Research Article

A novel approach to the crystal-field theory - the orbital magnetism in 3d-ion compounds

*R. J. Radwanski**

Center of Solid State Physics; S^{nt} Filip 5, 31-150 Krakow, Poland
Institute of Physics, Pedagogical University, 30-084 Krakow, Poland

Z. Ropka

Center of Solid State Physics; S^{nt} Filip 5, 31-150 Krakow, Poland

(12.07.2001, cond-mat/0307575 23 July 2003, published 29 December 2006)

We point out that the orbital magnetism has to be taken into account in the description of real 3d-ion compounds. According to the developed by us the Quantum-Atomistic Solid-State (QUASST) theory in compounds containing open 3d-/4f-/5f-shell atoms there exists a discrete atomic-like low-energy electronic structure that predominantly determines electronic and magnetic properties of the whole compound. The relatively weak intra-atomic spin-orbit coupling is fundamentally important as it governs the low-energy discrete electronic structure.

PACS: 75.10.Dg; 71.70.Ch
Keywords: crystal field, spin-orbit coupling, orbital magnetism

I. INTRODUCTION

An unexpected discovery of high-T_c superconductivity in 3d-ion oxides in 1986 has revealed the shortcomings of our understanding of the 3d magnetism. Today still we do not have consistent understanding of electronic and magnetic properties of 3d-ion containing compounds. Many of 3d-ion oxides belong to the class of compounds called the Mott insulators that exhibit the insulating state in the presence of the unfilled d shell. Despite of very different theoretical concepts there is still no consensus how to treat electrons in the unfilled shell. The standard

* http://www.css-physics.edu.pl; Email: sfradwan@cyf-kr.edu.pl

band picture encounters serious difficulties - it often predicts the metallic state for systems that are in fact insulators, for instance for La_2CuO_4 and NiO [1–4]. The very characteristic feature of the present literature description of the 3*d*-ion magnetism is the spin-only description with the neglect of the orbital magnetism. This erroneous, according to us, view is related to the widely-spread conviction about the quenching of the orbital moment in 3*d*-atom compounds. This observation made in 1934 by Van Vleck is valid, however, only in the first-order approximation - we show that it is the highest time in the 3*d* solid-state physics to "unquench" the orbital moment.

In the present paper we would like to put attention to the essential importance of the orbital magnetism for the description of electronic and magnetic properties of compounds containing open shell atoms, in particular with the 3*d* shell.

II. THEORETICAL OUTLINE

According to developed by us the Quantum-Atomistic Solid-State (QUASST) theory [5, 6] we treat n d electrons in the incomplete shell as forming strongly-correlated atomic-like electron system $3d^n$. In a zero-order approximation these electron correlations within the incomplete 3*d* shell are accounted for by the two phenomenological Hund's rules, 1^o) the resultant spin quantum number S of the lowest term of the whole $3d^n$ system is maximal and 2^o) the resultant orbital quantum number L is maximal provided the condition 1^o. These rules yield for the $3d^6$ electron configuration, for instance, the term ^5D with $S = 2$ and $L = 2$ as the ground term. This term is 25-fold degenerated in the $|LSL_zS_z\rangle$ space like it was discussed for the Fe^{2+} ion in $FeBr_2$ [7]. This degeneracy is removed by i) the crystal field (CEF) interactions and ii) by the intra-atomic spin-orbit coupling. Despite of the fact that for the 3*d* ions the spin-orbit coupling is by two-orders of magnitude weaker than the CEF interactions we do not apply the perturbation method, as is usually made in literature, but treat the CEF and spin-orbit interactions on the same footing.

III. RESULTS AND DISCUSSION

The calculated electronic structure of the 3*d*-ion with the $3d^n$ configuration, $1 \leq n \leq 9$, are collected in Figs 1 and 2 for the octahedral symmetry of the crystal field. These calculations have been performed with the realistic octahedral crystal field parameter (the T_{2g}-E_g splitting

