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FROM ATOMIC PHYSICS TO SOLID-STATE PHYSICS: MAGNETISM AND ELECTRONIC STRUCTURE OF $PrNi_5$, $ErNi_5$, $LaCoO_3$ AND UPd_2Al_3*

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A consistent physical understanding of electronic, magnetic and spectroscopic properties of $PrNi_5$ and $ErNi_5$ is obtained with treating the f electrons as highly-correlated. The fine electronic structure, related with the atomic-like states and determined by the crystal-field and spin-orbit interactions, has been evaluated by means of different experimental techniques. The importance of the higher-order charge multipolar interactions and the local symmetry of the crystal field for the realized fine electronic structure and for the ground state are pointed out. We point out that a significant success of the crystal-field theory indicates on the substantial preservation of the atomic-like structure of the open-shell atoms even when they become part of solid.

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1. Introduction

In this paper we are interested in compounds containing atoms of transition metals of the iron group, of lanthanides and of actinides. These atoms contain $3d$, $4f$ and $5f$ open shells. The aim of this lecture is to provide the evidence for the existence of the discrete energy electronic states in solid-state compounds containing open-shell atoms. The most evidence exists for compounds containing lanthanides (La-Yb) though there is growing evidence for the existence of the discrete energy states in $3d$- and $5f$-atom compounds. It turns out from our studies that this discrete energy spectrum is associated

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with the atomic-like fine electronic structure of the open-shell atom involved. The revealed fine electronic structure is related to the energy excitations in the range 0–10 meV. The discussed states are substantially populated with the increasing temperature (thermal population). For convenience, we use the energy scale in K (1 meV = 11.6 K). Thus, we should realize that in the solid-state physics we are interested in relatively low energies. In solid-state physics we try to understand electronic and magnetic properties of a solid at room temperature and below, including the absolute-zero properties. The room-temperature energy corresponds to 25 meV (290 K). Comparing it with energies of the atomic-physics interest we can say that in solid-state physics we are interested in the very low energy scale. It means that in solid-state physics we are interested in the fine structure of the atomic ground state.

Lanthanide(= Rare Earth, RE) systems are a subject of very intensive studies, both experimental and theoretical [1,2]. Most of them exhibit properties useful for industrial applications. Let us mention, for instance, the hard magnetic materials for the permanent-magnet industry ($Nd_2Fe_{14}B$, $SmCo_5$, Nd_2Co_{17},...), magnetostrictive materials ($TbFe_2$,...), and laser materials like the neodymium or erbium lasers, where RE atoms are introduced as impurities to a transparent matrix (*e.g.* CaF_2, $CaWO_4$, YAG-$Y_3Al_5O_{12}$,...), as in $PrCl_3$. The $RE\,Cu_2O_4$- and $RE\,Ba_2Cu_3O_7$-based compounds exhibit high-temperature superconductivity [3,4]. Among $3d$ compounds we can mention $LaMnO_3$ (with a colossal magnetoresistance), $LaCoO_3$, CrO_2 (as recording tapes), TiO_2, V_2O_3, La_2CuO_4 (the parent compound for high-temperature superconductors), NiO, FeO and $FeBr_2$. Among the actinides, we mention UO_2, UPd_2Al_3, UGa_2, $NpGa_2$ and $NpPd_2Al_3$.

From theoretical point of view there is a prolonged discussion about the role played by the f electrons in f-atom containing compounds. Such terms as mixed-valence or heavy-fermion behaviour ($CeAl_3$, ...) have become already a landmark of exotic and scientifically intriguing phenomena. In the mixed-valence and the Fermi liquid (and related) theories a significant delocalization of the f electrons, leading to a non-integer value of f electrons, plays a crucial role. At the same time, there is a growing number of rare-earth compounds describable within the crystal-field (CEF) model. In the CEF model, applied by the present authors, f electrons are treated as fully localized with the integer value of valency. A similar discussion concerns the treatment of $3d$ electrons.

There are thousands of rare-earth compounds. The main subdivision is related to the electrical behaviour — they are or they are not conductive. Compounds of the first group are intermetallic compounds (here we can mention $ErNi_5$, $PrNi_5$, $TbFe_2$, Ho_2Co_{17}, $RE\,Al_2$ ...). Compounds of the second group are insulators (here RE_2O_3, $PrCl_3$, and NdF_3 can be mentioned).

