

On the crystal field in the modern solid-state theory[♣]

*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
(cond-mat/0504199, 8 April 2005; published 30 March 2007)*

We point out the high physical correctness of the use and the concept of the crystal-field approach, even if is used to metallic magnetic materials of transition-metal 3d/4f/5f compounds. We discuss the place of the crystal-field theory in modern solid-state physics and we point out the necessity to consider the crystal-field approach with the spin-orbit coupling and strong electron correlations, as a contrast to the single-electron version of the crystal field customarily used for 3d electrons. We have extended the strongly-correlated crystal-field theory to a Quantum Atomistic Solid-State Theory (QUASST) to account for the translational symmetry and inter-site spin-dependent interactions indispensable for formation of magnetically-ordered state. We have correlated macroscopic magnetic and electronic properties with the atomic-scale electronic structure for ErNi₅, UPd₂Al₃, FeBr₂, LaCoO₃ and LaMnO₃. In QUASST we have made unification of 3d and rare-earth compounds in description of the low-energy electronic structures and magnetism of open 3d-/4f-/5f-shell electrons. QUASST offers consistent description of zero-temperature properties and thermodynamic properties of 4f-/5f-/3d-atom containing compounds. Our studies indicate that it is the highest time to unquench the orbital magnetism in 3d oxides.

PACS: 71.70.Ch, 75.10.-b

Keywords: Crystal Field, spin-orbit coupling, Heavy fermion, magnetism, 3d oxides

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

I. INTRODUCTION

The use and the concept of the crystal-field approach, if used to metallic magnetic materials, has been recognized as erroneous by the Highest Scientific Council of the Polish Government (CK ds SITN, later in short CK) in its decision BCK-V-O-819/03 on 31.05.2004. The full decision, in Polish and in part in English, is available on www.css-physics.edu.pl. This reproach we denote as No 1. Such a formulation of the reproach should not be read that this Council agrees that the use and the concept of the crystal-field approach, if used to nonmetallic magnetic materials, is correct. The above decision is somehow in a common line of depreciation of the crystal field (CEF) theory in the modern solid-state theories. Let mention, that a recently edited (2003) book of Mohn "Magnetism in the solid state" [1], being an overview of presently-in-fashion magnetic theories, mentions only one position on the localized magnetism: a book of Van Vleck from 1932 [2] (apart of this shortage the book is very nice and we highly recommend it). Diagrams of Tanabe-Sugano [3], known already 50 years, are not exploited in the modern solid-state physics theories for description of 3d-ion compounds and the orbital magnetic moment only recently starts to draw the proper attention. Theoretical approaches yielding continuous wide 1-10 eV energy bands for 3d/4f/5f states overwhelm the present solid-state theory. On other side the CEF approach, yielding the discrete electronic structure for 3d/4f/5f electrons with details at least 1000 times smaller, below 1 meV, is often recalled by experimentalists in order to analyze obtained experimental results. Thus, one can say that there is at present a large gap between theory and experiment in description of 3d/4f/5f states.

In this paper we would like to discuss the place of the crystal-field theory in the modern solid-state physics, to clarify our understanding of the crystal field approach and to inform about the administrative interference to Physics in judging the physical correctness, rather incorrectness, of the crystal-field theory to metallic magnetic materials. We claim that the simplest and most natural theoretical approach, as the CEF theory is, has not been exploited enough for showing its physical adequacy and its total theoretical rejection is premature.

We by years openly formulate the need of taking into account the crystal field in description of 3d/4f/5f compounds, even these exhibiting the heavy-fermion phenomena (mainly 4f or 5f compounds) and insulating 3d oxides. In order to avoid undeserved critics we do not claim that CEF explains everything but we claim that CEF effects should be clarified at first (properly!!!) in any analysis of physical properties of any transition-metal compound. Also we do not claim to invent the crystal-field theory - we point out its importance in the specific social conditions of the end of the XX and the beginning of the XXI century,

when the crystal-field theory is somehow prohibited and rejected from magnetic theories.

The biggest problem in this discussion is related to a fact that the crystal-field theory has within the magnetic community in last 30 years a special place - being continuously rejected from the scientific life permanently appears as an unavioded approach for explanation of properties of real compounds. The crystal-field theory is in the modern solid-state theory like an unwilling child, 75 years old already.

II. FURTHER ADMINISTRATIVE DETAILS

The above mentioned objection was the only one scientific reproach in the administrative decision CK-04 towards the disqualification of the scientific activity of R. J. Radwanski. These scientific achievements account for a date of 7 May 2001 126 publications in international journals from the SCI philadelphia list and two promoted doctors. The full list of these publications is available on www.css-physics.edu.pl. There are also further 19 publications to 31.12.2004. See also 51 internet papers in ArXiv/cond-mat. In an earlier decision BCK-V-P-1262/02 of 24.03.2003, denoted latter as CK-03, CK has formulated another reproach, No 2, that "the used by Radwanski crystal-field approach is oversimplified, and the agreement of calculations with experiments is accidental."

These two decisions have been undertaken by means of opinions with the negative conclusion of Prof. Prof. H. Szymczak (November 2001), J. Sznajd (February 2003), Prof. A. M. Oles (December 2003) and of J. Klamut (April 2004). For the final decision two last opinions have been crucial. All of the referees belong to the best polish solid-state physicists and magneticians, so such opinions deserve on the serious attention by the magnetic community, not only polish but the international one. Opinions with the positive conclusion of Prof. Prof. K. Krop (October 2001), R. Mienas (April 2002) and K. Wysokinski (December 2002) have been found insufficient, in light of four negative opinions, to provide evidence for substantial scientific achievements required by the Polish law.

III. CRYSTAL FIELD IN MODERN SOLID-STATE PHYSICS AND ITS EXTENSION TO QUANTUM ATOMISTIC SOLID STATE THEORY

These decisions and objections become a part of the long-lasting world discussion going on about the use and the applicability of the CEF approach. This discussion lasts already 75 years as the CEF theory has

been started in 1929 by Bethe and followed by Kramers, Van Vleck and many, many others. Despite of 75 years and in meantime (1936-1938) formulation of the competitive band theory there is no consensus within the modern solid-state physics on the description of compounds containing transition-metal atoms with open 3d/4f/5f shells. These compounds exhibit so exciting phenomena like heavy-fermion behaviour at low temperatures and unexpected, in frame of band models, insulating ground state of 3d monoxides. In such scientific circumstances the decision of CK disqualifying the crystal-field theory is, according to us, premature and simply harmful to Physics. The most important is a fact, that important polish physicists by means of CK like to solve a serious scientific problem by means of the administration decision. From such a point of view this decision is a curious one as the European civilization already 370 years ago has learnt that no administrative inquisition-like decision, even of the highest level, can solve any scientific problem. We add that nobody has questioned in a scientific way anyone of our published papers!!! We admit that we suffer often an unscientific treatment of our submissions by Editors, who often find them simply not suitable without a clear scientific formulation of objections. We are sure, however, that a good science will always win, i.e. will show its physical adequacy and the conceptual fertility, and we also know from the history of science that good theories suffer often seriously for a pretty long time. Thus we continue our studies by more than 20 years and we are optimists. As violation of scientific rules we presume the rejection to publish a Comment, that corrects a recently published paper. In a consequence, for instance, oversimplified electronic structures of 3d ions, without strong correlations and without the spin-orbit coupling, still appear in *Phys. Rev. Lett.* and *Phys. Rev. B* despite of our (not suitable) submission "Relativistic effects in the electronic structure for 3d paramagnetic ions" PRL-LS 6925 from 1997 (available at ArXiv cond-mat/9907140).

