Research Article

From atomic physics to solid-state physics: the case of LaMnO$_3$

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Magnetism and the low-energy electronic structure of LaMnO$_3$ are discussed starting from the atomic physics for the Mn^{3+} ion. We derived the discrete energy spectrum associated with the localized electron atomic-like crystal-field states of the Mn^{3+} ions. We take into account two Hund's rules, the spin-orbit coupling and crystal-field interactions. The derived discrete energy spectrum, in the scale of 1 meV, contrasts the continuous energy spectrum yielded by band theories. According to our atomic-like approach the d electrons in LaMnO$_3$ form the highly-correlated electron system $3d^4$ described by two Hund's rules quantum numbers S=2 and L=2. We take into account the local off-cubic Jahn-Teller distortion and the formation of the magnetic state. The resulting electronic structure is completely different from that presented in the current literature. The superiority of our model relies in the fact that it explains consistently properties of LaMnO$_3$, the insulating and magnetic ground state as well as thermodynamics, using well-established physical concepts. The model, that we call the Quantum Atomistic Solid-State Theory (QUASST), can be applied to other $3d$-/$4f$-/$5f$-atom containing compounds.

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Magnetism of compounds containing $3d$ atoms and, related to it, the nature of the low-energy, < 2 eV, electronic structure is still under very strong debate, see, e.g., Ref. [1] and references therein. The understanding of the magnetism and of the electronic structure is very closely related to a general problem "how to treat d electrons in $3d$-atom containing compounds". The fundamental controversy "how to treat d electrons" starts already at the beginning - should they be treated as localized or itinerant. Directly related to this problem is the structure of the available states: do they form the continuous energy spectrum like it is in the band picture or do they form the discrete energy spectrum typical for the localized states. Moreover, recently a concept of the orbital ordering has appeared in discussion of $LaMnO_3$ as it was presented in Science in April 2000. $LaMnO_3$ belong to the class of compounds known as Mott insulators in which, as it was formulated in Ref. [1], the internal degrees of freedom, associated with the spin and orbital ones, survive. The group of compounds known as Mott insulators reaches thousands and attracts the scientific interest by more than 50 years, from both theoretical and application point of view. The interest to $LaMnO_3$-based compounds has increased considerably after revealing its colossal magnetoresistance properties [1, 2]. Despite of enormous activities, both theoretical and experimental, understanding of the colossal magnetoresistance and, related to it, of the magnetism is still rather poor. We will present here an understanding of $LaMnO_3$ that differs substantially from that presented in [1], though we also use the term "orbital". In order to avoid a misunderstanding already at the beginning we say that authors of Ref. [1], despite of advocating for the orbital physics, quench the orbital angular momentum - in contrary, we point out the fundamental importance of the orbital angular momentum in the formation of the magnetism and of the electronic structure. The importance of low-energy electronic structure relies in the fact that it determines physical properties of real systems. These physical properties are of the application interest. Thus, we reveal also the orbital physics but it is fundamentally different one from that presented by authors of Ref. [1]. However, thanks the paper [1] the reader becomes familiar with present difficulties in the understanding of $3d$-atom compounds - very often one could get an impression, completely erroneous, that in the XXI century physicists know everything.

We try to understand properties of compounds containing open-shell $3d$-atoms taking as the start the atomic physics. In $LaMnO_3$ the manganese atoms are in the trivalent state as is anticipated from the compensated valences $La^{3+}Mn^{3+}O_3^{2-}$. Such the ionic picture is confirmed by the experimentally observed insulating ground state. The Mn^{3+} ion
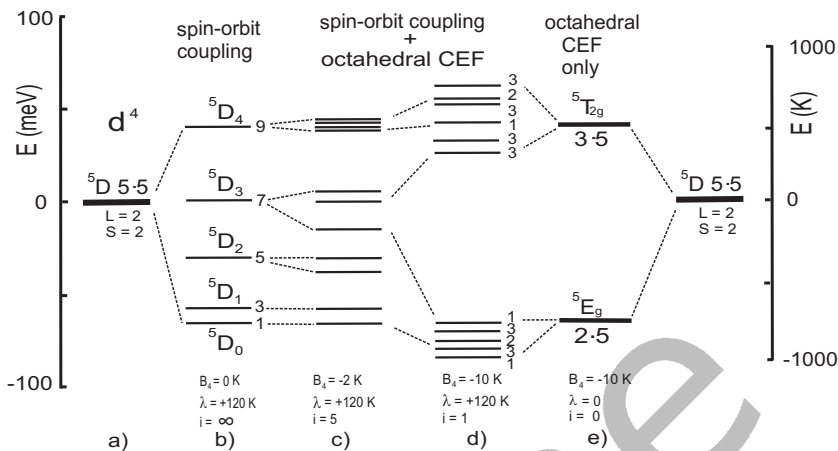
FIG. 1: The calculated influence of the strength of the octahedral crystal field, B_4, on the atomic states of the Mn^{3+} ion (MnIV), shown in part (b). i denotes the ratio of the overall spin-orbit effect (10 λ) to the overall crystal-field effect (120 $|B_4|$). In a real system, like $LaMnO_3$, i amounts to about 0.05-0.10 as the crystal-field interactions largely prevail the spin-orbit interactions and the CEF parameter B_4 amounts to -150 K.