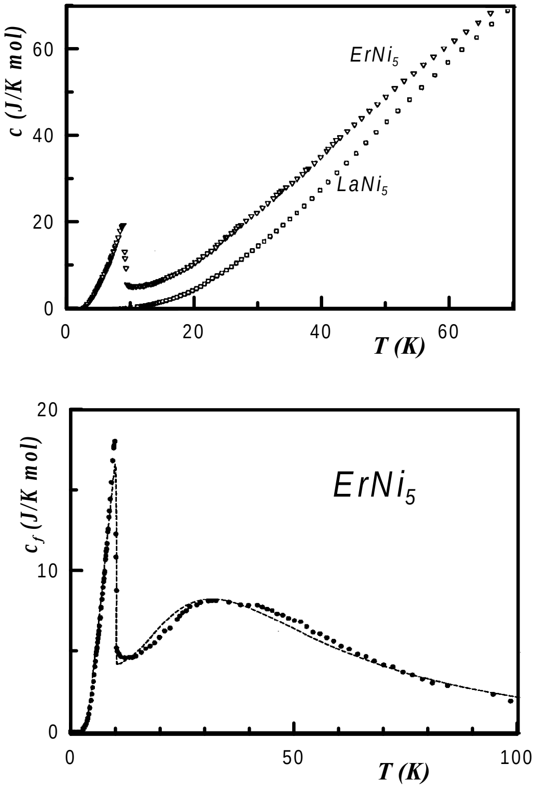

Fig. 1. (a) — temperature dependence of the heat capacity of single crystalline $\mathrm{ErNi_5}$ and $\mathrm{LaNi_5}$ (experiment). (b) — temperature variation of the contribution of the f subsystem to the heat capacity of $\mathrm{ErNi_5}$ derived as the difference of the molar specific heat of $\mathrm{ErNi_5}$ and $\mathrm{LaNi_5}$. 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 [5].

In order to focus our interest let us concentrate on $\mathrm{ErNi_5}$, an exemplary compound that belongs to the wide class of $\mathrm{RE\,Ni_5}$ compounds. The existence of these compounds with all rare-earth elements, *i.e.* 12 compounds with the same hexagonal crystallographic structure, makes this series very useful for systematic studies not only for the one compound but also for the whole series. Because of that the change, suggested by the crystal-field model, of the CEF parameters from one compound to another, can be tested. The CEF parameters represent the strength of the charge multipolar interactions of the aspherical 4f cloud with the aspherical charge surrounding. The $\mathrm{RE\,Ni_5}$ compounds with magnetic rare-earth elements *i.e.* from Ce to Tm are magnetic except $\mathrm{PrNi_5}$. The highest value for T_C of 32 K is found for $GdNi_5$. It indicates the dominant role of the rare-earth spin in the formation of the magnetic state (de Gennes factor $S(S+1)$ is the largest for the Gd^{3+} ion). The nickel ions are non-magnetic as we can infer from YNi_5 and $LaNi_5$. They both are Pauli paramagnets though with the exchange-enhanced susceptibility.

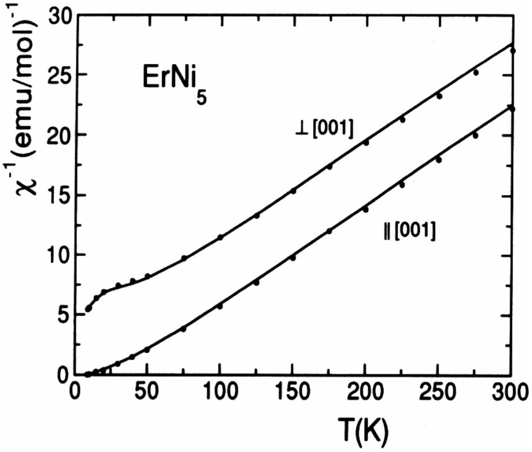

Fig. 2. Temperature dependence of the paramagnetic susceptibility along the principal directions of the hexagonal $ErNi_5$. The calculated results (lines) fully reproduce experimental data (closed circles). Violation of the Curie–Weiss law should be noticed at low temperatures [5].