Theoretical hypothesis of our 20 years research can be formulated as: macroscopic properties of compounds containing open-shell 3d/4f/5f atoms are predominantly determined by the low-energy discrete electronic structure, with separations below 1 meV. These states originate from atomic-like energy states of 3d/4f/5f ions. For description of these atomic-like states the local surroundings, crystal-field, spin-orbit and strong intra-atomic correlations have to be taken into account. As for description of a crystalline solid it is necessary to consider at least the translational symmetry and inter-site interactions, in particular spin-dependent interactions indispensable for formation of magnetically-ordered state, we have extended the CEF theory to an Quantum Atomic Solid State Theory (QUASST) [4, 5]. The CEF theory is, however,

the basic ingredient of QUASST, particularly important for the physical understanding and the overall scientific paradigm. Coming out with QUASST we would like to skip somehow the crystal-field theory that has got a negative meaning in the solid-state physics, becoming a synonym of the oversimplified point-charge model. We hope that magnetic theoreticians give some credit for QUASST to allow showing its applicability and usefulness for understanding of transition-metal compounds.

The crystal field gives explanation for the physical origin of the observed low-energy electronic structure, yielding their nature and a well-defined number. Strong intra-atomic correlations assure that these states are describable for an atom being the full part of a solid like in the free ion. It means that in QUASST we assume that the atomic-like integrity is preserved even when the given atom becomes the full part of a solid. It is a very strong assumption but taking into account that it is based on the generally-accepted concept of the atomistic construction of matter surely is worth to be thoroughly studied. We are consequently doing it in the Center of Solid State Physics in Krakow. The valency of the atom in a solid depends on the partner(s) and the stoichiometry. It can be 3+ in case of Pr_2O_3 , but 4+ for PrO_2 . In metallic PrNi_5 , without judging the formal stoichiometry of Pr and Ni atoms, the observed discrete electronic structure turns out to be related to the $4f^2$ configuration occurring formally in the Pr^{3+} ion.

IV. THE CEF APPROACH AND QUASST IN CONVENTIONAL 4f

Among others Radwanski and Franse in years 1984-1995 have put a substantial contribution to show the physical adequacy of the CEF approach to conventional 4f compounds, like $\text{Ho}_2\text{Co}_{17}$, $\text{Dy}_2\text{Co}_{17}$, $\text{Nd}_2\text{Fe}_{14}\text{B}$, ErNi_5 , DyNi_5 , NdNi_5 , PrNi_5 , .. All of them are metallic. All are magnetic, apart of PrNi_5 down to 1 K. By physical adequacy we understand a highly consistent description of physical properties. Let focus on (anisotropic) magnetic properties of all above mentioned compounds. For it we correlated macroscopic properties, like value of the magnetic moment and its direction in the crystal, with atomic-scale properties like localized states with (low-)energies and eigenfunctions. By it we could prove that the observed huge anisotropy is predominantly of the single-ion origin. The derived CEF-like electronic structure from high-field magnetization measurements have been later positively verified by specific heat measurements [6]. A conical structure of $\text{Nd}_2\text{Fe}_{14}\text{B}$ below 140 K has been nicely described within the CEF theory revealing the importance of higher-order CEF interactions [7]. The importance of

higher-order CEF interactions is manifest again in the first-order metamagnetic transition at 17 T.

The model analysis of the overall temperature dependence of the specific heat is shown in Fig. 1. Fig. 2 shows the fine electronic structure of the $4f^{11}$ configuration (the Er^{3+} ion) associated with the $^4I_{15/2}$ ground multiplet. The perfect description both in magnetic and paramagnetic state with the λ peak at T_c should be noted. Concluding ErNi_5 we say that in metallic magnetic compound coexist localized electrons having discrete states with conduction electrons originating from outer shells of Er and Ni. Magnetic and electronic properties are predominantly governed by localized electrons with states determined by CEF interactions.

The CEF theory at the start points two things. One, that a solid is not a homogeneous jellium (magma) but there exists varied in space the electrostatic potential obviously due to charge polarized atoms and electrons (the simplest version is a charge point ionic model). Secondly, a 3d/4f/5f paramagnetic atom serves as an atomic-scale agent to probe this potential. The CEF theory points out the multipolar character of this electrostatic potential. It is reflected in subsequent orders of CEF parameters (quadrupolar - B_2^0 , B_2^2 parameters; octupolar - B_4^0 , B_4^4 , , dodehexapolar B_6^0 , B_6^6 , ..). For a paramagnetic ion this multipolar potential causes the splitting of its ionic electronic structure. This splitting is a hallmark of the CEF theory. This splitting in case of 4f compounds is surprisingly well describable making use of the total angular momentum quantum number J as the good quantum number. Actually, we should work with the all-term electronic structure instead of the one, Hund's rule, ground multiplet only. The successful approximation with only one multiplet is due to the strong spin-orbit coupling that causes the excited multiplet to lie at least 0.3 eV above the ground multiplet preventing its substantial thermal population at, say, room temperature. Energies of this electronic structure can be later verified by, for instance, specific heat measurements and by spectroscopic measurements using inelastic neutron scatterings. The eigenfunction of the ground state bears information about the magnetic moment, its value and the direction, a fact that we strongly employ in our studies.

