lattice | Parent (bare) compounds | SC |
|------------------------|-------|------|-------------|---------|-------------------------|----|
| 3d¹ (e¹_{1g}) : ²E | Tetra | – | e²_{g} : ³A_{2g} | S = 0 | ? | ? |
| 3d² (t_{2g}²_{e}) : ⁵E | Octa | HS | e²_{g} : ³A_{2g} | S = 3/2 | (Ca, Sr)FeO₃ | NIS, SD |
| Mn³⁺, Fe⁴⁺ | | | | | RnO₃ | Tc, (?) |
| 3d⁶ (e_{1g}²_{1g}) : ⁵E | Tetra | HS | e²_{g} : ³A_{2g} | S = 5/2 | (LaFeAsO, . . .) | NIS, SD |
| Fe²⁺, Co³⁺ | | | | | LiFeAs | Tc ≤ 56 K |
| 3d⁷ (t_{2g}²_{1g}) : ²E | Octa | LS | e²_{g} : ³A_{2g} | S = 0 | (RnO₃ | ? |
| Co³⁺⁺⁺, Ni³⁺⁺⁺ | | | | | AgNiO₂ | |
| 3d⁹ (t_{2g}²_{1g}) : ²E | Octa⁺ | – | b²_{g} : ³A_{1g} | S = 0 | (La₂CuO₄, . . .) | NIS, SD |
| Cu²⁺ | | | | | YBa₂Cu₄O₈ | Tc ≤ 135 K |

(v) At variance with d¹, d⁷, and d⁹ systems, the d⁴ and d⁶ systems reveal an unavoidable coexistence of the spin–triplet bosons and a magnetic lattice.

All these results are summarized in table 1, where we have added examples of 3d systems with optimal 3dⁿ configurations in tetrahedral (Tetra), octahedral (Octa) or tetragonally distorted octahedral (Octa⁺) crystal field. Figure 3 illustrates the final electronic configurations and two-particle e² transport for the disproportionation reaction in optimal d¹, d⁴, d⁷, d⁹ systems.

Our consideration supports and generalizes a purely electronic motivation for ‘negative U’ centers, which was based on a stabilization of the electron-rich closed-shell configurations, such as ns² or nd¹⁰, through the charge excitation effects or those of half-filled configurations, such as nd³, through the exchange–correlation effects (Hund’s rule) [8]. The approach explains the missing oxidation states of ions in the s¹ electronic configuration and predicts the disproportionation, or charge-transfer instability, in systems with ions having nominally m¹ (Hg²⁺, Tl²⁺, Pb³⁺, Bi⁴⁺), d⁹ (Cu²⁺), d⁴ (Mn³⁺, Fe⁴⁺), d⁶ (Fe²⁺, Co³⁺) valence electronic configuration.

In the above we proceed with a conventional approach to the electronic structure of the 3d compounds that implies a predominantly 3d antibonding character of the molecular t₂g and e₉ orbitals in octahedral MO₆ or tetrahedral MO₄ clusters. The electron and spin density in these clusters is distributed between the 3d ion and ligands, which should be taken into account, in particular, when addressing a so-called ‘partial’ disproportionation such as Ni⁴⁺⁺⁺⁺⁺–Ni⁴⁺⁺⁺ in RnO₃ [12]. However, upon lowering the crystal field symmetry and anomalous strengthening of the dp-hybridization at the end of the dⁿ series the situation can change in several important points. A remarkable example is provided by quasi-2d cuprates, where we proceed with a strong axial distortion of the CuO₆ octahedra, actually with square CuO₄ plaquettes (D₄h point symmetry) as a basic element of the crystal and electronic structure. A single-hole b₁g(∞ d²₋₋₋₋) state of the Cu²⁺ ion is typical for the square-planar coordination.
of oxygen ions whereas a two-hole Cu$^{3+}$ state with the same coordination of oxygen ions seldom exists. Instability of Cu$^{3+}$ ions with a 3d$^9$, or two-hole 3d$^2$ configuration is obviously related to a strong inter-electron (hole) repulsion. However, the two-hole state in the CuO$_4$$^{2-}$ center being a cluster analog of the Cu$^{3+}$ ion can be stabilized by the location of the additional hole to low-energy predominantly O 2p molecular orbitals, thus providing a sharp suppression of the inter-electron (hole) repulsion with a relatively small loss in the one-hole energy. In 1988 Zhang and Rice [44] proposed that the doped hole forms a well isolated local spin and orbital $^1\text{A}_{1g}$ singlet state which involves a phase-coherent combination of the 2p$\sigma$ orbitals of the four nearest neighbor oxygens with the same $b_{1g}$ symmetry as for a bare Cu 3d$^9$-$e^2-g^2$ hole. The spin and orbital singlet $^2\text{L}_{1g}$, $^1\text{A}_{1g}$, or Zhang–Rice singlet, may be viewed as a local hole composite boson. In other words, the disproportionation $3\text{d}^9 + 3\text{d}^9 \rightarrow 3\text{d}^{10} + 3\text{d}^8$ in the tetragonally distorted octahedral 3d$^9 = 3\text{d}^1$ (Cu$^{2+}$) systems gives rise to a system of composite hole $S = 0$ bosons whose spin and orbital structure provide maximal values of the effective boson transfer integral and minimal boson effective mass, which provide optimal conditions for the disproportionation driven high-$T_C$ superconductivity. Such a situation is unlikely to be realized for the d$^1$ configuration in a tetrahedral crystal field because of a weak p–d covalency. Thus, our analysis shows that in fact only the d$^9$ system can be a major candidate for maximal $T_C$'s.