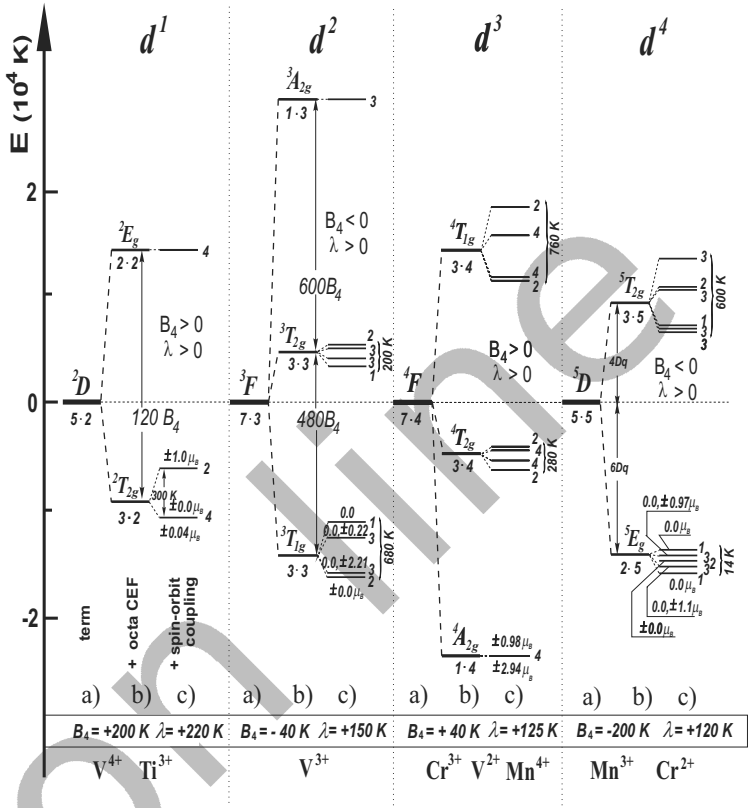

FIG. 1: The calculated electronic structure of the $3d^n$ configurations of the $3d$ ions, $1 \leq n \leq 4$, in the octahedral crystal field (b) and in the presence of the spin-orbit coupling (c). According to the Quantum Atomistic Solid-State theory the atomic-like electronic structures, shown in (c), are preserved also in a solid. (a) - shows the Hund's rule ground term.

amounts to 2.2 eV for the $3d^1$ system) and the intra-atomic spin-orbit coupling ($|\lambda|$= 220-1200 K). Indeed, the octahedral crystal field strongly dominates the effect of the spin-orbit coupling. The most important outcome is a fact that the electronic structure is much more complex than

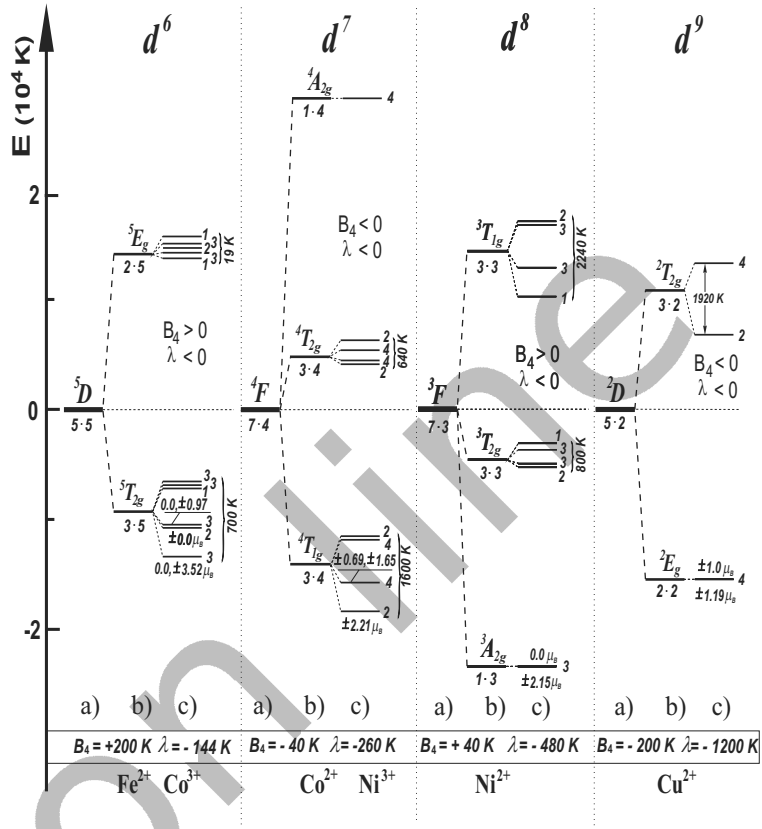

FIG. 2: The calculated electronic structure of the $3d^n$ configurations of the $3d$ ions, $6 \leq n \leq 9$, in the octahedral crystal field in the presence of the spin-orbit coupling. According to the Quantum Atomistic Solid-State theory these atomic-like electronic structures are preserved also in a solid.

presently discussed in the literature (Fig. 3). Such schematic structures like that shown in Fig. 3 are discussed even quite recently [3, 8–14]. It is evident that our results are basically different confirming the fundamental scientific novelty of our approach in description of $3d$-atom containing compounds.

