

Research Article

The quantum atomistic solid-state theory[♠]

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The quantum atomistic solid-state theory (QUASST) is developed for compounds containing open-shell $3d$, $4f$ and $5f$ atoms and points out the existence in a solid of the atomic-like discrete electronic structure determined by the crystal-field and spin-orbit interactions. These low-energy localized states determine electronic and magnetic properties of $3d/4f/5f$ atom containing compounds. QUASST accounts for very strong correlations within $3d/4f/5f$ electrons. QUASST unifies the description of $3d/4f/5f$ atoms and their compounds and allows to bridge the atomic physics and the solid-state physics.

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The aim of the quantum atomistic solid-state theory (QUASST) is the consistent physical model description of electronic, magnetic and spectroscopic properties of solids containing atoms with an incomplete electronic shell, namely $4f$, $3d$ and $5f$ shells. Surely at present most evidence for the physical adequateness of QUASST exists for rare-earth systems - we are quite convinced also about the substantial applicability of QUASST to $3d$ - and $5f$ -atom compounds. In presenting QUASST we

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will concentrate on $4f$ -atom compounds but the same should hold for $5f$ - and $3d$ -atom compounds. Among different properties of interest we can mention the magnetic moment, its value and its direction at 0 K and at ambient temperatures, temperature dependence of the heat capacity and of the paramagnetic susceptibility, the anisotropy of magnetic properties. Surely we are interested in the energy spectrum of available electronic states and their nature. Surely we think about the formation of the magnetic moment, its spin and orbital contributions, as well as a symmetry breaking during the formation of the magnetic state.

QUASST accepts a picture called sometimes ionic, but we have to say that, according to us, this ionic model never was clearly formulated. Even, when it and the crystal-field (CEF) theory are sometimes used they are very often misleadingly used, in particular in case of $3d$ ions.

The basic ideas of the CEF theory (put forward by Bethe in 1929) - the existence of the discrete energy states for the paramagnetic open-shell $4f$ atoms and the importance of the local symmetry - is taken as the main ingredients in the construction of the more general theory for the solids - the quantum atomistic solid-state theory. The basic idea of QUASST is that i) the paramagnetic atoms preserve much of their atomic properties also being the full part of a solid. Otherwise - $4f/3d/5f$ atoms exist also in a solid. The novelty of this simple idea can be understood if one remembers that in the presently-in-fashion modern theories of solids atoms somewhere disappear. It is clearly visible in the band theories, more often recently used for the description of systems with open-shell atoms, that yield the continuous energy spectrum.

We should explain that in different compounds different ionic states of the paramagnetic atom can be formed. Pr is, for instance, trivalent in Pr_2O_3 , PrAl_2 and in PrNi_5 but is tetravalent in PrO_2 . The different ionic states we consider as different states of the atom. The good description of PrNi_5 and ErNi_5 [1, 2], that are intermetallics, indicates that there exists the Pr^{3+} and Er^{3+} ions (more exactly, the atomic-like f^2 and f^{11} systems) despite of the conduction band electrons. It means, that we can have the clearly defined ionic state, with the well-defined integer number of $4f$ electrons, in an intermetallic compound. Then, apart of the description of the Pr^{3+} ions we should discuss properties of conduction electrons. In RENi_5 their contribution to the heat capacity and to the paramagnetic susceptibility is small and is the trivial function of temperature. Similarly to the Pr states, trivalent or tetravalent, the Co atom in CoO is in the divalent state but it is in the trivalent state in LaCoO_3 .