Above, we did not consider the energy stability of the final disproportionated ‘negative-$U$’ state. It should be noted that together with a sizable recombination energy this implies well isolated ground states of d$^{n\pm1}$ configurations.

4. Electron–hole Bose liquid with spin–triplet $\varepsilon = 1$ local composite bosons

We have presented a unified approach to the disproportionation phenomenon in different 3d compounds, although we did not touch upon such important points as electron and lattice polarization effects, vibronic coupling, and the role played by the spin and orbital degrees of freedom. All these can strongly deform the phase diagram of the 3d compounds from the predictions of the purely charge order parameter model.

The minimal model of the EHBL phase does not imply intervention of the spin degrees of freedom only in quasi-2d cuprates. Indeed, the model considers such a cuprate to be a system of the spin and orbital singlet $^1\text{A}_{1g}$ local S-bosons moving on a lattice formed by hole centers with the well isolated spin-and-orbital singlet Zhang–Rice $^1\text{A}_{1g}$ ground state. For all other ‘optimal’ 3d$^9$ systems listed in table 1 we arrive at an unavoidable spin–triplet $s = 1$ structure of the composite local bosons moving on the spin (bare octa-HS d$^4$ and tetra-HS d$^6$ configurations) or spinless (bare tetra-d$^1$ and octa-LS d$^7$ configurations) lattice. In the absence of the external magnetic field the effective Hamiltonian of such an electron–hole Bose liquid takes the form of the Hamiltonian of the quantum lattice Bose gas of the triplet bosons with an exchange coupling [19]:

\[
\hat{H} = \hat{H}_{QLBG} + \hat{H}_{ex} = \sum_{i\neq j, m} t_{ij}(ii)\hat{B}_{im}^\dagger\hat{B}_{jm} + \sum_{i\neq j} V_{ij}n_in_j - \mu \sum_i n_i + \sum_{i\neq j} j^{hh}_{ij}(\hat{S}_i \cdot \hat{S}_j) + \sum_{i\neq j} j^{bb}_{ij}(\hat{S}_i \cdot \hat{S}_j) + \sum_i j^{bb}_{i0}(\hat{S}_i \cdot \hat{S}_0). \tag{18}
\]

Here $\hat{B}_{im}^\dagger$ denotes the $s = 1$ boson creation operator with a spin projection $m$ at the site $i$; $\hat{B}_{im}$ is the corresponding annihilation operator. The boson number operator $\hat{n}_{im} = \hat{B}_{im}^\dagger\hat{B}_{im}$ at site $i$ due to the condition of the on-site infinitely large repulsion $V_{ii} \rightarrow +\infty$ (hardcore boson) can take values 0 or 1.

The first term in (18) corresponds to the kinetic energy of the bosons, where $t_{ij}(ii)$ is the transfer integral. The second one reflects the effective repulsion ($V_{ij} > 0$) of the bosons located on the neighboring sites. The chemical potential $\mu$ is introduced to fix the boson concentration: $\hat{n} = \frac{1}{N} \sum_i \hat{n}_i$. For the EHBL phase in the parent system we arrive at the same number of electron and hole centers, namely, to $n = \frac{1}{2}$. The remaining terms in (18) represent the Heisenberg exchange interaction between the spins of the hole centers (term with $j^{bb}_{ij}$), spins of the hole centers and the neighbor boson spins (term with $j^{bb}_{ij}$), boson spins (term with $j^{bb}_{ij}$), and the very last term in (18) stands for the intra-center Hund exchange between the boson spin and the spin of the hole center. In order to account for the Hund rule one should consider $j^{bb}_{ij}$ to be an infinitely large ferromagnetic.