As a strong confirmation of the CEF approach we take the possibility of prediction of magnetic properties of the isostructural compound with another rare-earth atom. Using the single-ion scaling we had predicted in 1986, for instance, a value of the transition field of 26 T for $\text{Dy}_2\text{Co}_{17}$ basing on 19 T for $\text{Ho}_2\text{Co}_{17}$. In years 1991-1995 a remarkably consistent description within the CEF approach has been obtained for the RNi_5 series, both zero-temperature properties and thermodynamics. All of the

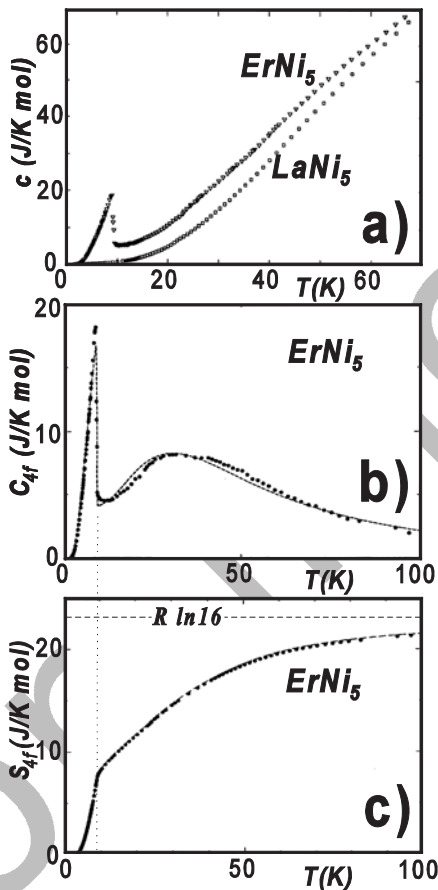


FIG. 1: Magnetic phase transition in ErNi_5 . a) Temperature dependence of the experimental heat capacity of single crystalline ErNi_5 and LaNi_5 ; b) Temperature variation of the contribution of the f subsystem to the heat capacity of ErNi_5 (points - experimental data [6]). The dotted line shows the f -subsystem contribution calculated for the atomic-like discrete energy spectrum determined by the strong spin-orbit coupling, CEF and spin-spin interactions [8].

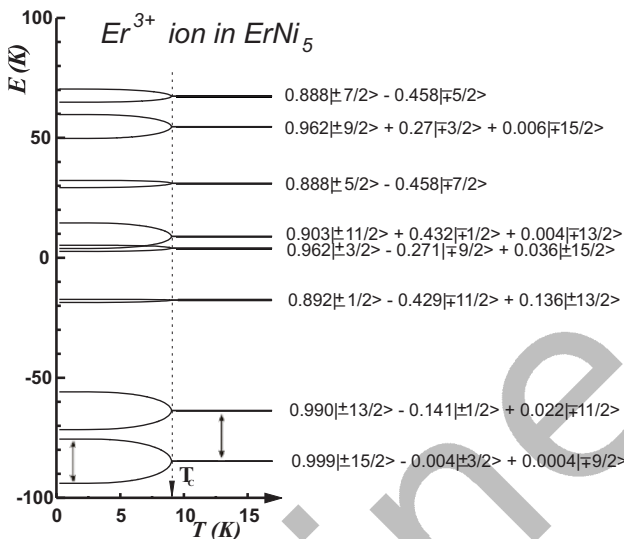


FIG. 2: The calculated fine electronic structure of the $4f^{11}$ configuration (the Er^{3+} ion) in $ErNi_5$. Below T_c of 9 K the magnetic state is formed what becomes visible by the splitting of Kramers doublets [8].

above mentioned compounds, except $PrNi_5$, are magnetically ordered. Thus, the calling the applied approach as the CEF approach is only a nick-name pointing out the fundamental role of CEF states for the magnetic and electronic properties. Of course, a magnetic order cannot be obtained within the purely CEF approach. However, we know what happens to CEF states when the magnetic order is formed. The magnetic state develops on the CEF states. In fact, all of the analysis of RNi_5 compounds illustrate the action of the QUASST theory.

Sub-Conclusion: there is wide experimental evidence for the existence of CEF states in rare-earth (4f) compounds, both metallic and ionic. From our studies of ionic compounds we can mention Nd_2CuO_4 and $ErBa_2CuO_7$.

V. EXTENSION OF THE CEF APPROACH TO ACTINIDES (5f COMPOUNDS)

Just after the first experimental results on newly discovered in group of Prof. Frank Steglich heavy-fermion metal UPd_2Al_3 Radwanski and Franse in 1992 have described the specific heat, from 4 to 300 K, as

related to the $5f^3$ (U^{3+}) configuration. We have managed to describe the overall temperature dependence with a Schottky-like peak at 50 K and a λ -type peak related to the antiferromagnetic state formed at T_N of 14 K. This energy level scheme has been confirmed by INS experiment of Krimmel/Steglich in 1996 [9] as we pointed out in year of 2000 [10]. The observation of well-defined localized CEF excitations in heavy-fermion metal UPd_2Al_3 we take as great confirmation of our atomistic approach. With great pleasure we have noted in year of 2001 a change of mind of Fulde and Zwicknagl from the itinerant picture for all f electrons to a dual model with two fully localized f electrons [11]. Two or three localized electrons we treat as a minor problem, because the main theoretical difference is related to the itinerant or localized point of view. For the scientific honesty we have to mention that the problem of localized states in UPd_2Al_3 is not yet over - another German group of Lander with coworkers quite recently claim that there is no evidence for the localized states in UPd_2Al_3 [12]. Just after appearance of these doubts we again clearly defined our point of view and our interpretation with the $5f^3$ configuration [13].

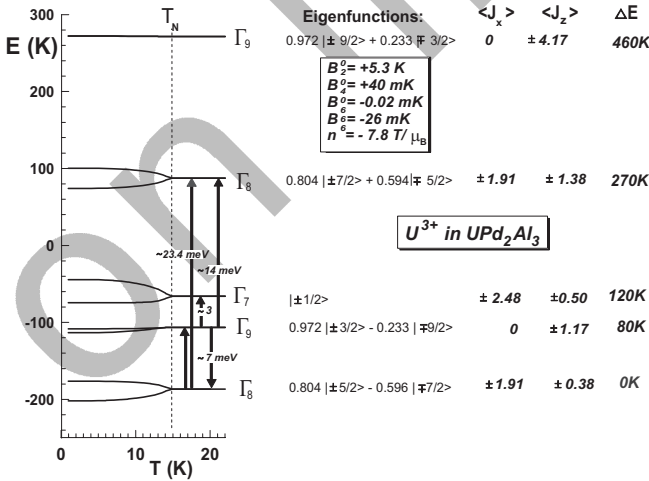


FIG. 3: Energy level scheme of the $5f^3$ (the U^{3+} ion) in UPd_2Al_3 taken from Refs [10, 13]. Arrows indicate transitions which we have attributed to excitations revealed by inelastic-neutron-scattering experiments of Krimmel *et al.* [9].

We prefer 3 f electrons owing to the intrinsic dynamics of the Kramers system, states of which are established by the atomic physics (in partic-

ular the number of states and their many-electron atomic-like nature). We can add that no one succeeded in description of the observed transitions and other properties to the $5f^2$ configuration with the similar consistency to ours.