in $LaMnO_3$, in contrast to the free ion, experiences additionally the crystal-electric-field (CEF) potential. This crystal-field potential at the Mn site depends on the charge distribution in its vicinity, that in the crystalline material is very anisotropic. The effect of the crystal field has a lot in common with the well-known in the atomic physics the Stark effect, Of course, in a crystal solid the Stark effect is much more complex due to the multipolar character of the electrostatic potential, with the importance of higher-order multipolar interactions than dipolar and quadrupolar ones. Moreover, Nature with the decreasing temperature involves further effects - a lattice distortion, magnetic interactions, that often lead to the magnetic state, and/or a site differentiation with respect to the local surroundings and the local symmetry. All these effects are experimentally observed in $LaMnO_3$, indeed, and these effects are computable in our approach. In a crystal there can be also a site differentiation with respect to the local charge - this effect involves, however, quite significant energies and we think that the charge degree of freedom does not play the significant role in the perfectly-stoichiometric $LaMnO_3$. In general, all the above-mentioned effects cause the subsequent lifting of the degeneracy of the free-atom states as well as the lowering energy of the ground state and a quite substantial spreading of the
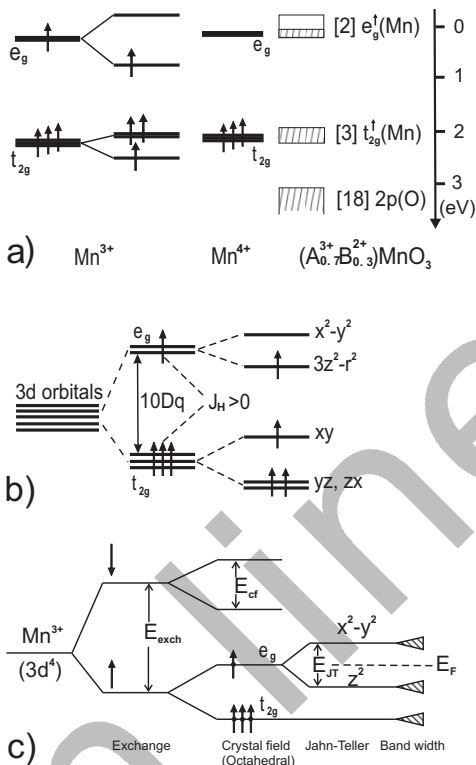
FIG. 2: a) Electronic structure of Mn^{3+} in octahedral coordination, before and after Jahn-Teller distortion and of Mn^{4+} in octahedral coordination; on the right the electronic structure for ferromagnetic manganites with x=0.3 with the formation of bands is shown, after Ref. 7; b) Splitting of the five-fold degenerate atomic $3d$ levels into lower t_{2g} and higher eg states. The particular Jahn-Teller distortion further lifts each degeneracy as shown, after [8, 9]; c) Energy level scheme for $LaMnO_3$ shown in Fig. 1 of Ref. [2]. Following Ref. [2] the values of E_{exch}, E_{cf} and E_{JT} from density functional calculations are around 3 eV, 2 eV and 1.5 eV respectively. Typical bandwidth is 1.5-2.0 eV. Jahn-Teller split orbitals, with the Fermi level lying between them, is a reason in this picture of the insulating ground state.