Generally speaking, this model Hamiltonian describes a system that can be considered as a Bose-analog of the one orbital double exchange model system [45].

A more or less simple manifestation of spin degrees of freedom is anticipated for tetra-d$^1$ and LS-octa-d$^7$ configurations, where we proceed with spin–triplet composite bosons, however, moving on the spinless lattice.

Estimates for different superexchange couplings given the bond geometry typical for manganites such as LaMnO$_3$ [19] predict antiferromagnetic coupling of the nn hole centers ($j^{hh} > 0$), antiferromagnetic coupling of the two nearest neighbor bosons ($j^{hh} > 0$), and ferromagnetic coupling of the boson and the nearest neighbor hole centers ($j^{hh} < 0$). In other words, we arrive at a highly frustrated system of triplet bosons moving in a lattice formed by hole centers; when the hole centers tend to order G-type antiferromagnetically, the triplet bosons tend to order ferromagnetically both with respect to their own site and their nearest neighbors. Furthermore, nearest neighboring bosons strongly prefer an antiferromagnetic ordering. Lastly, the boson transport prefers an overall ferromagnetic ordering.

Competition of the Heisenberg exchange and the bosonic double exchange in ‘optimal’ systems, such as ferrates (Ca, Sr)FeO$_3$ or manganites R%MnO$_3$ with bare octa-HS d$^3$ configurations of the transition metals, can be easily demonstrated on an example of the d$^3$–d$^2$ pair, or EH-dimer. The net spin of the EH-dimer is $S = S_1 + S_2$, where $S_1 (S_1 = \ldots$
5/2) and \( S_2 \) (\( S_2 = 3/2 \)) are spins of Fe\(^{3+} \) and Fe\(^{5+} \) (Mn\(^{2+} \) and Mn\(^{4+} \)) ions, respectively. In the nonrelativistic approximation the spin structure of the EH-dimer will be determined by isotropic Heisenberg exchange coupling

\[
V_{\text{ex}} = J (S_1 \cdot S_2),
\]

with \( J \) being an exchange integral, and the two-particle charge transfer characterized by a respective transfer integral which depends on spin states as follows:

\[
\frac{5}{2} \frac{3}{2}; \frac{5}{2} \frac{5}{2}; SM | \hat{H}_B | \frac{5}{2} \frac{3}{2}; SM = \frac{1}{20} \delta(S + 1) t_B.
\]

where \( t_B \) is a spinless transfer integral. Making use of this relation we can introduce an effective spin-operator form for the boson transfer as follows:

\[
\hat{H}_{B}^{\text{eff}} = \frac{t_B}{20} \left[ 2(S_1 \cdot \hat{S}_2) + S_1(S_1 + 1) + S_2(S_2 + 1) \right].
\]

This can be a very instructive tool both for qualitative and quantitative analysis of boson transfer effects, in particular, the temperature effects. Both conventional Heisenberg exchange coupling and unconventional two-particle bosonic transfer, or bosonic double exchange, can be easily diagonalized in the net spin \( S \) representation, so that for the energy we arrive at

\[
E_S = \frac{J}{2} \left[ S(S + 1) - \frac{25}{2} \right] \pm \frac{1}{20} S(S + 1) t_B,
\]

where \( \pm \) corresponds to two quantum superpositions \(| \pm \rangle \) written in a spin representation as follows

\[
|SM \rangle \pm = \frac{1}{\sqrt{2}} \left( \frac{5}{2} \frac{3}{2}; SM \pm \frac{3}{2} \frac{5}{2}; SM \right).
\]

with \( s \) - and \( p \)-type symmetry, respectively. It is worth noting that the bosonic double exchange contribution formally corresponds to a ferromagnetic exchange coupling with \( J_B = -\frac{1}{10} t_B \).