The derived electronic structure accounts, apart of the INS excitations, also surprisingly well for the overall temperature dependence of the heat capacity, the substantial uranium magnetic moment and its direction. We make use of a single-ion like Hamiltonian, the same as has been used for ErNi_5 , for the ground multiplet $J=9/2$ [6, 16]:

$$H = H_{CF} + H_{f-f} = \sum \sum B_n^m O_n^m + n_{RR} g^2 \mu_B^2 \left(-J \langle J \rangle + \frac{1}{2} \langle J \rangle^2 \right)$$

The first term is the crystal-field Hamiltonian. The second term takes into account intersite spin-dependent interactions (n_{RR} - molecular field coefficient, $g=11/8$ - Lande factor) that produce the magnetic order below T_N what is seen in Fig. 3 as the appearance of the splitting of the Kramers doublets and in experiment as the λ -peak in the heat capacity at T_N .

The splitting energy between two conjugate Kramers ground state agrees surprisingly well, both the value of the energy and its temperature dependence, to a low-energy excitation of 1.7 meV at $T=0$ K observed by Sato *et al.* [14, 15], which has been attributed by them to a magnetic exciton. Thus, we are convinced that the $5f^3(\text{U}^{3+})$ scheme provides a clear physical explanation for the 1.7 meV excitation (magnetic exciton) - this excitation is associated to the removal of the Kramers-doublet ground state degeneracy in the antiferromagnetic state.

For actinides we also should mention the consistent description ($5f^3$, U^{3+}) of a ferromagnetic metal UGa_2 , T_c of 125 K, both zero-temperature properties (magnetic moment of $2.7 \mu_B$ lying in the hexagonal plane, $T_c=125$ K) and thermodynamics (temperature dependence of the specific heat and of anisotropic paramagnetic susceptibility) [16]. Later this description has been extended to NpGa_2 ($5f^4$, Np^{3+}), isostructural easy axis ferromagnet properties of which has been described using the single-ion correlation (Stevens factors) [17].

Recently in autumn of 2003 a well-defined localized excitation has been observed in heavy-fermion metal YbRh_2Si_2 . Sichelschmidt from F. Steglich group has managed to observe in this heavy-fermion metal at temperature $T=1.5$ K an ESR signal typical for the localized Yb^{3+} ion [18]. The observation of the ESR signal is a large surprise as YbRh_2Si_2 was regarded as a prominent heavy-fermion metal with the Kondo temperature T_K , of 25-30 K. The Kondo model does not expect localized states to exist at temperatures lower than T_K , whereas temperature of

1.5 K is more than 10 times smaller than T_K . Surely, such the observation calls for the rejection, or at least a substantial revision of the Kondo lattice theory. We are convinced that this revision will go to our CEF based understanding of the heavy-fermion phenomena with the importance of the local Kramers doublet ground state. Just after the Sichelschmidt/Steglich discovery we have described the g tensor and derived two sets of CEF parameters for Γ_6 and Γ_7 CEF ground states [19].

Sub-conclusion: We take these examples as further evidence for the applicability of the CEF-based approach to actinides and anomalous 4f/5f compounds. Our basic idea for the localized CEF origin of heavy-fermion phenomena has been formulated already in 1992 [20]. A report of CSSP-4/95 "Physics of heavy-fermion phenomena" [21] has been widely distributed to the leading scientists over 400 copies, including the International Board of SCES-94 and SCES-95. Our CEF-based interpretation of the heavy-fermion phenomena has been put in 1995 to the scientific protection of the Prezes of the Polish Academy of Science.

VI. ANOMALOUS PROPERTIES AND HEAVY-FERMION BEHAVIOR

In our understanding of anomalous 4f/5f compounds the localized Kramers doublet ground state plays the essential role [20, 21]. A lattice of Kramers ions with the local Kramers doublet ground state is the physical realization of the anisotropic spin liquid postulated *ad hoc* in heavy-fermion theories. According to us, the heavy-fermion behavior is related to difficulties in the removal of the Kramers doublet degeneracy. The local Kramers doublet is always formed for a strongly-correlated odd-number electron system. The removal of the Kramers degeneracy is equivalent to the formation of the magnetic state, characterized by breaking of the time-reversal symmetry. There can be different reason for this difficulty in the removal of the Kramers degeneracy (this difficulty can be called as a quantum entanglement of two Kramers conjugate states) causing its removal at low temperatures only. The Kramers-doublet degeneracy has to be removed before the system approaches zero temperature. In this view heavy-fermion state is a magnetic state. In contrast to well-defined magnetic/paramagnetic transition characterized by the lambda-type peak in the specific heat the magnetic state in heavy-fermion compounds is not uniformed, being of the spin-fluctuation type. There is a site-to-site change of value of the Kramers doublet splitting. Associated with it is a site-to-site change of the value of the local magnetic moment and its direction. Thus one can model such magnetic state by a statistical distribution

of the 0-0.3 meV splittings and of Kondo temperatures. In QUASST heavy-fermion excitations are neutral spin-like excitations between conjugate local Kramers states. These thermal excitations are associated with the reversal of spin. In our picture f electrons (exactly f electron states) are localized, whereas f excitations looks like itinerant (no one can say which exactly atom becomes excited). Our explanation with localized f electrons is unpopular within the magnetic community which prefers itinerant f electrons. If f electrons would be really itinerant than the conductivity of a heavy-fermion compound would be larger than the reference La/Y/Lu compound. But in experiment is always opposite - the resistivity of a heavy-fermion compound is always larger than the reference system. Finally we can add that in QUASST CEF-like f states do not lie at the Fermi energy. The Fermi surface is established for itinerant conduction electrons only. Moreover, in QUASST the heavy-fermion like phenomena at low temperatures can occur also in ionic compounds. This analysis of anomalous and heavy-fermion behavior in transition-metal compounds was not a subject of evaluation by CK - here it was added for the completeness reasons.

VII. 3d IONIC COMPOUNDS

In 1996 we have realized that a standard approach to electronic structures and magnetism of 3d-ion compounds substantially differ from that used in rare-earth compounds. Namely, owing to the weakness of the spin-orbit coupling, in 3d compounds the spin-orbit coupling has been customarily ignored. As a consequence the magnetic moment was essentially of the spin-type only whereas the electronic structure was built from the orbital-only states. Moreover, the concept of electronic structures and magnetism was built on single-electron states, t_{2g} and e_g orbitals known from the octahedral crystal field, with neglecting intra-atomic electron correlations among d shell. In 1997 we have performed calculations for the spin-orbit effect on the electronic states of 3d paramagnetic ions in the octahedral crystal field revealing a variety of low-energy states, Fig. 4 [22, 23]. For these calculations we have taken into account strong correlations among electrons in the 3d shell by considering many-electron states and two Hund's rules. These structures have been put in 2000 to the scientific protection of the President of the American Physical Society.

According to the Quantum Atomistic Solid-State theory the atomic-like electronic structures, shown in (c), are preserved also in a solid. The shown states are many electron states of the whole d^n configuration. At zero temperature only the lowest state is occupied. The higher states

become populated with the increasing temperature. In Fig. 4 on the lowest levels the magnetic moment (in μ_B) are written. They are not integer. It means that a general conviction that the localized model gives the magnetic moment of the unpaired n localized d electrons as $2n\mu_B$ (or $(10-2n)\mu_B$) is not true.