lowest states. In our atomic-like CEF approach [3, 4] four d electrons in the open $3d$ shell of the Mn^{3+} ion form the highly-correlated atomic-like $3d^4$ electron system. These strong correlations among the $3d$ electrons we account for, in a zero-order approximation, by the Russell-Saunders (LS) coupling scheme and two Hund's rules. These two Hund's rules
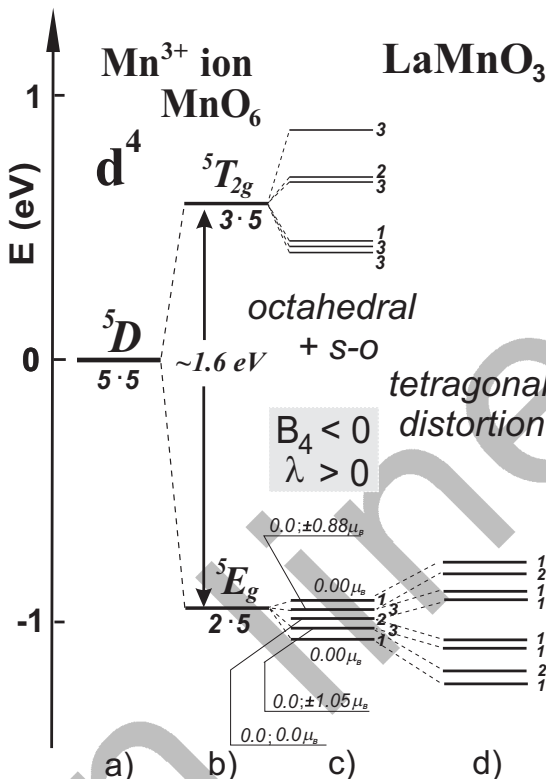
FIG. 3: The calculated fine electronic structure of the Mn^{3+} ion in the MnO_6 octahedron, realized in $LaMnO_3$, produced by the octahedral crystal field in the presence of the intra-atomic spin-orbit coupling (c) and by extra tetragonal distortion (d). The degeneracy and the magnetic moment of the states are shown. The fine splittings in c) and d) are not to the left-hand scale.

yield for the d^4 system from 14 atomic terms the ground term ^5D with S = 2 and L = 2. The states of the free ion are shown in Fig. 1b - in the free ion there is only the spin-orbit coupling active. Fig. 1b shows states for the free Mn^{3+} ion denoted in the atomic physics as Mn IV. The 25 states of the lowest atomic term are grouped into 5 multiplets as we know from the atomic physics and the 3rd Hund's rule. The 3rd Hund's rule yields the total angular momentum number J of 0, 1, 2, 3, and 4, with the ground multiplet $^5D_0$. The NIST Atomic Spectra Database [5] provides their energies at 0, 12.3, 35.6, 68.5 and 109.8 meV they can be quite well described by the spin-orbit coupling constant of 11.6 meV.

In a solid under the action of the usually dominant cubic crystal field, the ^{5}D term splits into the orbital triplet $^5T_{2g}$ and the orbital doublet ^5E_g with the energy separation Δ of about 1-3 eV. In the octahedral oxygen-anion surrounding of the Mn^{3+} ion, realized in the perovskite-like structure of $LaMnO_3$, the orbital doublet ^5E_g is lower as is shown in Fig. 1e. The lower ^5E_g ground subterm comes out from *ab initio* calculations of the hexadecapolar potential, denoted as the A_4 CEF coefficient, at the Mn site in the oxygen-anion octahedron. The A_4 CEF coefficient in the center of the oxygen-anion octahedron is positive. The A_4 CEF coefficient together with the Stevens factor β for the $3d^4$ system, of -2/63 (Stevens factors are, in fact, proportional to the respective multipolar moments of the aspherical $3d$-electron cloud), yields the negative value of the octahedral CEF parameter B_4 and consequently the ^5E_g ground subterm. The negative sign for B_4 has been derived already a pretty long time ago by Abragam and Bleaney ([6], see page 374) in discussion of the electron paramagnetic resonance (EPR) of $3d$-doped insulators. However, this result has been completely forgotten in the nowadays solid-state physics as in the nowadays discussion of $3d$-atom compounds figures like those presented in Figs 2a,b,c [7–10] with the t_{2g} ground orbitals and excited e_g orbitals are always considered (for one $3d$ electron, the $3d^1$ system β is positive, of 2/63).