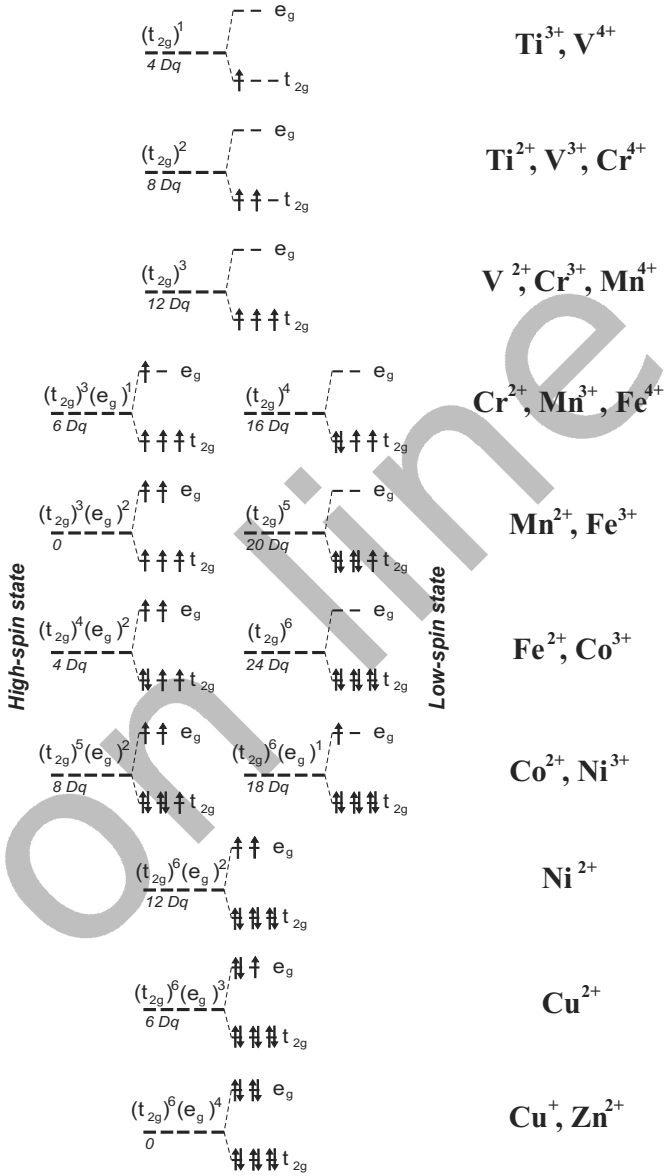

FIG. 3: Electronic structures of 3*d*-ions in high- and low-spin states in the octahedral crystal field. Such the structures are discussed in the present literature [3, 8–14], but - according to our studies - they are not physically adequate.

In Figs 1 and 2 are also shown values of the magnetic moment of the ground state. These moments are i) not integer and ii) much different from those expected for the spin-only moment, i.e. an integer value equaling to $2n\ \mu_B$. In many cases the moment is zero or close to zero indicating the possibility of the formation of the non-magnetic state. The degenerated ground states can be a subject to an off-cubic distortion according to the Jahn-Teller theorem. This effect has been widely discussed for $LaCoO_3$ [15], for instance, that is non-magnetic down to lowest temperatures. The trigonal off-cubic crystal-field distortion of the octahedral complex CoO_6 occurring in the perovskite structure of $LaCoO_3$ causes the splitting of the lowest triplet, shown in Fig. 2 for the $3d^6$ system, into the non-magnetic singlet and the magnetic doublet with the singlet lower. Recently it has been unambiguously proved that such the singlet-doublet structure, with a splitting of 0.6 meV only, is realized in $LaCoO_3$ indeed [16], but there is about 12 meV lower another singlet as the ground state. This singlet ground state is a $^1A_1$ subterm originating from the ^1I term, that lowers so much its energy due to substantial octahedral crystal-field interactions. The octahedral CEF turns out to be about 25% stronger than we originally thought (instead of B_4 of 200 K it turns out to be of 260 K) [16], but these octahedral CEF interactions are still not so strong to break intra-atomic correlations among electrons within $3d$ shell (the preservation of intra-atomic correlations among electrons within $3d$ shell is our meaning of "atomistic"; these strong intra-atomic correlations allow to work with many-electron quantum numbers S and L of the whole $3d^n$ configuration instead of single-electron states with s_i and l_i). A significantly good description of the experimentally derived quasi-triplet states with its behavior in magnetic fields up to 30 T applied along different main crystallographic directions [16] proves the high physical adequacy of the used by us intermediate CEF approach to 3d-ion compounds in contrary to the generally use strong CEF approach. Despite of a non-Hund's rule ground state in $LaCoO_3$ the QUASST theory is still valid for $LaCoO_3$ as the $^1A_1$ subterm is the term expected from the atomic physics. In fact, we never expected that in a solid electronic states will be so thin, in the energy scale below 1 meV, and so well characterized by the atomic physics. At present we take Electron-Paramagnetic(Spin)-Resonance (ESR) results on $LaCoO_3$ as a significant evidence for the application of QUASST to $3d$-atom containing compounds.