We see that the cumulative effect of the Heisenberg exchange and the bosonic double exchange results in a stabilization of the \( S = 4 \) high-spin (ferromagnetic) state otherwise (see figure 4). As in the conventional (one-electron) double exchange model [46] the latter frustration between the Heisenberg exchange and the bosonic double exchange stabilizes a noncollinear ordering in bulk systems.

5. Discussion

Our approach provides a comprehensive understanding of the well established disproportionation in ferrates (Ca, Sr)Fe\(_3\)O\(_5\) and nickelates RNiO\(_3\) with octa-HS d\(^7\) and octa-LS d\(^2\) configurations of the transition metals. It is worth noting that the flexible perovskite structure of both compounds facilitates a screening of the effective correlation parameter \( U_{dd} \). In (Ca, Sr)FeO\(_3\) the effect is believed to strengthen due to a large enough polarizability of the Ca\(^{2+} \) or Sr\(^{2+} \) ions while in RNiO\(_3\) we deal with a sizable reduction of the effective \( U_{dd} \) due to a strong Ni–O covalency.

An incommensurate helicoidal spin ordering observed both in CaFeO\(_3\) and SrFeO\(_3\) up to very low temperatures can be explained as a result of a competition between conventional exchange coupling and the bosonic double exchange in EH dimers \( M^\pm \leftrightarrow M^\mp \). Interestingly, the helicoidal spin ordering gives rise to a full (SrFeO\(_3\)) or partial (CaFeO\(_3\)) suppression of the charge order, resulting in a metallic or insulating temperature dependence of the resistivity, respectively [47].

In any case, both the theoretical and experimental study of the phase diagram for the (Ca, Sr)FeO\(_3\) system deserves further work, especially with the specific aim of searching for possible superconductivity.

The nominal electronic HS-octa-configuration d\(^4\) of the Fe\(^{4+} \) ion is analogous to that of the Mn\(^{3+} \) ion in perovskite (ortho)manganites RmMnO\(_3\), which implies similar disproportionation features. Indeed, similarly to ferrates (Ca, Sr)FeO\(_3\) the orthomanganites RmMnO\(_3\) reveal a high-temperature metallic phase, which may be associated with a fully disproportionated \( R(Mn^{2+}Mn^{4+})O_3 \) phase [18, 19], or EHBL system. Such a conclusion is particularly supported by an anomalously small magnitude of the thermopower. Interestingly, under spin ordering this manganite phase in contrast with the ferrates could become a ferromagnetic
**EHBL metal** as bosonic double exchange in manganese EH dimers overcomes the Heisenberg exchange in favor of the ferromagnetic spin state [19]. In other words, we deal with the high-spin ferromagnetic ground state of the EH-dimer (see figure 4(a)), while in ferrates we have the low-spin ferrimagnetic state (see figure 4(b)). However, upon actually lowering the temperature one observes a first-order phase transition at \( T = T_{JT} \) \( (T_{JT} \approx 750 \text{ K in LaMnO}_3) \) from the high-temperature fully disproporportionated metallic EHBL phase to a low-temperature orbitally ordered insulating phase with a cooperative Jahn–Teller ordering of the occupied \( e_g \)-orbitals of the Mn\(^{3+}\)O\(_6\) octahedra, accompanied by A-type antiferromagnetic ordering below \( T_N \) \( (T_N \approx 140 \text{ K in LaMnO}_3) \) [18, 19]. In other words, the vibronic (Jahn–Teller) coupling in the bare (parent) Mn\(^{3+}\) phase suppresses the anticipated charge order and promotes a recombination \( M^\pm \rightarrow M^0 \) transition.

Interestingly the non-isovalent substitution and/or non-stoichiometry seems to revive the disproporportionated phase, and such manganites along with a metallic ferromagnetism with a colossal magnetoresistance reveal many properties typical for superconducting materials. These are: a steep jump of the specific heat, gap opening in tunneling, and a giant proximity effect. Several manganite samples were shown to exhibit a negative diamagnetic susceptibility in a wide temperature range up to room temperature [48]. To explain many experimental manifestations of superconductivity, Kim [49] has proposed a superconducting condensation in manganites. In this scenario, colossal magnetoresistance in La\(_{1−x}\)Sr\(_x\)MnO\(_3\) is naturally explained by the superconducting fluctuations with increasing magnetic fields. This idea is closely related to the observation of an anomalous proximity effect between superconducting YBCO and a manganese oxide, La\(_{1−x}\)Ca\(_x\)MnO\(_3\) or La\(_{1−x}\)Sr\(_x\)MnO\(_3\) [50], and also the concept of a local superconductivity manifested by doped manganites [51].