The low-energy electronic structure has been calculated by us from the single-ion-like Hamiltonian, considered within the 25-fold spin-orbital space (the $|LSL_zS_z\rangle$ space), containing simultaneously the crystal-field (of the optional symmetry) and the spin-orbit coupling [11]. The structure shown in Figs 1c,d and 3c is obtained for the purely octahedral symmetry but in the presence of the spin-orbit coupling. The splitting of the ^5E_g subterm is the spin-orbit effect. It depends on the strength of the spin-orbit coupling and in case of the Mn^{3+} ion the splitting of the ^5E_g subterm is quite small, of 2-10 meV. The further splitting is produced by the tetragonal off-octahedral distortion, relevant to the situation realized in $LaMnO_3$. As seen from Fig. 3d the distortion decreases the energy of the ground state. Thus, the distortion can go spontaneously and satisfies the Jahn-Teller theorem.

In the magnetic state the magnetic inter-site interactions overweighs the temperature disordering. We have performed self-consistent calculations considering the magnetic interactions within the molecular-field approximation for two cases, for the magnetic structure with the magnetic moments along the tetragonal c axis and for moments within the tetragonal plane along the a or b axis. The same value for the molecular-field coefficient n of 17.7 K/μ_B^2 (=26.35 T/μ_B) produces the magnetic order below 95 K for moments along the tetragonal axis and below
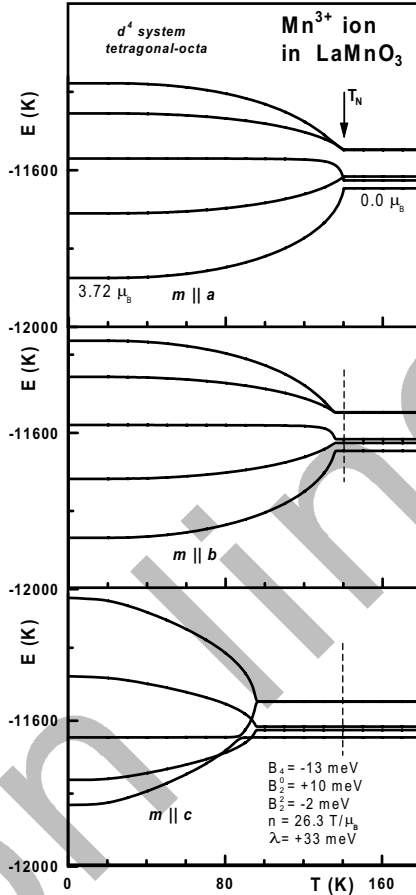
FIG. 4: Calculated temperature dependence of the lowest part, 5 states from Fig. 3d, of the fine electronic structure of the Mn^{3+} ion in $LaMnO_3$ in the magnetic state calculated for moments along a, b and c directions. The highest ordering temperature with 140 K is obtained for the magnetic moments along the a axis like it is in the reality. Only 5 states originating from the ^5E_g subterm are shown, other 5 are about 100 meV above and show quite similar behavior. This 100 meV splitting is mainly caused by the tetragonal distortion.

132 K/140 K for the magnetic order with moments along b/a axis, respectively, see Fig. 4. Of course, the ordering occurs for the moment alignment with the highest ordering temperature. Thus, our theoretical result with the preference of $LaMnO_3$ to order magnetically with mo-
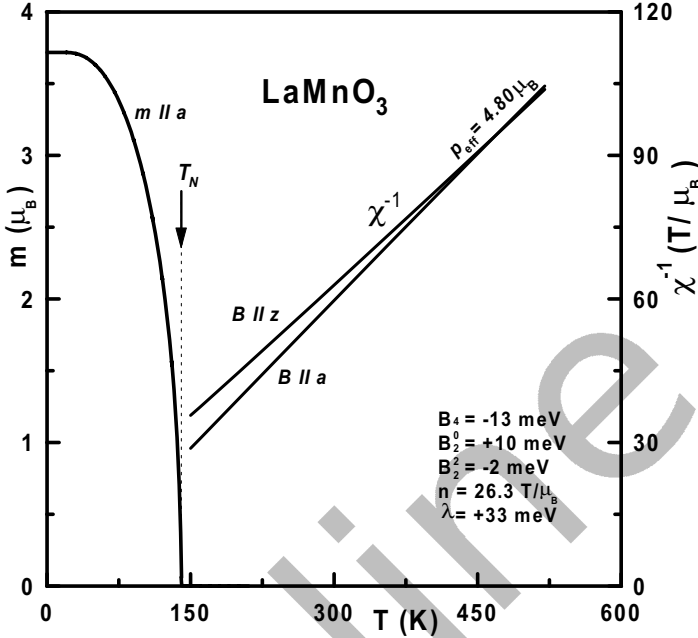
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FIG. 5: Calculated temperature dependence of the ordered magnetic moment, $T < T_N = 140$ K, and of the paramagnetic susceptibility for two main crystallographic directions.