By the preservation of the atomic structure we understand that the Pr^{3+} ion, for instance, has the atomic-like $4f^2$ system (other electrons

are in closed inner shells). It means that the intra-atomic interactions are strong enough to preserve this highly-correlated electronic system also when the atom becomes the part of a solid and undergoes interactions with surroundings. Similarly, six $3d$ electrons of the Co^{3+} ion in Mott insulator LaCoO_3 form the highly-correlated $3d^6$ electronic system. Thus ii) n $4f/3d/5f$ electrons form the highly-correlated $4f^n/3d^n/5f^n$ electronic system. Subsequently we have the term and multiplet structure known from the atomic physics. The intra-atomic correlations lead to iii) the ground term of the $4f^n/3d^n/5f^n$ system with the resultant S and L given by Hund's rules. Then we work in the $(2S+1)(2L+1)$ space. In case of $4f$ and $5f$ ions this space is further reduced (due to the existence of the large spin-orbit coupling) to the $(2J+1)$ space, where J for the lowest multiplet is given by the 3^{rd} Hund's rule. QUASST points out iv) the importance of the intra-atomic spin-orbit (s-o) coupling. So far the $4f$ ions are described within the large s-o limit whereas the s-o coupling has been largely ignored for $3d$ ions. There is a highest time to take into account the finite, though quite large, s-o coupling in description of rare-earth ions and the non-zero, though relatively weak, s-o coupling for the $3d$ ions. It turns out that the large s-o limit used in the description of rare-earth ions is quite physically adequate - it means that taking into account the finite s-o coupling does not introduce the revolution in the low-energy part of the electronic structure, but allows to explain, for instance, the appearance of the higher multiplets at the finite energies (the excited multiplet for the Sm^{3+} ion lies at 120 meV only as detected by inelastic-neutron-scattering experiments of Furrer *et al.* [3]). However, in case of the $3d$ ions taking into account the s-o coupling, even of the small value, causes the completely new low-energy electronic structure, in parts c of Figs 1 and 2, and dramatically changes the shape of eigenfunctions in comparison to the situation with $\lambda_{s-o} = 0$, shown in the parts b of Figs 1 and 2. In fact, the smaller value of the s-o coupling the lower energy scale in the electronic structure appears and the lower temperature range, where anomalies of electronic and magnetic properties appear [4].

QUASST points out v) the existence of the discrete electronic structure associated with the atomic-like states of the $4f^n/3d^n/5f^n$ systems in a solid. In fact, this is the main postulate of the QUASST theory.

QUASST points out vi) the importance of the atomic scale symmetry on the electronic structure, in particular on the realized ground state and its magnetic moment, both the value and the direction. This electronic structure determines the electronic and magnetic properties macroscopically observed both at zero temperature as well as at ambient temperatures.