Strong evidence of the revived EHBL phase below the first-order phase transition \( M^\pm \rightarrow M^0 \) from the high-temperature EHBL phase to the low-temperature AFM insulating phase has been obtained very recently by Nath et al [52]. The authors observed an electric-field driven destabilization of the insulating state in a nominally pure LaMnO\(_3\) single crystal with a moderate field which leads to a resistive state transition below 300 K. The effect has been explained as a bias driven percolation-type transition between two coexisting phases, where the majority phase is a charge and orbitally ordered polaronic AFM insulating phase and the minority phase is a bad metallic EHBL phase [52].

Very recently, distinct signatures of high-temperature disproporportionated EHBL phases have also been revealed in other manganites, such as LaMn\(_y\)O\(_{12}\) [53] with quadruple perovskite structure and YBaMn\(_2\)O\(_6\) [54]. A dramatic suppression of the Curie–Weiss susceptibility in the undistorted phase of LaMn\(_y\)O\(_{12}\) above \( T_{JT} \approx 650 \text{ K} \) is explained by a picture of long-lived low-spin \( S = 1 \) EH dimers (see figure 4(b)) formed by the charge transfer between neighboring Mn sites [53]. High-temperature electron spin resonance studies of A-site ordered mixed-valence manganite YBaMn\(_2\)O\(_6\) [54] have revealed two problems. First, in the metallic high-temperature phase the ESR signal stems only from all Mn\(^{3+}\) core spins. Second, the ESR linewidth obeys the Korringle-like linear high-temperature increase over a wide temperature range of 400 K, clearly pointing to a truly metallic state. Both findings strongly support our suggestion of the high-temperature EHBL phase of manganites being a system of spin–triplet composite \( e_g^2 \) bosons moving on a lattice of spin-3/2 Mn\(^{4+}\) centers. Furthermore, one may speculate that the Korringle-like behavior of the ESR linewidth could be a signature of such a charge-disproportionated picture [54]. Our prediction of the disproporportionation driven high-\( T_c \) superconductivity in the HS-d\(^0\) octa systems needs a more direct validation for the hole doped manganites such as La\(_{1−x}\)Sr\(_x\)MnO\(_3\).

The high-temperature metallic phase of rare earth nickelates RNiO\(_3\) with an LS-octa-d\(^7\) configuration of Ni\(^{3+}\) ions resembles that of orthomanganites, however, with a Pauli-like magnetic susceptibility, and evidences a full d–d disproporportionation. Yet the low-temperature behaviors of manganites and nickelates differ greatly. For rhombohedral LaNiO\(_3\) the system remains metallic down to 1.5 K, whereas orthorhombic RNiO\(_3\) \( (R = \text{Pr}, \ldots, \text{Lu}) \) exhibits a first-order phase transition to a charge ordered insulating state upon cooling below \( T_{CO} \), spanning from 130 K for \( \text{Pr} \) to \( \sim 550–600 \text{ K} \) for heavy rare earths. Both the lighter and heavier orthorhombic RNiO\(_3\) compounds are very similar from the point of view of their local electronic and magnetic CO state, despite the strong change of the metal-to-insulator NO–CO transition temperature. All these exhibit clear signatures of the charge-disproportionated state, with two types of Ni centers corresponding to alternating large Ni\(_{10}\)\(^6\)\(^2+\) (Ni\(^{2+}\) center) and small Ni\(_8\)\(^6\)\(^{4+}\) (Ni\(^{4+}\) center) octahedra strongly differing in magnetic moments \( (\sim 2 \mu_B \) and \( \sim 0 \), respectively). Regarding the magnetic order, these nickelates adopt an antiferromagnetic structure defined by the propagation vector \( (1/2, 0, 1/2) \) at a transition temperature \( T_N \) spanning from 130 to \( \sim 200 \text{ K} \). Antiferromagnetic ordering can be explained by a rather strong superexchange \( nnn \) (next-nearest neighbor) coupling of magnetic \( S = 1 \) Ni\(^{2+}\) centers. Unfortunately, the antiferromagnetism stabilizes the charge order and suppresses the superconductivity.