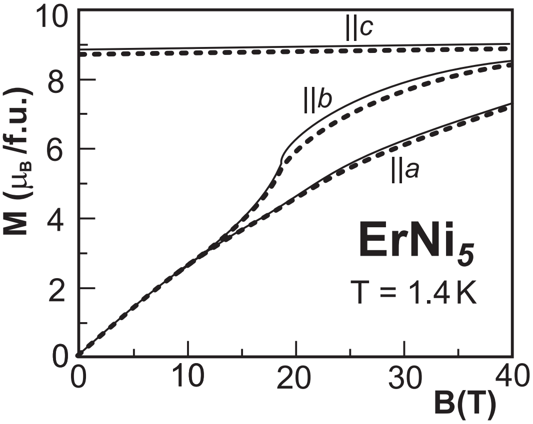

Fig. 3. The high-field magnetization curves at 1.5 K for single crystalline $ErNi_5$ measured along the main hexagonal directions. The calculated results (lines) fully reproduce experimental data [5].

Some experimental results for $ErNi_5$ are presented on Figs 1–3. Inspecting these figures please know that we would like to understand the overall temperature dependence of the heat capacity seen in Fig. 1 noting that the heat capacity of $ErNi_5$ is substantially larger than that of $LaNi_5$ and exhibits a λ type of peak at 9 K.

We would like to find the reason for the violation of the Curie–Weiss law at low temperatures in the temperature dependence of the paramagnetic susceptibility, Fig. 2.

We would like to know the origin of so anisotropic behaviour in the externally applied magnetic fields as we see in Fig. 3.

Surely we would like to know how the magnetic order forms at T_C of 9 K and why the ordered magnetic moment is so large as 8.5 μ_B or is extremely small in other compounds, or even zero like in case of the Pr^{3+} ion in $PrNi_5$. We would like to know ... — there are really a lot of interesting questions concerning the rare-earth compounds. These are some example questions that we put on in the discussion of rare-earth compounds. The similar questions are of interest in the studies of actinides and $3d$-atom compounds.

The presented properties of $ErNi_5$ are very well understood on the quantitative level as originating from the discrete energy states of the Er^{3+} ion, 11 f electrons of which are treated as forming the highly-correlated electron system $4f^{11}$. For the description of its states we need to remind the atomic-physics knowledge. We should explain also that in different compounds different ionic states of the paramagnetic atom could 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.

2. A brief reminder about the atomic physics

The atomic $4f$ states of the highly-correlated $4f^n$ system in the RE^{3+} ion are grouped in electronic terms that are the states with the same value of total S and L. For the case of $4f^2$ system, relevant to the Pr^{3+} ion, the possible terms are: ^3H, ^3F, ^3P, ^1I, ^1G, ^1D and ^1S. The associated degeneracy amounts to 33, 21, 9, 13, 9, 5 and 1, respectively. One can check that the total degeneracy of all terms amounts to 91 as should be. It was Hund who inspecting a great number of atomic spectra has formulated in 1929 two phenomenological rules, known at present as Hund's rules, for finding the ground term. Namely, he pointed out that the ground term is characterized by *(i)* the maximal possible value of S and *(ii)* the maximal possible value of L provided the maximal S condition is fulfilled. For the case of the Pr^{3+} ion with $2f$ electrons we have $S = 1(= 1/2 + 1/2)$ and $L = 5(3 + 2)$ and the ground term is denoted as ^{3}H. The ground terms of all rare-earth ions are collected in textbooks (*e.g.* C. Kittel, *Introduction to Solid State Physics*, ch.14).

For the case of the Pr^{3+} ion we have still the problem of the 33-fold degeneracy of the ^{3}H ground term. However, we are somehow lucky that for the rare-earth ions (not for the $3d$ ions) these states are grouped into multiplets characterized by the quantum number of the total angular momentum J. From the quantum mechanics we know that as a result of the adding of two momenta S and L we have $|L-S| \leq J \leq L+S$. In case of the discussed Pr^{3+} ion J can be 4, 5 and 6. The substates of the term with the same value of J are called a multiplet. According to the 3rd Hund's rules *(iii)* the ground multiplet is characterized by the smallest J for the electronic system with less than the half-filled f shell and with the largest J for systems with more than half-filled f shell. Thus the ground multiplet of the Pr^{3+} ion is $^3H_4$. The further splitting of this 9-fold degenerated ground multiplet is the subject of CEF interactions. The associated energy excitations of say 25 meV are the subject of solid-state physics considerations and of further considerations of the present lecture. The multiplet degeneracy depends on the J value of the ion involved and amounts to 6 (Ce^{3+} and Sm^{3+}), 8 (Gd^{3+} and Yb^{3+}), 9 (Pr^{3+}, also U^{4+}), 10 (Nd^{3+}, also U^{3+} and Np^{4+}), 13 (Tb^{3+} and Tm^{3+}), 16 (Dy^{3+} and Er^{3+}) and 17 (Ho^{3+}).