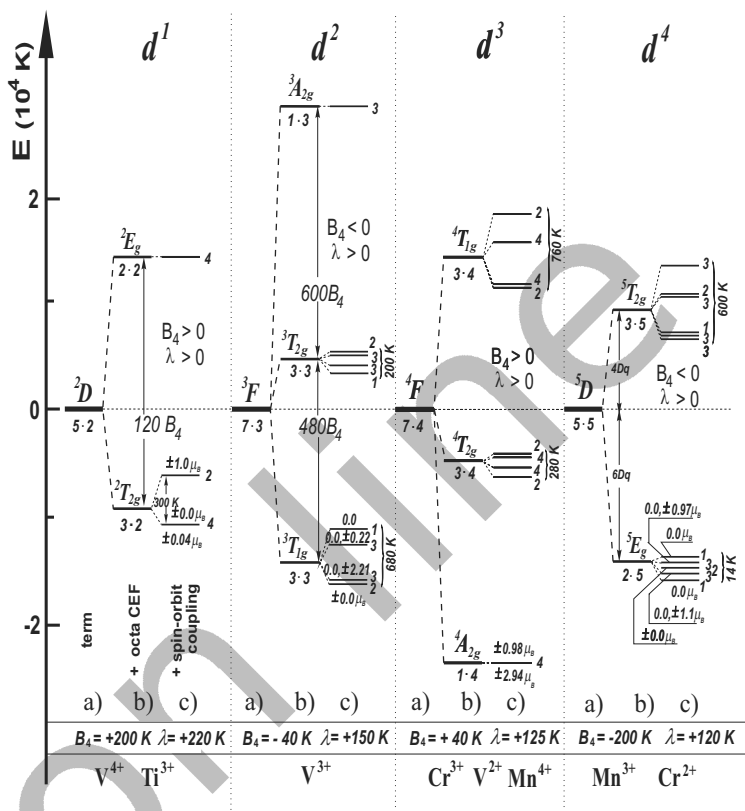


FIG. 1: The calculated atomic-like electronic structure of the highly-correlated $3d^n$ ($4d^n$), $1 \leq n \leq 4$, electron systems in the octahedral crystal field in the presence of the spin-orbit coupling (c). a) - the Hund's rule term and b) its splitting due to the octahedral crystal-field. The highly-correlated $3d^n$ ($4d^n$) electron system is described by two Hund's rules quantum numbers and the calculations are performed for the same strength of the crystal field whereas the spin-orbit coupling constant varies from $+220$ K for $3d^1$ system to 1220 K for the $3d^9$ system. The degeneracy of the states is shown as well as the magnetic moment of the ground state. For the $4d^n$ systems the spin-orbit coupling constant is larger by factor 3-4. According to the Quantum Atomistic Solid-State theory these atomic-like electronic structures are preserved also in a solid.

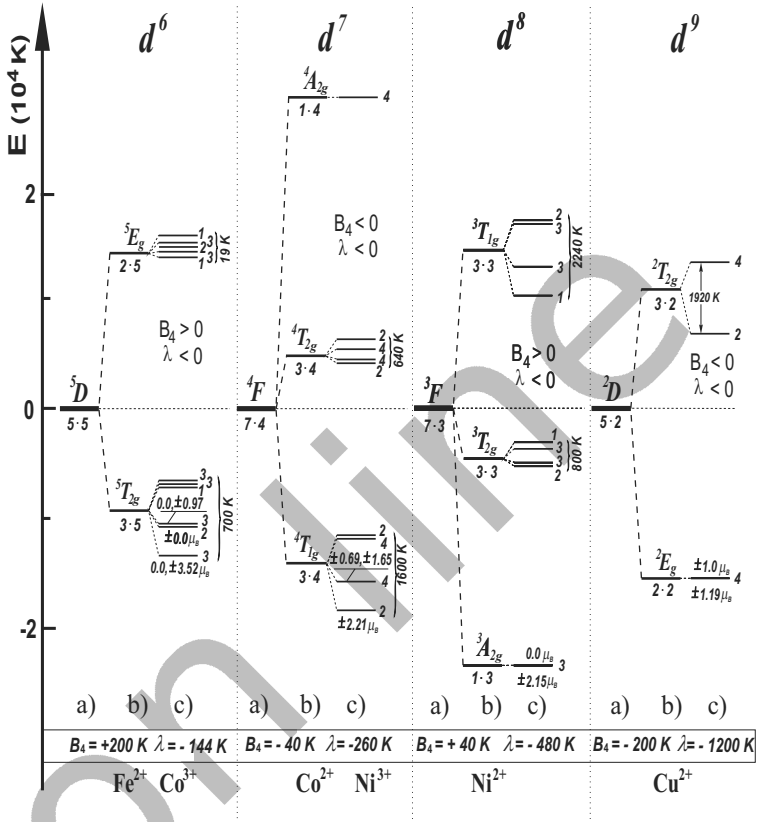


FIG. 2: The calculated electronic structure of the $3d^n$ configurations of the $3d$ ions, $6 \leq n \leq 9$, in the octahedral crystal field in the presence of the spin-orbit coupling (c). a) - the Hund's rule term and b) its splitting due to the octahedral crystal-field. The highly-correlated $3d^n$ ($4d^n$) electron system is described by two Hund's rules quantum numbers and the calculations are performed for the same strength of the crystal field whereas the spin-orbit coupling constant varies from +220 K for $3d^1$ system to 1220 K for the $3d^9$ system. The degeneracy of the states is shown as well as the magnetic moment of the ground state. For the $4d^n$ systems the spin-orbit coupling constant is larger by factor 3-4. According to the Quantum Atomistic Solid-State theory these atomic-like electronic structures are preserved also in a solid.