ments along the a axis is in nice agreement with the experimental observation. In the magnetic state a molecular field is set up self-consistently. Its value is calculated to be 98 T at zero temperature. The electronic structure in the magnetic state, shown in Fig. 4, and its temperature dependence can be experimentally verified as it affects many physical properties like temperature dependence of the heat capacity, of the paramagnetic susceptibility χ, of the magnetic-moment value. The energy separations should be detected by energy spectroscopy experiments like Raman spectroscopy, for instance. In fact, we take the results of the Raman spectroscopy [12] revealing a number of well-defined energy excitations as a confirmation of our atomistic model [13]. Thus, according to us the interpretation of peaks observed in Raman spectra in the energy region up to 200 meV as orbital waves (orbitons) [12] is incorrect. In the light of the present studies there is no doubt that in this energy region one should expect single-ion-like excitations associated with atomic-like states of the Mn^{3+} ion.

The obtained value of the ordered magnetic moment at zero temper-

ature amounts to 3.72 μ_B. It is built up from the spin moment of +3.96 μ_B and from the orbital moment of -0.24 μ_B. The opposite sign of the spin and orbital moments mimics somehow the 3rd Hund rule. We point out that the opposite sign of the spin and orbital moments comes out directly in our calculations and is related to the positive sign of the intra-atomic spin-orbit coupling. The effective moment calculated from the computed χ^{-1} *vs* T plot, in the 300-400 K region amounts to 4.89 μ_B (c direction) and 4.65 μ_B (a direction), see Fig. 5. It is only slightly smaller value than the spin-only value of 4.90 μ_B what is a surprise owing to the fact that we take the full quantum orbital value L into calculations. The small orbital contribution to the susceptibility is caused by the weak spin-orbit coupling. This small orbital contribution has been recognized already in 1935 by Van Vleck and has led him to a widely-known statement about the quenching of the orbital moment in 3d-atom compounds, in contrast to rare-earth-atom compounds. We would like to point out that the relatively small orbital moment contribution to the susceptibility does not mean that the orbital quantum number L can be ignored as it yields completely physically-different electronic structure, as one can see comparing Fig. 2 and Fig. 3. The χ^{-1} *vs* T plot is practically the straight line in most cases the existence of the fine electronic structure causes the violation of the Curie-Weiss law and very anomalous χ *vs* T dependence like it is calculated for LaCoO$_3$ [11].