This approach called a strongly-correlated crystal field approach [23] is in contrast to the single-electron crystal-field approach customarily presently used. By doing it we have made unification of 3d and rare-earth compounds in description of the low-energy electronic structures and magnetism, of course keeping the relevant strength of the spin-orbit coupling. We have calculated the low-energy electronic structure and correlate it with magnetic and electronic properties, e.g. ${}^3T_{1g}$ of the V^{3+} ion in $LaVO_3$ and 5E_g of the Mn^{3+} ion in $LaMnO_3$. In SCES-02 there was a reproach to us that these ground subterms are incorrect owing to literature t_{2g}^2 and $t_{2g}^3e_g$ configuration, with the e_g orbital higher whereas derived by us 5E_g subterm is lower. Despite of our long explanations, explaining lower and capital symbols, the papers have been rejected - the International Advisory Board have been informed about this controversy by the Chairman of SCES-02. Just after, our solution with the ground subterm ${}^3T_{1g}$ for the V^{3+} ion ($3d^2$ configuration) in $LaVO_3$ or V_2O_3 and 5E_g for the Mn^{3+} ion ($3d^4$ configuration) in $LaMnO_3$ has been put to the scientific protection of the Rector of the Jagiellonian University in Krakow and of the AGH University of Mining and Metallurgy. Recently A. M. Oles, the vice chairman of SCES-02, has admitted the correctness of our ground states in $LaVO_3$ (V_2O_3) and in $LaMnO_3$. We await for further scientific steps.

We have clarified the electronic structure and magnetism of $LaCoO_3$ [24]. It turns out that relatively strong octahedral crystal field yields the breaking of Hund's rules establishing the ground subterm 1A_1 originating from 1I term that in the free Co^{3+} ion lies 4.45 eV above the ground term. However, the octahedral crystal field interactions are too weak to break intra-atomic correlations and to create conditions for the applicability of the single-electron approach. It means that the experimentally observed states are still described within the atomistic QUASST approach. By perfect reproduction of the ESR results of Noguchi from 2002 [25] on the excited triplet we have proved that this triplet is a part of the ${}^5T_{2g}$ sub-term, originating from the high-spin 5D term. It means that there is no intermediate spin-state, with $S=1$, despite of theoretical LDA-U calculations of Korotin et al. from 1996 [26] and a numerous literature on this subject. Thus, we have confirmed the substantial physical applicability of the atomistic CEF-based Tanabe-Sugano diagrams, existing already 50 years, applicability of which have

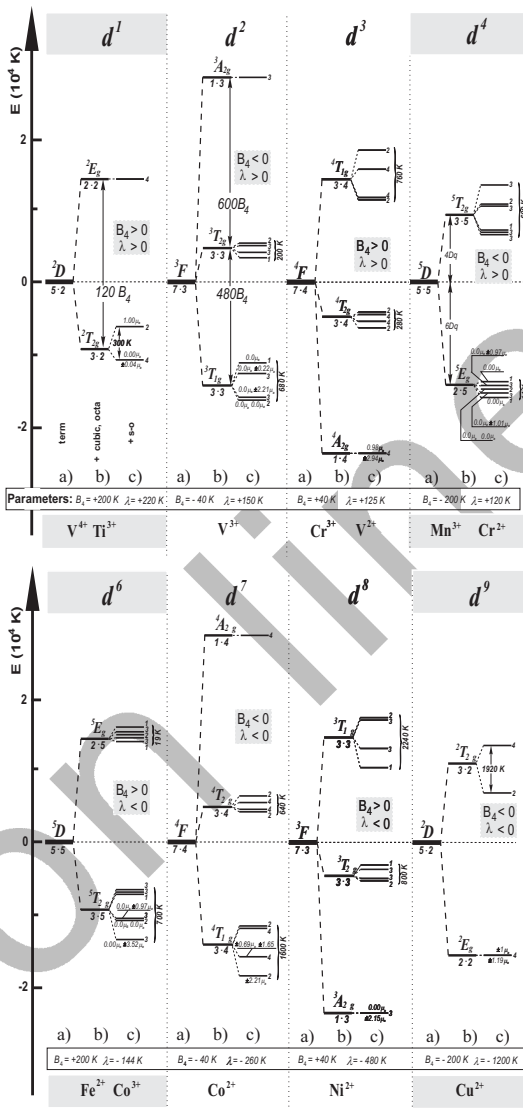


FIG. 4: The calculated electronic structure of the $3d^n$ configurations of the 3d ions, $1 \leq n \leq 9$, in the octahedral crystal field (b) and in the presence of the spin-orbit coupling (c). (a) - shows the Hund's rule ground term. Levels in (c) are labeled with degeneracies in the LS space whereas in (b) the degeneracy is shown by the orbital spin degeneracy multiplication. The spin-orbit splittings are drawn not in the energy scale that is relevant to CEF levels shown in figures b [22, 23].

been questioned by band-structure calculations. The breaking of the Hund's rules in LaCoO_3 results from the extraordinary small Co-O distance, of 192 pm. In CoO , for instance, the Co-O distance amounts to 217 pm. This smaller distance by 13% causes increase of B_4^0 parameter by 85% owing to the R^{-5} dependence of the octupolar CEF interactions.

We have calculated the orbital moment in NiO [27], CoO [28], FeBr_2 and LaMnO_3 [29]. We have derived highly anisotropic properties of these compounds in full agreement with the experimental evidence. In Fig. 5 we present the calculated temperature dependence of the specific heat of FeBr_2 both in the paramagnetic and antiferromagnetic state with the λ -peak at T_N of 14 K [30]. For description we use the similar Hamiltonian as shown above. The formation of the magnetic state is related with the splitting of the lowest quasi triplet. It is worth to add that this quasi-triplet is the excited quasi-triplet discussed above for LaCoO_3 . The Fe^{2+} and Co^{3+} ions are isoelectronic $3d^6$ systems. Despite of the hexagonal lattice symmetry of FeBr_2 and the slightly distorted cubic structure of LaCoO_3 in both these compounds the local symmetry is octahedral. We would like to turn attention that the good reproduction of the overall specific heat means, in fact, the counting of atoms. The reproduction of the absolute value indicate that all atoms equally contribute to the observed property. It means, though it could sound unbelievably, that all Fe atoms have the same electronic structure. We think that it is an effect of the blind action of the simple physical laws.