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QUASST points out vii) the strong interplay of the magnetic state of a paramagnetic ion and the symmetry of the electric field produced by surrounding charges. The electric field produced by surrounding charges within the CEF community is known as the crystal field. The well-known example is the Pr^{3+} ion in PrNi_5 . It is the local symmetry of the crystal field that produces the non-magnetic state of the paramagnetic atom. Within the CEF community this effect is discussed in the connection to the Kramers and the Jahn-Teller theorems. The CEF interactions can substantially reduce the local magnetic moment also in case of the Kramers ions. It has been found that the hexagonal symmetry CEF can produce even a non-magnetic Kramers-doublet ground state for the highly-correlated f^3 system [5, 6]. It has been also shown that viii) for the $3d$ -ion compounds the Jahn-Teller theorem has to be considered within the spin-orbital space in contrary to the orbital-only space considered so far. Thus, our treatment makes unification with the rare-earth ions where the Jahn-Teller theorem is customarily considered within the spin-orbital space. In fact, such the treatment came to the rare-earth magnetism in a very natural way with the acceptance, after the works of Hund (1925) and Van Vleck (1929, 1932), that J is the good quantum number for $4f$ ions. Simultaneously the works of Van Vleck (1932), Schlapp and Penney (1932) have introduced the "quenching" of the orbital moment in the $3d$ ions that gave a start for the (erroneous) consideration of $3d$ -ion magnetism as related to the spin-only moment.

QUASST, providing the discrete electronic structure, ix) enables the calculation of whole thermodynamics. The obtained temperature dependences of the heat capacity and of the paramagnetic susceptibility are in remarkably good agreement with experimental data for continuously increasing great number of compounds [1, 2, 7–12]. Our understanding of $4f/3d/5f$ -atom compounds is close to an original idea of Van Vleck from 1932 [13] that electronic and magnetic properties are largely determined by the atomic-like electronic structure.

QUASST points out x) the multipolar character of the electric field existing in a solid. The higher-order CEF interactions are very important. Higher-order CEF parameters reflect multipolar charge interactions. The parameters B_2^n , B_4^n and B_6^n , for instance, are associated with the quadrupolar, octupolar and hexadecapolar interactions, respectively, and all of them have enormous influence on the realized electronic structure. Note, that their influence cannot be treated as the subsequent expansion terms.

QUASST xi) distinguishes the atomic-like properties of the single atom and the macroscopic properties. In the simplest case the molar heat capacity is obtained from the single-ion heat capacity by multi-

plying by the Avogadro number. The same holds for the paramagnetic susceptibility and for the ordered magnetic moment. This is justified only in case of the simplest crystallographic structures and for the ferromagnetic state. In general, there can be in the crystal structure a few non-equivalent sites with the different lattice point symmetry. The further site differentiation can occur by the symmetry of the local crystal field. The principal axis of the electric field gradient can differ from site to site forming, for instance, the zig-zag structure. The local zig-zag structure is very typical for perovskite-like structures (LaMnO_3 , Sr_2RuO_4) where the tilt and rotations of local octahedra are commonly experimentally found. As the symmetry can be very low the principal axis of the quadrupolar (B_2^m), octupolar (B_4^m) and hexadecapolar (B_6^m) interactions is necessary to consider too. It makes the direct correlation between the atomic-like properties and macroscopic properties not always straightforward for low-symmetry compounds.

QUASST postulates xii) the lowering symmetry with the lowering temperature as much as possible as the general rule (the extension of the Jahn-Teller theorem). It causes that with the lowering temperatures we should take into account more and more inequivalent sites and more complex multipolar charge interactions what makes the CEF and QUASST calculations much more troublesome.

xiii) The magnetic state is related to the time-reversal symmetry (TRS) breaking that can be traced at the atomic scale as the Zeeman-like effect [1, 2, 8–10]. The nicest illustration for it is the splitting of the Kramers doublet ground state. The formation of the magnetic state is somehow forced by the lowering-energy demand - this lowering energy is nicely visible even in the atomic scale in case of the Kramers doublet ground state. In case of a non-Kramers system the existence of a closely-lying localized state helps the formation of the magnetic state (like for the d^4 systems in the octahedral surrounding).

