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

R. J. Radwanski

Center for Solid State Physics, S'nt Filip 5, 31-150 Krakow, Poland,
Institute of Physics, Pedagogical University, 30-084 Krakow, Poland

Z. Ropka

Center for Solid State Physics, S'nt Filip 5, 31-150 Krakow, Poland

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 No: 75.10.D; 71.70.E

Keywords: crystal field, spin-orbit coupling, orbital magnetism

An unexpected discovery of high-Tc 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 band picture encounters serious difficulties - it often predicts the metallic state for systems that are in fact insulators, for instance for La$_2$CuO$_4$ and NiO [1,2,3,4]. The very characteristic feature of the present literature description of the 3d-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 3d-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 3d 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 3d shell.

According to developed by us the Quantum-Atomistic Solid-State (QUASST) theory we treat n d electrons in the incomplete shell as forming strongly-correlated atomic-like electron system 3dn. In a zero-order approximation these electron correlations within the incomplete 3d shell are accounted for by the two phenomenological Hund’s rules, 1°) the resultant spin quantum number S of the lowest term of the whole 3dn system is maximal and 2°) the resultant orbital quantum number L is maximal provided the condition 1°. These rules yield for the 3d6 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 |LSLzS_z⟩ space like it was discussed for the Fe2+ ion in FeBr2. This degeneracy is removed by i) the crystal field (CEF) interactions and ii) by the intra-atomic spin-orbit coupling. Despite the fact that for the 3d 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. The calculated electronic structure of the 3d-ion with the 3dn configuration, 1 ≤ n ≤ 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 T2g-Eg splitting amounts to 2.2 eV for the 3d1 system) and the intra-atomic spin-orbit coupling (|λ| = 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 presently discussed in the literature (Fig. 3). Such schematic structures like that shown in Fig. 3 are discussed even quite recently. It is evident that our results are basically different confirming the fundamental scientific novelty of our approach in description of 3d-atom containing compounds.

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
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.

moment, i.e. an integer value equalling 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
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.

is non-magnetic down to lowest temperatures. This non-magnetic ground state is caused in the atomic scale. The Co$^{3+}$ ion can become non-magnetic due to the trigonal off-cubic crystal-field distortion of the octahedral complex CoO$_6$ occurring in the perovskite structure of LaCoO$_3$. The trigonal distortion causes the splitting of the lowest triplet, shown in Fig. 2
FIG. 3: Electronic structures of 3d-ions in high- and low-spin states in the octahedral crystal field. Such the structures are discussed in the present literature [3, 8, 9, 10, 11, 12, 13, 14], but - according to our studies - they are not physically adequate.

for the 3d⁶ 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 LaCoO₃ indeed [16], but there is about 12 meV lower another singlet as the ground state. This singlet ground state is a ¹A₁ 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 3$d$ shell (the preservation of intra-atomic correlations among electrons within 3$d$ 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 3$d^m$ 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 3$d$-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 3$d$-atom containing compounds.

The orbital moment comes out from the intra-atomic spin-orbit coupling. We have calculated the orbital moment in NiO (3$d^8$), for instance [17] finding the orbital moment $m_O=+0.54\ \mu_B$ and the spin moment $m_S=+1.99\ \mu_B$. In FeBr$_2$ we have found $m_O=+0.80\ \mu_B$ and $m_S=+3.52\ \mu_B$ [7]. In 3$d^1$ system $m_O=-1.00\ \mu_B$ and $m_S=+0.99\ \mu_B$. It is worth to remind that the large orbital magnetism occurs in 4$f$ and 5$f$ 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$_2$RuO$_4$ [18]. The Ru$^{4+}$ ion is the 4$d^4$ electron system, but than much larger value for $\lambda$ 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$_2$RuO$_4$, 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 4$d$ shell.