Recently we describe consistently NiO within the strongly-correlated CEF approach reconciling its insulating ground state, the value and the direction of the magnetic moment in the antiferromagnetic state below 525 K and thermodynamic properties [31]. In particular we have calculated the overall electronic specific heat with the lambda-type peak at T_N and a substantial heat with the overall entropy of $R \ln 3$ fully released at T_N . We have quantified crystal-field (the leading parameter $B_4 = +21$ K), spin-orbit (-480 K, i.e. like in the free ion [32]) and magnetic interactions (B_{mol} of 503 T and $n = -200$ T/ μ_B). In our approach $E_{dd} \gg E_{CF} (=2.0$ eV) $\gg E_{s-o} (=0.29$ eV) $\gg E_{mag} (=0.07$ eV). The orbital and spin moment of the Ni^{2+} ion in NiO has been calculated within the quasi-atomic approach. The orbital moment of $0.54 \mu_B$ amounts at 0 K in the magnetically-ordered state, to about 20% of the total moment ($2.53 \mu_B$). Despite of using the full atomic orbital quantum number $L=3$ and $S=1$, the calculated effective moment from the temperature dependence of the susceptibility amounts to 3.5 - $3.8 \mu_B$, i.e. only 20 % larger value than a spin-only value of $2.83 \mu_B$.

We take as great confirmation of the strongly-correlated crystal field approach that the electronic structure through the series of compounds

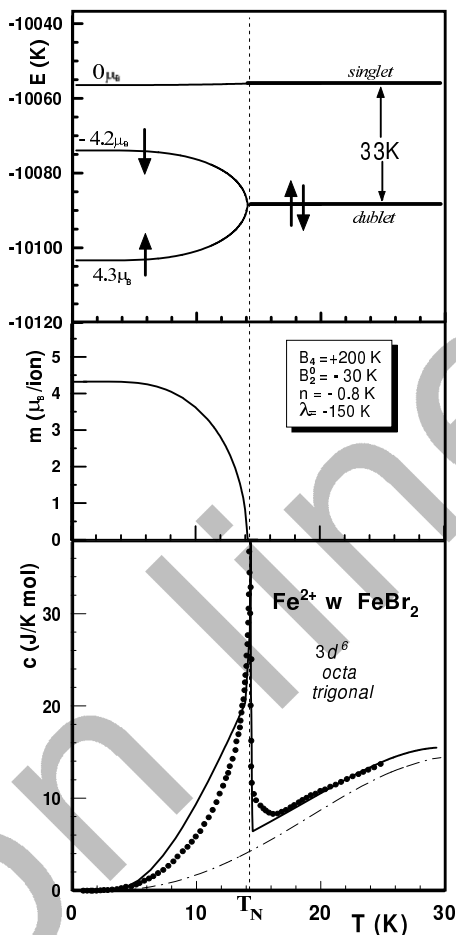


FIG. 5: Magnetic phase transition in FeBr_2 . a) temperature dependence of the 3 lowest energy levels originating from the ${}^5T_{2g}$ subterm of the Fe^{2+} ion; b) temperature dependence of the magnetic moment of the Fe^{2+} ion; c) temperature variation of the contribution of the d subsystem to the molar heat capacity. The points represent the experimental data [30].

results from the symmetry of the transition-metal surroundings. For instance, in all of above mentioned compounds the closest surroundings has predominantly the octahedral symmetry. As a consequence the ground state subterm alternates as the octupolar moment of the $3d^n$

configuration.

VIII. DEVELOPMENT OF PHYSICS

Everybody can see that our understanding of the electronic structure and magnetism of transition-metal compounds is along the well-established in solid-state physics paradigm. By pointing out the importance of the crystal field we call for a larger attention to local atomic-scale effects. In the present situation of the administrative reproaching of the use and the concept of the crystal-field approach if applied to magnetic metallic compounds we call to members of the international physical community. We have to turn to the international community, because by years Polish physicists can not settle up a problem and by years after the first negative Szymczak's opinion of 2001 subsequent opinions are written in very loosely language. For instance in the opinion of A.M. Oles, crucial for the final negative decision, there is only one (!!) verifiable statement, that fitting of the only one physical property is not reliable. We fully agree with this general Oles statement, but it does not touch the scientific approach of Radwanski, where always we analyze many properties for one compound and look for the consistency with other isostructural compounds. Other reproaching statements of Oles are not scientifically conclusive in the sense that these statements contain always "seems to", "probably" or "likely". Even a reproach of H. Szymczak, obviously erroneous, about description of the trigonal off-octahedral distortion used by Radwanski cannot be clarified. In our paper by Ropka and Radwanski in *Phys. Rev. B* (63 (2001) 172404), Ref. 1 on the list of our publication from 2001, we have described the trigonal off-octahedral distortion, at the end of the first page, by the $B_2^0O_2^0$ term added to the octahedral Hamiltonian written for the z axis along the cube diagonal (reproach No 3). This procedure has been simply erroneously questioned by Szymczak in 2001, but there was no one to clarify it. According to normal scientific rules Szymczak has been obliged to write a Comment to the Editor of *Phys. Rev. B* and to inform publicly the scientific community about incorrectness before writing an unsubstantiated reproach to the Governmental Scientific Committee. (In fact, the simplest was to send e-mail to Radwanski, and trying to explain the controversy.) An unscientifically made reproach cannot be clarified now. Later, four referees did not clarify this erroneous reproach - we take it as an evidence for their scientific dishonesty. At present instead of the simple clarifying the erroneous decision of CK, the easiest would be the correction by Szymczak, the Polish magnetic community keeps a long-lasting splendid quiet. This unscientific be-

havior is partly related to the dominant administrative position of H. Szymczak in the Polish physics and a lack of respect for basic scientific rules in Polish physics. We hope that these problems will be discussed in the coming magnetic conferences in Poland, in Wroclaw, 19-21 May 2005, on "Anomalous properties of strongly correlated systems" chaired by D. Kaczorowski and in Poznan, 25-29 June 2005 on "Physics of Magnetism" chaired by Krompiewski and R. Micnas.

We submit this problem also to Prof. E. Bauer, the Chairman of the incoming SCES-05 Conference to be held in 26-30 July 2005 in Vienna, and to all members of the International Advisory Board. In particular, we turn to well-experienced physicists: M. Abd-Elmeguid, P. Alekseev, J. Allen, M.C. Aronson, P. Coleman, M. Continentino, B. Coqblin, A. de Visser, C. Di Castro, Z. Fisk, J. Flouquet, A. Fujimori, P. Fulde, J. Gomez-Sal, H. Harima, H. Johannesson, B. Johansson, C. Lacroix, A. Loidl, G. Lonzarich, M.B. Maple, F. Marabelli, K.A. McEwen, A.J. Millis, J.A. Mydosh, Y. Onuki, G. Oomi, R. Osborn, M. Reiffers, T.M. Rice, T.F. Rosenbaum, E.V. Sampathkumaran, H. Sato, G.A. Sawatzky, V. Sechovsky, J. Sereni, M. Sigrist, J. Spalek, F. Steglich, T. Takabatake, J.D. Thompson, K. Ueda, D. Vollhardt, H. v. Lohneysen, V. Zlatič. All of us knows that the magnetism of transition-metal compounds is still under scientific discussion and any administration decision about the incorrectness of the crystal-field-based approach to magnetic metallic materials is premature and harmful to physics. A reproach that "the used (crystal-field) approach is too simplified" with a simultaneous statement that "the obtained agreements with experimental data are accidental" is illogical. We are ashamed that such strong administrative interference to Physics happens in Poland, a country of the long tradition of freedom. We are lucky that apart of the administration we have another great authority - the Pope John Paul II. By last 20 years he teaches about the truth, the values, the dignity and the freedom in everyday life and in Science.