xiv) Energies involved in the formation of the magnetic state are relatively weak. For NiO with T_N of 525 K the energy gain amounts to 3.25 kJ/mol (=33.5 meV/ion) [11]. It is much smaller than the Stoner splitting I , that is of order of 0.6-1.2 eV.

xv) The molecular field B_{mol} is quite small. In case of NiO B_{mol} amounts to 510 T [11] and the effect of this field is visible in the atomic-like discrete electronic structure. The Stoner splitting of 1 eV would correspond to a field of more than 4000 T. Our value is much more realistic.

a) QUASST makes the unification in the theoretical description of the 3d and 4f ions.

b) QUASST makes the unification in the theoretical description of the

5*f*- and 4*f*-ion compounds. Very good description of electronic, magnetic and spectroscopic properties of UPd₂Al₃ [8], UGa₂ [9], NpGa₂ [10] and NpPd₂Al₃ have been obtained within the CEF theory with the trivalent state of the actinide ions. The remarkably good applicability is really surprise knowing that all of these compounds are metallic. Moreover, UPd₂Al₃ exhibits at low temperatures superconductivity and the heavy-fermion behavior.

c) QUASST starts the discussion of the correlation among the *d* and *f* electrons from the very-strongly correlated limit.

d) QUASST recognizes that the strong correlation discussed for the 3*d*/4*f*/5*f* compounds are predominantly of the intra-atomic origin.

e) QUASST starts the description of a solid from the description of the involved atoms.

f) QUASST bridges the atomic physics and the solid-state physics. One can ask: "Is this atomic idea a new one in the solid-state physics?" Yes and no. No, as most of experimentalists naturally discuss their results in terms of local properties. Yes, as according to our knowledge no one has been able to openly resist to presently-in-fashion solid-state physics theories that simply ignore the existence of the atom in a solid arguing that the solid is so many-body object and that there are so strong intersite correlations that the individuality of atoms is lost. In the standard band-structure calculations the *f* and *d* electrons are taken as itinerant forming a band. In the band there is a continuum of the energy states within 1-5 eV. In our model there are discrete states with energy separations even less than 1000 times smaller (1 meV, but 0 in case of Kramers ions). No, as there are some text books written about the crystal field, let mention a book of Abragam and Bleaney [14] or Ballhausen [15]. Yes, as they applied the CEF approach to some diluted 3*d* systems, not to the concentrated ones. Yes, as they have not been consequent enough and by discussing different crystal-field approaches (weak, strong, ...) with further concepts (e.g. low- and high-spin states) they largely washed up the original idea. Please note that in the strong CEF approach the *n* 3*d* electrons are treated as largely independent, i.e. they do not form the highly-correlated 3*d*^{*n*} system in contrary to the present model. The electronic structures of the 3*d* ions resulting from the single-electron description are shown Fig. 3 - they are fundamentally different from our results, shown in the parts c of Figs 1 and 2. Our approach corresponds to the weak crystal-field approach (actually the intermediate crystal-field approach), but we point out the fundamental importance of the intra-atomic spin-orbit coupling, despite of its relative weakness for the 3*d* ions. Also yes, as at present this atomic-like picture is enormously prohibited in the leading physical journals and a little is