At variance with the charge transfer unstable perovskites ((Ca, Sr)FeO\(_3\), RMnO\(_3\), RNiO\(_3\)) the quasi-2d nickelates ANiO\(_3\) \( (A = \text{Ag, Li, Na}) \) reveal the existence of unconventional ground states stabilized by the frustrated triangular lattice geometry from a cooperative JT ordering of Ni\(^{3+}\) ions in NaNiO\(_3\) to a *moderately charge ordering* 3Ni\(^{3+} \rightarrow \) Ni\(^{2+}\) + 2Ni\(^{4+}\) in antiferromagnetic metal AgNiO\(_2\) [55]. In the case of LiNiO\(_2\) there could be competition between charge ordering and orbital ordering for the ground state, the nickel valency could be a mixture of 2+, 3+, and 4+ [56].

In all the CT-unstable 3d compounds with *optimal* electron configurations addressed above, the JT coupling in nearly octahedral complexes (FeO\(_3\), MnO\(_6\), NiO\(_6\)) competed with the charge disproportionation, and in several compounds this determined the orbitally ordered ground state and the low-temperature phase, thus suppressing the anticipated
superconductivity. The JT coupling reaches its maximal magnitude in Cu$^{2+}$ octahedral complexes, which seemingly should inhibit the disproportionation in Cu$^{2+}$ based cuprates. However, the giant JT distortion stabilizes the CuO$_4$ plaquette with a $b_{1g} \propto d_{x^2−y^2}$ hole ground state which can be a proper starting orbital for an in-plane hole transfer $b_{1g} \rightarrow b_{2g}$ in the CuO$_2$ planes of the quasi-2d cuprates. As a result we arrive at a disproportionation of $2\text{CuO}_4^{2−} \rightarrow \text{CuO}_2^{4−} + \text{CuO}_2^{4−}$ with the formation of a spin- and orbital singlet electron center CuO$_2^{4−}$ (analog of the Cu$^+$ ion) and a hole center CuO$_2^{5−}$ (analog of the Cu$^{3+}$ ion) in a Zhang–Rice $^{1}\text{A}_{1g}$ ground state. Full disproportionation within a CuO$_2$ plane results in a system of composite two-electron spin–singlet (S-type) bosons moving on the spin-0 lattice formed by hole CuO$_2^{5−}$ centers. We arrive at an EHBL system, which is the most favorable for the high-$T_c$ superconductivity. A comprehensive argumentation of the disproportionation scenario for quasi-2d cuprates is reported in [5].

At first sight the case similar to cuprates can be realized in a hypothetical quasi-2d nickelate with a system of well isolated Ni$_3^{3+}$O$_2$ planes, provided a low-spin $e_g^5 \epsilon_{g}$ configuration of the NiO$_2^{4−}$ center with the $b_{1g} \propto d_{x^2−y^2}$ electron ground state and a spin–singlet ZR-type configuration of the $e_g^2$-subshell of the electron NiO$_4^{6−}$ center. However, the latter condition seems unlikely to be realized in practice, therefore the perspectives of the cuprate-like superconductivity in nickelates appear to be very illusory [57].

In the above we addressed ‘optimal’ systems with bare octahedral $d^3$ complexes. What about predicted ‘optimal’ $d^1$ and $d^6$ systems with tetrahedral local symmetry? At present we have no literature data on such $d^1$ systems, whereas the systems with tetrahedral $d^0$, or more precisely, high-spin Fe$^{2+}$ complexes number tens of the so-called iron pnictides (‘FePn’, where Pn is As or P) and iron chalcogenides (‘FeCh’, where Ch includes S, Se, and Te) [58]. In fact, all these compounds are either superconductors or parent systems which turn into a superconducting phase, with $T_c$ values up to 56 K under nonisovalent doping and external or ‘chemical’ pressure.

All the families of iron-containing superconductors have two-dimensional planes of FePn$_4$ or FeCh$_4$ tetrahedra. The quasi-2d structure means that the iron compounds are in common with superconducting cuprates; however, the FePn/Ch superconductors are fundamentally different from the cuprates in several points. Firstly, concerning the coexistence of superconductivity with magnetism demonstrated at an unprecedented atomic scale.

Unlike the case of the high-$T_c$ cuprates, electrons in FePn/Ch layers are always itinerant and there is no Mott insulating state in the electronic phase diagram, though most of the FePn/Ch systems start with an AFM order as the parent phase. The magnetic order in FePn/Ch layers is an unconventional one, most likely a spin-density wave with strongly reduced mean values of a local effective spin.