We turn to the international physical community as we believe that all members of this community share our view that Science can develop only in the truth and in freedom. We call to physicists, our colleagues in searching for the scientific truth: We can differ in approaching to Physics and Science - but all of us agree that Science and Physics can develop only without administration interference for judging correctness of any scientific theory. We believe that the future proves the incorrectness of the administrative interference to physics and for the restoration of normal scientific conditions in physics. Independently on it, we will continue with the highest integrity our research on the magnetism and electronic structures of transition-metal compounds being open for sci-

ActAPhysica/0704.02 30 Mar 2007

entific discussions and critics.

We are grateful to all opponents - thanks them our studies turn out to be scientifically important despite of using at the start well-known atomistic approach and the 75 years old crystal-field theory. Being grateful to our opponents we cannot, however, accept discrimination and inquisition methods used in doing science. It is obvious that Science without ethic values becomes empty. If somebody is able to prove errors in the crystal-field approach is welcome to publish it openly. If somebody has something against me and my scientific activity is welcome to say it publicly, not to work with the help of administration methods like rejection of papers from the publication or the presentation on conferences. A great ethic problem appears if later he publishes quite similar things. We declare our deep will to cooperate with everybody in serving to built the scientific magnetic community and to search for the scientific truth.

IX. REMARKS ON THE CRYSTAL-FIELD THEORY

A strange scientific climate about the crystal-field theory in the modern solid-state paradigm comes from a widely-spread view within the magnetic community that it does not have the proper theoretical justification. An oversimplified point charge model is treated as an essence of the crystal-field theory. An indication in some cases that the point charge model is not sufficient to account for the crystal-field splittings was taken as the conclusive proof for the incorrectness of the crystal-field concept at all. According to us the theoretical background for the crystal-field theory is the atomic construction of matter. Simply, atoms constituting a solid preserve much of their atomic properties. One can say that the atomic-like integrity is preserved, after giving up partly or fully some electrons, and then the atomic identity serves as the good quantum number of the electron system. We are quite satisfied that the point-charge model provides the proper variation the ground states going on from one to another 3d/4f/5f atom. Different ionic states we consider as different states of the atom, though it is better instead of the ionic state to say about the electron configurations and their different contributions to magnetic, electronic, spectroscopic and optical properties. For instance, in metallic ErNi_5 there exists $4f^{11}$ electron configuration, often written as the Er^{3+} ion, that is found to be predominantly responsible for the magnetism and the electronic structure of the whole compound [6]; the other electrons of Er and Ni are responsible for the metallic behavior. We point out the multipolar character of the electric potential in a solid. It is very fortunate situation when a solid, with milliard of milliard of atoms (in America billion of bil-

lions), can be described with the single electronic structure. It is true, that the crystal-field theory being itself a single-ion theory cannot describe a solid with collective interactions. For this reason we came out with the Quantum Atomistic Solid State Theory and completed the crystal-field theory with strong intra-atomic correlations and intersite spin-dependent interactions. By pointing out the importance of the CEF theory we would like to put attention to the fundamental importance of the atomic physics (Hund's rules, spin-orbit coupling, ...) and local single-ion effects. It is worth remind that the source of a collective phenomenon, the magnetism of a solid, are atoms constituting this solid. Properties of these potentially-active atoms (open-shell atoms) are determined by local surroundings and local symmetry. Subsequently, these atomic moments, with spin and orbital parts, enter to the collective game in a solid. If somebody thinks that CEF and QUASST is too simple (in fact, it is not simple!!) should not blame authors for it, but Nature. Nature turns out to be simpler than could be!

Another wrong conviction about the crystal-field theory is that it was exploited already completely. In order to shown that this thinking is wrong we turn the reader's attention that the crystal-field approach used within the rare-earth and actinide community (4f and 5f systems) fundamentally differs from that used within the 3d community. The 4f/5f community works with J as the good quantum number whereas the 3d community "quenches" the orbital moment and works with only the spin S . Our description of a 3d-atom compound like FeBr₂ and LaCoO₃ one can find in Refs [30] and [24]. In case of the strongly-correlated crystal-field approach we work with many-electron states of the whole $4f^n, 5f^n, 3d^n$ configuration in contrary to single-electron states used in 3d magnetism and LDA, LSDA, and many other so-called *ab initio* approaches. Technically, strong correlations are put within the CEF theory, and in QUASST, by application of two Hund's rules. The *ab initio* calculations will meet the CEF (QUASST) theory in the evaluation of the detailed charge distribution within the unit cell and after taking into account strong intra-atomic correlations among electrons of incomplete shells and the spin-orbit coupling in order to reproduce the CEF conditions (two Hund's rules, also the third one for rare-earths and actinides).

We would like to mention that we are fully aware that used by us the Russell-Saunders LS coupling can show some shortages in case of actinides related to the growing importance of the j-j coupling. We are aware of many other physical problems which we could not mention here due to the length problem - finally we mention only that we can

reverse scientific problem in the solid state physics and use 4f/5f/3d compounds as a laboratory for the atomic physics for study 3d/4f/5f atoms in extremal electric and magnetic fields. In the solid-state physics we study the lowest part of the atomic structure, but extremely exactly.

The detailed electronic structure is predominantly determined by conventional interactions in a solid: the Stark-like effect by the crystalline electric field potential due to 3-dimensional array of charges in a crystal acting on the aspherical incomplete shell, and the Zeeman-like effect due to spin-dependent interactions of the incomplete-shell spin (atomic-like moment) with self-consistently induced spin surroundings. These states can become broaden in energy by different interactions (lowering of the local symmetry, thermal expansion, appearance of a few inequivalent sites, lattice imperfection, surface effects and other solid-state effects). Obviously, we should not think that discrete crystal field states mean that they are extremely thin lines. 3 or even 10 meV broad lines are still of the crystal-field origin. Underlying by us by many, many years the importance of the crystal field we have treated as an opposite view to the overwhelmed band structure view yielding the spreading of the f-electron (and mostly 3d-electron) spectrum by 2-5 eV.