The separation between multiplets depends on the strength of the intra-atomic Spin-Orbit (S-O) coupling. RE atoms are characterized by the strong S-O coupling — it assures that J serves as the good quantum number. The excited multiplets are usually well above 200 meV — the smallest separation occurs for the Sm^{3+} ion. A value of 120.6 meV has been recently experimentally revealed by inelastic-neutron-scattering (INS) in $SmBa_2Cu_3O_7$ [6].

An f paramagnetic ion, when placed in a solid, experiences the electric-field potential due to all charges constituting the solid. As an effect of this potential, that has multipolar character with important higher terms, the multiplet degeneracy of the partially filled f shell is lifted and different charge-formed (CF) ground states of the f subsystem are realized. In case of a Kramers system, the system with an odd number of electrons, the charge-formed ground state is always a doubly degenerate Kramers doublet. This Kramers degeneracy can be only removed by external or/and internal magnetic fields. The latter one originates from the Spin-Dependent (S-D) interactions. The resultant electronic structure for the f^{11} electronic system formed for the Er^{3+} ion in $ErNi_5$ is shown in Fig. 4. In case of the non-Kramers system, a system with even number of f electrons, the crystal field can realize the singlet ground state as it happens for the Pr^{3+} ion in $PrNi_5$, Fig. 5.

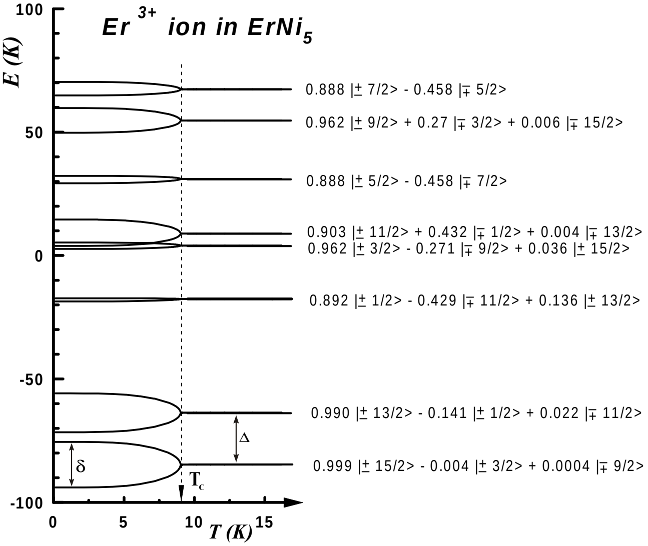

Fig. 4. The energy level scheme of the Er^{3+} ion in the hexagonal ErNi$_5$ under the action of the CEF interactions. All the levels are doublets as the Er^{3+} ion with $J = 15/2$ is a Kramers ion. These doublet states are split in the magnetically ordered state, below T_C of 9.2 K [5].

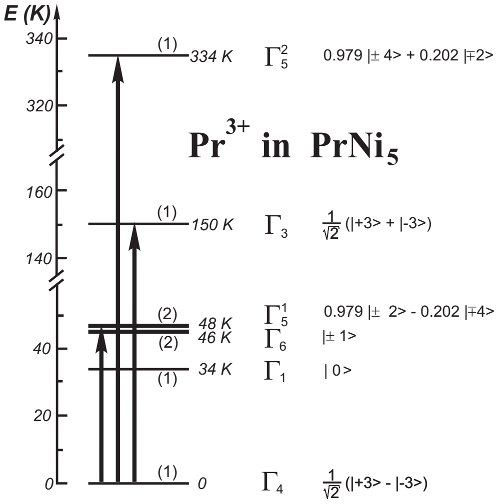

Fig. 5. The energy level scheme of the Pr^{3+} ion in the hexagonal non-magnetic PrNi$_5$ under the action of the CEF interactions [7]. Arrows indicate the transitions observed in the INS spectroscopy.