All the main features of the superconducting and normal states for the FePn/Ch compounds agree with our predictions of the disproportionation within the FePn/Ch layers accompanied by the formation of an EHBL system with a topological phase separation, e.g. formation of a multi-bubble system. However, in contrast with the spinless scenario for cuprates, in the FePn/Ch layers both composite electron $e_g^5$ bosons and the hole lattice have non-zero spins, $s = 1$ and $S = 5/2$, respectively. It means that the charge ordered bubbles are jointly magnetic bubbles with a complex nanoscale inhomogeneous spin structure. Accordingly, the FePn/Ch layers can be considered as a system of bubble carriers which carry both charge, ‘local superconductivity’, and a spin density. Moreover, the bubble formation is accompanied by strong nanoscale structural distortions, which can be detected by pair distribution function analysis [59].

In any case, finding high-$T_c$ superconductivity in the FePn/Ch compounds with the tetrahedral coordination of the iron Fe$^{2+}$ ($3d^6$) ions in the HS state and its coexistence with an unconventional magnetism can be a key argument supporting the disproportionation scenario [5]. Puzzlingly, our model implies the superconducting carriers in FePn/Ch compounds are composed of $e_g$ rather than $t_{2g}$ electrons as predicted by one-electron band models. Both cuprates and ferro-pnictides/chalcogenides are believed to be ‘bad’ EHBL metals.

6. Conclusion

We analyzed d–d disproportionation phenomena in materials with different 3d ions. We have shown that optimal conditions for the disproportionation driven high-$T_c$ superconductivity are realized only for several $d^0$ configurations. These are HS-$d^4$, LS-$d^7$, $d^9$ configurations given an octahedral crystal field, and $d^1$, HS-$d^6$ configurations given a tetrahedral crystal field. Interestingly, all these bare systems are characterized by E-type orbital degeneracy, i.e. these are prone to a strong Jahn–Teller effect. In all instances, the disproportionation reaction lifts the bare orbital degeneracy, that is, it has a peculiar ‘anti-Jahn–Teller’ character. All the optimal systems are characterized by a strong suppression of the one-particle transport, while after disproportionation these are characterized by an effective two-particle transport.

In any case, the optimal disproportionation schemes (see figure 3 and table 1) imply the participation of a spin degree of freedom. The proposed superconductivity in the $d^4$ and $d^6$ systems at variance with $d^1$, $d^3$, and $d^9$ systems is characterized by the unavoidable coexistence of the spin–triplet composite bosons and a magnetic lattice. Only quasi-2d cuprates in a ‘negative-U’ regime seem to represent a system of spin–singlet composite bosons moving on the spinless lattice. Their magnetic response could be explained by purely oxygen orbital magnetism if we take into account deviations from the simple Zhang–Rice model [29, 30]. Interestingly, our ‘spinless’ scenario for cuprates clearly opposes a spin/magnetic mechanism currently being a leading contender for the superconducting mechanism in the high-$T_c$ cuprates.

We argue that unconventional superconductivity observed in iron-based layered pnictides and chalcogenides with 1 The suggestion of the disproportionation driven superconductivity in iron pnictides was first made in 2008, see [42].
tetrahedrally coordinated Fe$^{2+}$ ions presents a key argument to support the fact that the disproportionation scenario is at work in these compounds. It is worth noting that the potential for high-$T_c$ appears to be greatest for undistorted FePn$_4$ tetrahedra [60]. Furthermore, observation of the high-$T_c$ superconductivity in these quasi-2d systems with undesirable spin degrees of freedom, both for the composite boson and the lattice, gives some hope of finding superconductivity in artificial 2d superlattices of all the ‘optimal’ configurations.

We did not consider here many important points of the disproportionation scenario, or make any comparisons with other model approaches, particularly the bipolaronic theory of Alexandrov [41]. Nevertheless, the model approach suggested is believed to provide a conceptual framework for an in-depth understanding on an equal footing with the physics of very different strongly correlated 3d systems, such as cuprates, manganites, nickelates, ferro-pnictides/chalcogenides and other systems with a charge-transfer instability and/or mixed valence. In particular, our paper provides a clear answer to the question, ‘what is so special about Cu in cuprates or Fe in Fe-based superconductors?’ and why, for example, BaMn$_2$As$_2$, which, with respect to many properties is situated between BaFe$_2$As$_2$ and the high-$T_c$ cuprates, is not a high-$T_c$ superconductor [60].

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