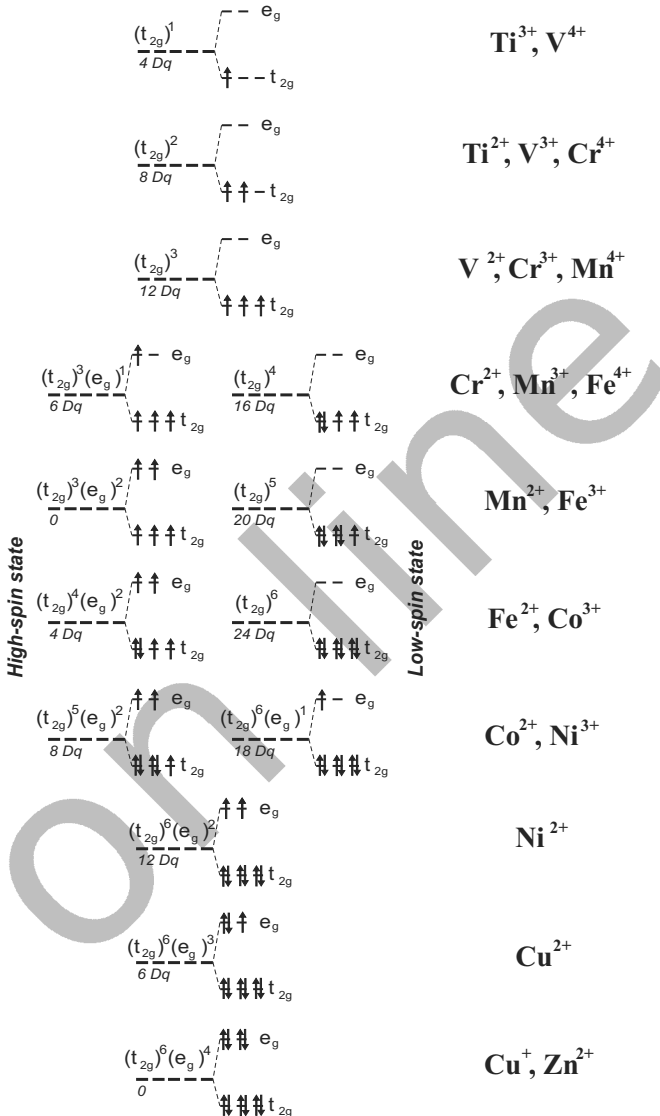


FIG. 3: The single-electron electronic structures of $3d^n$ ($4d^n$) electron systems. These strong crystal-field approach results are customarily recalled in the present discussion of properties of $3d$ -atom containing compounds. The violation of the 1st Hund's rule leads from the high-spin state to the low-spin state. In this description the 2nd Hund's rule and the orbital magnetism do not appear at all in contrast to the description shown in Figs 1 and 2.

said about the discrete states in the magnetic and strongly-correlated electron system conferences.

We would like to add, preceding unfounded critics, that we do not claim that everything can be explained only by single atoms but our point is that the proper, i.e. physically adequate starting point for the discussion of properties of a solid containing the open-shell atoms is the consideration of its atomic states. Our numerous computer experiments point out that e.g. the orbital moment has to be "unquenched" in the solid-state physics of $3d$ -atom containing compounds and our approach enables it. For instance, we have derived the orbital moment in NiO to be $0.54 \mu_B$ what amounts to 20 % of the total moment ($2.53 \mu_B$) [11]. Moreover, one should not consider our approach as the treatment of an isolated atom - we start the discussion of NiO from the consideration of the cation octahedra NiO_6 (more exactly - the d^8 system of the Ni^{2+} ion in the octahedral crystal field). The whole NaCl structure of NiO is built up from the edge sharing cation octahedra. The perovskite structure, for instance, is built up from the corner (and the edge) sharing cation octahedra along the c direction (in the a - b plane). Thus, such octahedra cover the whole macroscopic sample provided the perfect translational symmetry. The CEF parameters contain information about the interaction of the single ion with the whole charge surroundings. Our approach is in agreement with the general conviction about the importance of the electron correlations in description of open-shell compounds - in our approach we start from the very highly-correlated limit in contrary to a weak correlation limit of the LDA and LSDA approaches. In conclusion, on basis of the extended analysis of experimental results for the great number of compounds containing $4f$, $5f$ and $3d$ open-shell atoms we have developed the quantum atomistic solid-state theory. This theory points out the existence of the discrete electronic structure associated with atomic-like states of the involved $4f$, $3d$, $5f$ atoms. The existence of such the structure causes dramatic changes of the low-temperature electronic and magnetic properties like the formation (or not) of the local magnetic moment and its long-range magnetic order, temperature dependence of the magnetic susceptibility and of the heat capacity and according to us most of the experimentally observed anomalies originate from these discrete energy states. For the better illustration of our point of view the reader is asked to look into recent (1999) *Phys. Rev. Lett.* and *Phys. Rev. B* papers. In Ref. [16] authors, considering states of two $3d$ electrons of the V^{3+} ion in V_2O_3 , came out with the continuum electronic structure spread over 2.5 eV (Figs 2 and 3). In Ref. [17] two d electrons of the V^{3+} ion are considered to be largely independent. It shows that our quite reasonable atomic-like approach,