3. Examples

3.1. Non-magnetic RE compound: PrNi$_5$ *(non-Kramers Pr*$^{3+}$ *ion)*

The exemplary energy level scheme for the Pr^{3+} ion in the hexagonal symmetry of PrNi_5 is shown in Fig. 5. From magnetic experiments we know that PrNi_5 does not show magnetic order down to 0.5 K. Hence it is relatively the easy case — we try to describe its properties with CEF interactions only neglecting magnetic interactions. The energy scheme has the singlet ground state of the Pr^{3+} ion in agreement with the non-magnetic state of PrNi_5. The shown eigenfunctions $|\Gamma_i\rangle$ reflect the hexagonal symmetry — there is the mixing (hybridization) of the functions $|JJ_z\rangle$ with J_z different by 6.

Having the eigenvalues E_i (= energies) and the eigenfunctions $|\Gamma_i\rangle$ we can calculate thermodynamics of various electronic and magnetic properties by taking use of the Boltzmann distribution function. The main electronic property is the heat capacity (= the specific heat) and its temperature dependence. The main magnetic property is the magnetic susceptibility and its temperature dependence as well as the magnetic moment related with the magnetization and its temperature dependence. Having available energies we can calculate the canonical partition function.

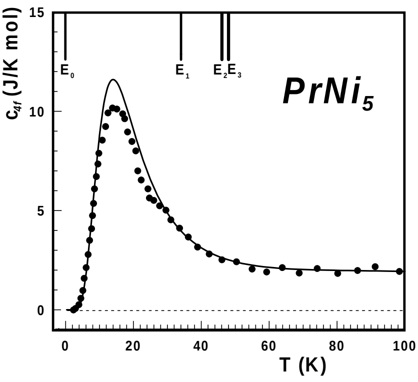

Fig. 6. Experimentally derived temperature dependence of the f-heat capacity of PrNi_5 together with calculations for the atomic-like discrete energy spectrum of the Pr^{3+} ions [7]. On top the energy position of the CEF states are shown.

The temperature dependence of the heat capacity calculated for PrNi_5 is shown in Fig. 6. There are also shown the experimental data and one can see that the agreement is quite nice. It is necessary to point out the overall agreement in the whole temperature range as well as of the absolute value. This later agreement indicates that the observed heat capacity comes out from all Pr ions — it means that all Pr ions exhibit practically the same energy level splitting. It is a surprise but it is the experimental fact.

Inspecting Fig. 6 one can find there the Schottky-type heat capacity named in the memory of Schottky who the first studied the heat capacity from a 2-level system, a system with available two temperature-independent levels separated by an energy interval of Δ. It can be shown that in such the case the heat capacity exhibits a maximum at T = 0.42 Δ with the maximal heat value of 3.6 J/K mol. In case of $PrNi_5$ the maximal heat reaches almost 3 times more ($\approx$ 10 J/Kmol) — it is related with 5, instead of one, closely lying excited states: Γ_1(singlet) and two doublets (Γ_6 and Γ_5).

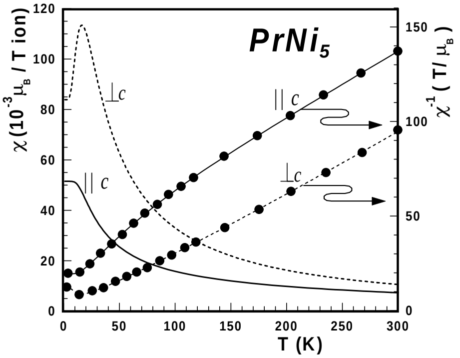

Fig. 7. Temperature dependence of the paramagnetic susceptibility along the principal directions of the hexagonal $PrNi_5$. The calculated CEF results lines) fully reproduce experimental data (closed circles) — in calculations the Pauli-like susceptibility $\chi_0 = 4 \cdot 10^{-3} \mu_B/T$-ion is taken into account. The violation of the Curie–Weiss law should be noticed at low temperatures [7].

The temperature dependence of the paramagnetic susceptibility calculated for $PrNi_5$ is shown in Fig. 7. There is visible large anisotropy of the paramagnetic susceptibility — $\chi(T)$ depends on the applied magnetic field direction. It reproduces well the experimental data. It is, however, necessary to mention that for the comparison of the experimentally-observed susceptibility of $PrNi_5$ and the CEF susceptibility of the Pr^{3+} ions we have to take into account the Pauli-like (= temperature independent) susceptibility χ_0 of $4 \cdot 10^{-3} \mu_B$/Tf.u. originating from the conduction electrons according to the formulae: $\chi_{\mathrm{exp}} = \chi_{\mathrm{CF}} + \chi_0$. The overall agreement in the whole temperature range as well as its absolute value indicates again that the observed susceptibility comes out from all Pr ions what is possible provided all Pr ions exhibits exactly the same energy level splitting. It is consistent with the conclusion from the heat capacity analysis.