X. CONCLUSIONS

We advocate for the high adequacy of use and the concept of the crystal field approach, even if applied to metallic magnetic materials of transition-metal compounds. By extension of the crystal-field theory to a Quantum Atomistic Solid-State theory (QUASST) we have made the unification of 3d and rare-earth compounds in description of the low-energy electronic structures and magnetism of open 3d/4f/5f shell electrons taking into account the local crystal field, the intra-atomic spin-orbit coupling and strong intra-atomic correlations. QUASST offers consistent description of zero-temperature properties and thermodynamic properties of 3d-ion containing compounds. We have calculated the orbital moment in 3d oxides (NiO, CoO, LaCoO₃, LaMnO₃, FeBr₂). Our studies indicate that it is the highest time to unquench the orbital magnetism in 3d -ion compounds. We claim that the first-principles and ab initio studies will be as long not successful as strong correlations assumed in the CEF approach will be not incorporated in the calculations. We do not claim to (re-)invent crystal-field theory, but we do not agree for the depreciation of the crystal field theory. We are convinced that the crystal-field theory with strong correlations is a fundamental ingredient of the modern solid-state paradigm.

♣ dedicated to the Pope John Paul II, a man of freedom in life and in Science.

- [1] P. Mohn, *Magnetism in the Solid State*, Solid State Sciences **134** (Springer-Verlag, Berlin) (2003).
- [2] J. H. Van Vleck, *Theory of electric and magnetic susceptibilities* (Oxford University Press) (1932).
- [3] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753 (1954); S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York) (1970).
- [4] R. J. Radwanski and Z. Ropka, *Acta Physica* **2**, 1 (2007); cond-mat/0010081 (2000) *Quantum Atomistic Solid State Theory*.
- [5] R. J. Radwanski, R. Michalski, and Z. Ropka, *Acta Phys. Pol. B* **31**, 3079 (2000).
- [6] R. J. Radwanski, N. H. Kim-Ngan, F. E. Kayzel, J. J. M. Franse, D. Gignoux, D. Schmitt, F. Y. Zhang, *J. Phys.: Condens. Matter* **4**, 8853 (1992).
- [7] R. J. Radwanski and J. J. M. Franse, *J. Magn. Magn. Mat.* **80**, 14 (1989).
- [8] R. J. Radwanski, R. Michalski, Z. Ropka, and A. Blaut, *Physica B* **319**, 78 (2002).
- [9] A. Krimmel, A. Loidl, R. Eccleston, C. Geibel and F. Steglich, *J. Phys.: Condens. Matter* **8**, 1677 (1996).
- [10] R. J. Radwanski, R. Michalski and Z. Ropka, *Physica B* **276-278**, 803 (2000); R. J. Radwanski and Z. Ropka, *Czech. J. Phys.* **54**, D295 (2004); cond-mat/0407453 (2004).
- [11] G. Zwickyagl, A. Yaresko and P. Fulde, *Phys. Rev. B* **68**, 052508 (2003); *Phys. Rev. B* **65**, 081103(R) (2002); G. Zwickyagl and P. Fulde, *J. Phys.: Condens. Matter* **15**, S1911 (2003).
- [12] A. Hiess, N. Bernhoeft, N. Metoki, G. H. Lander, B. Roessli, N. K. Sato, N. Aso, Y. Haga, Y. Koike, T. Komatsubara, and Y. Onuki, *J. Phys.: Condens. Matter* **18**, R437 (2006); cond-mat/0411041 (2004); N. Bernhoeft, A. Hiess, N. Metoki, G. H. Lander and B. Roessli, cond-mat/0411042 (2004).
- [13] R. J. Radwanski and Z. Ropka, *Acta Physica* **2**, 14 (2007); cond-mat/0412257 (2004), *Are there crystal field levels in UPd_2Al_3 ? We answer, THERE ARE*.
- [14] N. K. Sato, N. Aso, K. Miyako, R. Shiina, P. Thalmeier, G. Vareloglannis, C. Geibel, F. Steglich, P. Fulde, and T. Komatsubara, *Nature* **410**, 340 (2001).
- [15] F. Steglich, N. K. Sato, N. Aso, P. Gegenwart, J. Custers, K. Neumaier,

- H. Wilhelm, C. Geibel, and O. Trovarelli, *Physica B* **329-333**, 441 (2003).
- [16] R. J. Radwanski and N. H. Kim-Ngan, *J. Alloys Comp.* **219**, 260 (1995).
- [17] R. J. Radwanski, *J. Phys.: Condens. Matter* **8**, 10467 (1996).
- [18] J. Sichelschmidt, V.A. Ivanishin, J. Ferstl, C. Geibel, and F. Steglich, *Phys. Rev. Lett.* **91**, 156401 (2003).
- [19] R. J. Radwanski and Z. Ropka, cond-mat/0312725 (2003) *Crystal-field ground state for the localized f state in heavy fermion metal YbRh₂Si₂*.
- [20] R. J. Radwanski, *Acta Physica* **1**, 15 (2006); cond-mat/9906287 (1999); cond-mat/9911292 (1999) *Formation of the heavy-fermion state - an explanation in a model traditionally called localized* - presented at SCES-92 in Sendai as 8P92.
- [21] R. J. Radwanski, *Physics of heavy-fermion phenomena* - Report CSSP-17/94 and CSSP-4/95 distributed in about 400 egzemplaires among leading physicists at SCES-94 and SCES-95.
- [22] R. J. Radwanski and Z. Ropka, cond-mat/9907140 (1999) *Relativistic effects in the electronic structure for 3d paramagnetic ions*, submitted in 1997, May 30, to *Phys. Rev. Lett.* LE 6925.
- [23] R. J. Radwanski and Z. Ropka, in: *New Development in Field Theory*, O. Kovras, ed. (Nova Science 2006), 93 (2006); cond-mat/0404713 (2004) *Strongly-Correlated Crystal Field Approach to 3d oxides*.
- [24] Z. Ropka and R. J. Radwanski, *Phys. Rev. B* **67**, 172401 (2003); R. J. Radwanski and Z. Ropka, cond-mat/0404713 (2004).
- [25] S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, *Phys. Rev. B* **66**, 094404 (2002).
- [26] M. A. Korotin, S. Yu. Ezhov, I. V. Solovyev, V. I. Anisimov, D. I. Khomski, and G. A. Sawatzky, *Phys. Rev. B* **54**, 5309 (1996).
- [27] R. J. Radwanski and Z. Ropka, *Acta Phys. Pol. A* **97**, 963 (2000); cond-mat/0005471 (2000).
- [28] R. J. Radwanski and Z. Ropka, *Physica B* **345**, 107 (2004); cond-mat/0306695 (2003).
- [29] R. J. Radwanski and Z. Ropka, *J. Magn. Magn. Mater.* **272-276**, e259 (2004).
- [30] Z. Ropka, R. Michalski, and R. J. Radwanski, *Phys. Rev. B* **63**, 172404 (2001).
- [31] R. J. Radwanski and Z. Ropka, *Acta Physica* **1**, 26 (2006); cond-mat/0503407 (2005) *The atomic start description of NiO*.
- [32] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford), ch. 7 (1970).