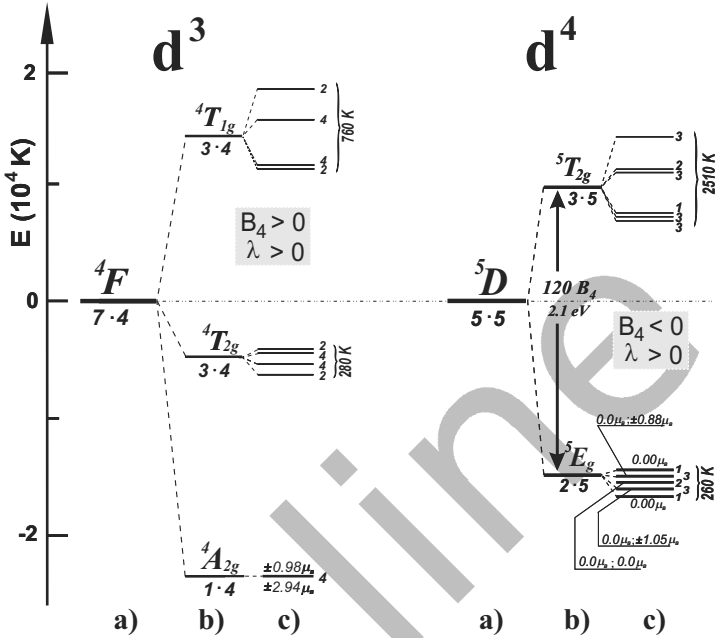


FIG. 4: The calculated atomic-like electronic structure of the highly-correlated $4d^3$ ($3d^3$) and $4d^4$ ($3d^4$) electron systems in the octahedral crystal field in the presence of the spin-orbit coupling. The electronic structure for the $4d^3$ ($3d^3$) and $4d^4$ ($3d^4$) systems is completely different.

yielding the description of the V^{3+} ion ($3d^2$ system) with the Hund's rules quantum numbers $S=1$ and $L=3$, is far from being accepted in presently-in-fashion theoretical approaches. In Ref. [18] the continuum electronic structure for six $3d$ electrons in FeO spreads over 8 eV (Fig. 8). In Refs [16–18] the orbital moment and the spin-orbit coupling is completely ignored. By this Letter we put the conjecture that in these cases the d electrons form the crystal-field discrete energy states with the importance of the s-o coupling. According to us in FeO, in the paramagnetic state, a quite similar structure to that presented in Ref. [4] and in Fig. 2 (for $3d^6$) is realized. In Ref. [19] the d and f electrons (in NiO and in Gd, respectively) are treated as itinerant (so according to us completely wrong). The continuous energy spectrum, spread over

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6 eV, for $4d$ electrons in recently-in-fashion compounds $\text{Sr}_3\text{Ru}_2\text{O}_7$ and $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ has been recently reported in Refs [20] and [21]. In these compounds the Ru atoms occur in the tetravalent (d^4) and pentavalent (d^3) states, but despite different valent state, band electronic structures are quite similar. In our approach the localized states for the d^3 (Ru^{5+}) and d^4 (Ru^{4+}) configurations are completely different as is shown in Fig. 4. Moreover, in our atomic approach there are 4-10 states in the energy range of 80 meV - an energy range that is 100 times smaller than the width of the d band in the band picture. Thanks these fundamental differences, both models can be experimentally verified in the future. We are convinced that the publication of our paper enables the open scientific discussion on the magnetism and on the electronic structure of $3d/4f/5f$ -atom containing compounds and we are ready for this discussion.

◆Dedicated to Hans Albert Bethe, the pioneer of the crystal-field theory, on his 95th birth anniversary (2 July 2001) with the best wishes.

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