The orbital moment comes out from the intra-atomic spin-orbit coupling. We have calculated the orbital moment in NiO ($3d^8$), for instance [17] finding the orbital moment m_O=+0.54 μ_B and the spin moment m_S=+1.99 μ_B. In $FeBr_2$ we have found m_O=+0.80 μ_B and m_S=+3.52

μ_B [7]. In $3d^1$ system m_O=-1.00 μ_B and m_S=+0.99 μ_B. It is worth to remind that the large orbital magnetism occurs in $4f$ and $5f$ systems.

According to the QUASST calculations the non-magnetic singlet seen in Fig. 1 for the d^4 system is responsible for the persistent non-magnetic state of Sr_2RuO_4 [18]. The Ru^{4+} ion is the $4d^4$ electron system, but than much larger value for λ has to be taken into calculations. We would like to note that despite the non-magnetic singlet ground state a magnetic state can be also formed in favorable situation - such the singlet-singlet ordering is well known in Pr compounds [19]. Such the magnetic state can be relatively weak, depending largely on the energy separation, exactly as it is the case of Sr_2RuO_4, where the energy separation becomes, in comparison to the Mn^{3+} ion in $LaMnO_3$, substantially larger due to the much stronger spin-orbit coupling in the $4d$ shell.

In discussion of the intriguing magnetism and superconductivity of UGe_2 we would like to refer to our studies of UGa_2 [20]. Magnetic and electronic properties of UGa_2 have been consistently described within the QUASST theory with the U^{3+} configuration coexisting with conduction electrons, that assure the metallicity. We have found magnetic properties of UGe_2 very similar to those of UGa_2 - the orthorhombic structure of UGe_2 is a distorted hexagonal structure of UGa_2. For instance, the direction of the uranium magnetic moment, in both compounds points to the same local direction. The calculated orbital and spin moments in UGe_2 amount to +2.45 μ_B and -1.05 μ_B yielding the total moment of 1.40 μ_B. In UGa_2 these values are +4.90 μ_B, -2.10 μ_B and +2.80 μ_B, respectively.

IV. CONCLUSIONS AND REMARKS

In conclusion, we point out that the orbital magnetism and the intra-atomic spin-orbit coupling has to be taken into account in the description of real $3d$-ion compounds. According to developed by us the Quantum Atomistic Solid-State theory in compounds containing open $3d$-/$4f$-/$5f$-shell atoms the discrete atomic-like low-energy electronic structure survives also when the $3d$ atom becomes the full part of a solid matter. The low-energy atomic-like electronic structure predominantly determines electronic and magnetic properties. Our QUASST approach is the extension of the crystal-/ligand-field theory [21] started in 1929 by Bethe and continued later by Kramers and Van Vleck, but somehow forgotten or improperly used recently (in the presently in-fashion one electron CEF approach single electrons are put subsequently on the purely octahedral t_{2g} and e_g states, as is shown in Fig. 3). In partic-

ular, the states shown in Figs 1 and 2 are **many-electron states of the whole $3d^6$ system** whereas at present most theoretical approaches consider n d electrons as largely independent. In description of the electronic structure and magnetism of $3d$-atom containing compounds the intra-atomic relativistic spin-orbit coupling plays fundamentally important role despite its relative weakness [22]. Our studies clearly indicate that it is the highest time to "unquench" the orbital moment in solid-state physics in description of $3d$-atom containing compounds. There is rapidly growing experimental evidence for the existence of the orbital moment, thanks X-ray synchrotron experiments, and QUASST enables its calculations using well-established physical concepts.

A note added during the referee process. This paper has been orally presented at IX School on High Temperature Superconductivity held in Krynica, Poland, in June, 10-14, 2001, that later has appeared in January 2002 as a special volume to Acta Physica Polonica B, pp 189-195, under editors of A. Szytula and A. Kolodziejczyk. The title of this paper has been changed from "Normal state of high-T_c superconductors - Orbital magnetism in $3d$-ion compounds" on the strong suggestion of the referee. Thanks it the title is more adequate, indeed, though we think that we are doing a quite conventional crystal-field approach (but in the intermediate, not strong, CEF regime), that has been unfortunately forgotten in the present solid-state physics.

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