Such the atomic-like approach to solids containing 3d open-shell atoms seems to be very natural but the existence in the modern solid-state physics of so many theoretical approaches ignoring somehow the atomic physics proves that the atomic-like approach is far from being in fashion. In the current literature in prestigious physical journals the fundamentally different descriptions of the electronic structure and the magnetism of LaMnO$_3$ usually appear. The main theoretical stream is related to the band description. The more experimentally oriented papers recall some ingredients of the localized description as illustrated in Figs 2a-c. There is a number of band-structure calculations, based on different versions of the local density (LDA, LSDA) [14–19] and Hartree-Fock approximations (HFA) [20, 21]. The band results are schematically shown in Fig. 6. The LDA/LSDA results are slightly different from the HFA results as far as the position of Mn 3d states with respect to the Fermi level and the nature of states at the Fermi level are considered, but both yield continuous energy spectrum for the 3d states spread over 10 eV. Pari *et al.* have pointed out that the LSDA yields incorrectly metallic ground state for LaMnO$_3$ [16]. Later this outcome was claimed to be incorrect [17] with an argument that a gap, needed for the insu-
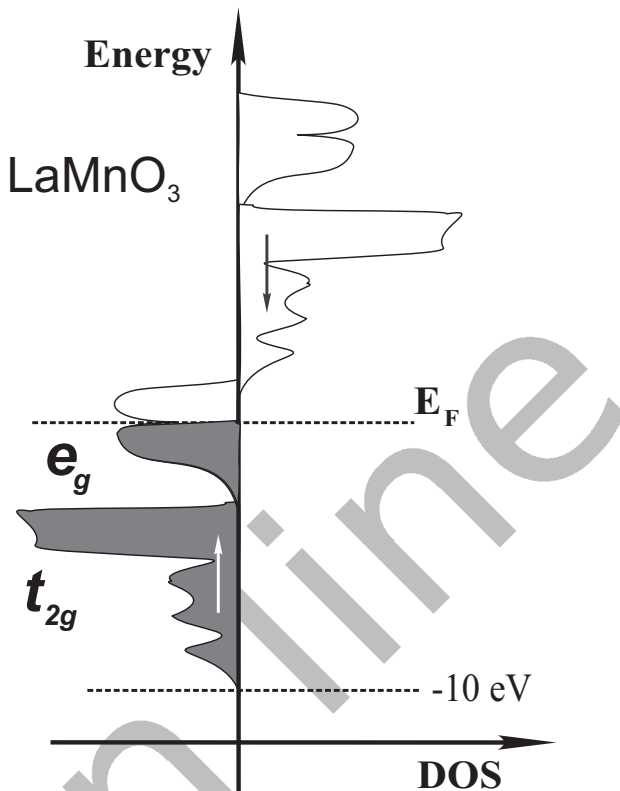
FIG. 6: Schematic description of the d states in LaMnO$_3$ within the band approach [14–21] obtained within the LSDA approach - there is the continuous energy spectrum. There is also some contribution from $2p$ states of oxygen. A slightly different picture is obtained within the Hartree-Fock approximation, but still d states form the continuous energy spectrum spread over 10 eV. A gap at the Fermi level is claimed to be formed due to the Jahn-Teller off-cubic distortion [17] - this mechanism seems to be ruled out after recent finding [28] that LaMnO$_3$ stays insulating despite of the closure of the J-T distortion.

lating state, within the band picture can be obtained by the Jahn-Teller distortion.

In the current localized-electron understanding 4 electrons (spins) of the Mn^{3+} ion are put subsequently one by one on the single-electron states formed for one d electron in the octahedral crystal field: three spins are put to t$_{2g}$ orbitals and the fourth occupies one of the higher e$_g$ orbitals (Fig. 2). Owing to one electron in the doublet e$_g$ orbitals one

can say that e_g is half filled and the e_g electron has got the orbital degree of freedom. According to Refs [7–10] such the electron/spin arrangement satisfies the first Hund's rule. In this approach the e_g electron plays the main role in the further description of properties of manganites [1] as the three t_{2g} electrons are thought to be largely bound.

The general shape of the bands presented in Fig. 6 can be somehow understood knowing the localized states of Figs 2a-c. The continuous energy spectrum looks like the smooth convolution on the available localized single $3d$ electron orbitals t_{2g} (fully occupied) and higher e_g orbitals (half-filled). The similarity of the band density of states and the energy level scheme of Figs 2a-c is related, according to us, to the single-electron treatment of the $3d$ electrons in both approaches. In contrast, the states shown in Figs 1 and 3 are many-electron states of the whole $3d^n$ electron system. At zero temperature only the lowest state is occupied. With increasing temperature higher states become thermally populated following the Boltzmann-distribution function. This temperature effect can be exactly calculated yielding thermodynamics, the temperature dependence of many physical properties like of the heat capacity, of the paramagnetic susceptibility (with the anisotropy), of the ordered moment and so on.