In discussion of the intriguing magnetism and superconductivity of UGe$_2$ we would like
to refer to our studies of UGa$_2$\textsuperscript{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 $\mu_B$ and -1.05 $\mu_B$ yielding the total moment of 1.40 $\mu_B$. In UGa$_2$ these values are +4.90 $\mu_B$, -2.10 $\mu_B$ and +2.80 $\mu_B$, respectively.

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 3$d$-ion compounds. According to developed by us the Quantum Atomistic Solid-State theory in compounds containing open 3$d$-/4$f$-/5$f$-shell atoms the discrete atomic-like low-energy electronic structure survives also when the 3$d$ 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 \textsuperscript{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 particular, the states shown in Figs 1 and 2 are \textbf{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 3$d$-atom containing compounds the intra-atomic relativistic spin-orbit coupling plays fundamentally important role despite its relative weakness \textsuperscript{22}. Our studies clearly indicate that it is the highest time to "unquench" the orbital moment in solid-state physics in description of 3$d$-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 preset solid-state physics.

[1] S. Yamaguchi, Y. Okimoto, and Y. Tokura, Phys. Rev. B 55, R8666 (1997).
[2] D. D. Sarma, N. Shanithi, S. R. Barman, N. Hamada, H. Sawada, and K. Terakura, Phys. Rev. Lett. 75, 1126 (1995).
[3] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998) (p.1049).
[4] M. A. Korotin, S. Yu. Ezhov, I. V. Solovyev, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B 54, 5309 (1996).
[5] R. J. Radwanski, R. Michalski and Z. Ropka, Acta Phys. Pol. B 31, 3079 (2000).
[6] R. J. Radwanski and Z. Ropka, *Quantum Atomistic Solid-State Theory*, http://xxx.lanl.gov/abs/cond-mat/0010081.
[7] Z. Ropka, R. Michalski, and R. J. Radwanski, Phys. Rev. B 63, 172404 (2001).
[8] M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuiller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, and F. Villain, Coordination Chemistry Rev. 190-192, 1023 (1999).
[9] P.A. Cox, *The electronic structure and chemistry of solids* (Oxford Science) 1998 (p. 150, Fig. 5.11).
[10] J. E. Huheey, *Inorganic Chemistry* (Harper&Row, New York) 1983 (pp 375-412).
[11] A. Bielanski, *Podstawy Chemii Nieorganicznej* (PWN, Warszawa, in Polish) 1997 (p. 495); also Edition 2002, p. 504
[12] R. M. Ibarra, R. Mahendiran, C. Marquina, B. Garcia-Landa, and J. Blasco, Phys. Rev. B 57, R3217 (1998).
[13] J. M. D. Coey, M. Viret, L. Ranno, and K. Ounadjela, Phys. Rev. Lett. 75, 3910 (1995).
[14] Y. Tokura and Y. Tomioka, J. Magn. Magn. Mater. 200, 1 (1999).
[15] Z. Ropka and R. J. Radwanski, Physica B 312-313, 777 (2002).
[16] Z. Ropka and R. J. Radwanski, Phys. Rev. B 65, 172401 (2003).
[17] R. J. Radwanski and Z. Ropka, Acta Phys. Pol. A 97, 963 (2000).
[18] Z. Ropka, R. J. Radwanski, and A. J. Baran, Electronic structure and magnetism of \( \text{Sr}_2\text{RuO}_4 \), Physica C \textbf{387} (2003) 262.

[19] R. Michalski, Z. Ropka, and R. J. Radwanski, J. Phys.: Condens. Matter \textbf{12}, 7609 (2000).

[20] R. J. Radwanski and N. H. Kim-Ngan, J. Magn. Magn. Mater. \textbf{140-144}, 1373 (1995).

[21] A. Abragam and B. Bleaney, \textit{Electron Paramagnetic Resonance of Transition Ions} (Clarendon, Oxford) 1970 (pp 365-471).

[22] R. J. Radwanski and Z. Ropka, \textit{Relativistic effects in the electronic structure for the 3d paramagnetic ions}, \url{http://xxx.lanl.gov/abs/cond-mat/9907140}. 