Our description of the electronic structure of $LaMnO_3$ proceeds within the intermediate crystal-field regime in contrary to the current-literature view that prefers the strong crystal field regime in the description of $3d$-atom compounds. According to our picture, the crystal field does not break the intra-atomic arrangement of electrons within the $3d$ shell. This our approach is in sharp contrast to the strong CEF regime that is the base for the single-electron description discussed previously with Figs 2 and 6. It means, that we think that the intra-atomic structure of an paramagnetic atom is largely preserved even when this atom becomes the full part of a solid - on this basis we have developed a Quantum Atomistic Solid-State Theory (QUASST) for compounds containing open $3d$-/$4f$-/$5f$-shell atoms [3]. This weak crystal-field approach, known within the rare-earth CEF community as the CEF approach, has been often successfully applied to $3d$-ion doped systems, when $3d$ ions are introduced as impurities, in interpretation of, for instance, electron-paramagnetic-resonance experiments [5, 22, 23]. We have successfully applied this approach to a $3d$-ion system where Co/Fe/Ni ions are the full part of a solid forming $LaCoO_3$, $FeBr_2$ or NiO [11, 13, 24–26]. Of course, in our picture the crystal field is much stronger (about 5 times) than the spin-orbit coupling as is generally accepted in the $3d$ magnetism, but this relatively weak spin-orbit coupling has enormous influence on the formed electronic states and $3d$-atom magnetic moment

[27].

We would like to point out that the presented approach should not be considered as the treatment of an isolated ion - we consider the cation in the octahedral crystal field. This octahedral crystal field is predominantly associated with the oxygen octahedron MnO_6. The perovskite structure is built up from the corner sharing octahedra MnO_6 - thus such the atomic structure occurs at each cation due to the translational symmetry. The strength of the crystal field interactions is determined by the whole charge surroundings, not only by the nearest oxygen octahedron. It makes that the CEF approach looks like a single-ion approach but in fact it describes the coherent states of the whole crystal. The parameters used are fully physical: the octahedral CEF parameter B_4 = -13 meV, the tetragonal B_2^0 = +10 meV, the orthorhombic B_2^2 = - 2 meV and the spin-orbit coupling λ = +33 meV. They yield overall effect of 1.6, 0.10, 0.002 and 0.33 eV, respectively. In general, it turns out that the electronic structure and the magnetism is governed by quite small energies.

In conclusion, we have presented the localized electron atomic-like crystal-field approach to the $3d$-electron states in $LaMnO_3$ that yields the discrete energy spectrum associated with the atomic-like states of the Mn^{3+} ions. We take into account two Hund's rules and the on-site spin-orbit coupling. The resulting electronic structure, with 10 states originating from the ^5E_g subterm, is completely different from that presented in the current literature. Our CEF-like model takes into account very strong correlations within $3d$ electrons that form highly-correlated electron system $3d^4$. These strong correlations are accounted for by two Hund's rules yielding S = 2 and L = 2. Our studies have revealed strong correlations between the local magnetic moment (its value and the direction) and the local distortions (more generally - the local symmetry of the crystal-field potential). Our atomic-like approach provides in the very natural way the insulating ground state for $LaMnO_3$ independently on the lattice distortions - it is in agreement with the recent experimental observation [28], that $LaMnO_3$ stays insulating despite of the disappearance of the J-T distortion. If so, it means that the objection arisen by Pari *et al.* [16] is a serious objection to the applicability of the band theory to $LaMnO_3$. The presented understanding with quantum mechanical level splittings concurs with the discussion of the physical origin of quantum phase transitions [29] as well as with early ideas of Bethe, Van Vleck and Kramers. The superiority of our model in description of $LaMnO_3$ relies in that it consistently describes both zero-temperature properties and thermodynamics, and it makes use of well-defined physical concepts. Good description of many elec-

tronic and magnetic properties within the many-electron CEF model indicates that the band-structure calculations have to be oriented into the very strong intra-atomic $d - d$ correlation limit in order to get the ground state in agreement with two Hund's rules and to take into account the intra-atomic spin-orbit coupling. We are convinced that it is the highest time in the solid-state physics to "unquench" the orbital moment for the description of compounds containing $3d$ atoms.

Added 28 Sept 2007:

1. here we use $\lambda = 33$ meV, now we think that λ should be about 12 meV; it influences only slightly numerical results of our paper - the main results on the discrete electronic structure are the same,

2. this paper has been written after long discussion with Phys. Rev. Lett. and Phys. Rev. B Editors on discrete electronic states in LaMnO$_3$ - as is documented in the subsequent paper and the attached correspondence; the referee and Editors have rejected our paper arguing errors in our computer program claiming that the ^5E_g state is not splitted (see p. 24 and 27) - after long discusions and extra our results (p. 26, 28-30, 32-33) the referee has admitted that our calculations are correct writting "I am full of apologies to the author. I tried to make a simple estimate of the spin-orbit effects but made a trivial error ...." (page 31).

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