Inspecting Fig. 7 one can find that the high-temperature susceptibility follows quite well the Curie–Weiss law ($\chi(T) = C/(T - \Theta)$) that is recognized at the χ^{-1} *vs* T plot as the straight line. From the slope of this line one can derive the value of the effective moment, in $\mu_{\rm B}$, as $p^2_{\rm eff} = 3k_{\rm B}\Delta T/\Delta\chi^{-1}$. Such the derived value is usually compared with the free-ion value expected for the ground state with the maximal value of J_z, that equals $p^2_{\rm eff}$ (free ion)$= g^2\mu^2_{\rm B}J(J+1)$. These calculations reproduce also the low-temperature susceptibility. Thus the reason for the departure from the Curie (Curie–Weiss) law is the existence of the fine electronic structure related with the Pr^{3+} ions.

3.2. Magnetic RE compound: ErNi$_5$ (Kramers Er^{3+} ion)

ErNi$_5$ orders ferromagnetically below 9 K. The Er^{3+} ion existing in ErNi$_5$ is the Kramers electronic system $4f^{11}$. The Hund's rules yield the ground multiplet $^4\mathrm{I}_{15/2}$ with $J = 15/2$, $S = 3/2$ and $L = 6$ and the Lande factor $g = 6/5$. The overall degeneracy is 16. The energy level scheme of thef^{11} system in the crystal field of the hexagonal symmetry contains 8 Kramers doublets, see Fig. 4, where the energy structure for the Er^{3+} ion in ErNi$_5$ has been shown. Such the doublet structure is in agreement with the Kramers theorem that says that the (crystalline-)electric field cannot fully remove the degeneracy of the states of the systems with an odd number of electrons, in general of fermions, *i.e.* particles with own internal spin $s = 1/2$. It means that the ground state of an odd-electron system in the electric field of the lowest symmetry is at least a doublet. For the Pr^{3+} ion with the even number (= 2) of the f electrons the ground state realized by the electric field can be a singlet, like it was in PrNi$_5$. The degeneracy of the Kramers doublet is lifted only by the magnetic field, external or internal. This internal field is set up in the magnetically-ordered state that is realized in ErNi$_5$ below 9 K and in NdNi$_5$ below 7 K.

The microscopic mechanism for the magnetic interactions is still under strong discussion. Despite of the detailed mechanism for the magnetic interactions and the formed magnetic structure these magnetic interactions surely involve the atomic spins. Thus we use the name spin-dependent (S-D) interactions. The S-D interactions between f-electron subsystems are mediated by conduction electrons as is discussed in the Kondo and RKKY interactions. In ionic systems concepts of the double exchange or the superexchange, the direct or indirect exchange are discussed. We will treat these S-D interactions by the mean-field (MF) approximation and by considering the RE moments. It is justified as when J is the good quantum number then the magnetic moment ($\mu = -g_L\,\mu_{\rm B}\,J$) and the spin is proportional to $J(S = (g_L - 1)\,J)$. Thus the single-ion-like Hamiltonian of the RE$\,^{3+}$ ion can be written in the form:

$$\begin{aligned} H \;&=\; H_f + H_{f-f} = \sum_n\sum_m B^m_n\check{O}^m_n + ng^2_L\mu^2_{\rm B}\left(-J\langle J\rangle + \tfrac{1}{2}\langle J\rangle^2\right) \\ &\quad + g_L\mu_{\rm B}\vec{J}\cdot\vec{B}_{\rm ext}\,. \end{aligned}$$

The first term is the CEF Hamiltonian written for the lowest multiplet given by Hund's rules. The second term represents the spin-dependent interactions between the RE^{3+} ions written in the MF approximation, where n denotes the molecular-field coefficient. The last term enables calculations of the influence of the external magnetic field B_{ext}. The internal molecular field amounts to $B_{\mathrm{mol}} = n \cdot \mu$. This field produces the splitting of the charge-formed Kramers-doublet ground state at each f site in the magnetically-ordered state below 9 K as is shown in Fig 4. This field has been calculated to be 1.5 T at 0 K for $\mathrm{ErNi_5}$ [5]. A field of 350 T, for example, has been evaluated to be in $\mathrm{Nd_2Fe_{14}B}$. $\mathrm{Nd_2Fe_{14}B}$ exhibits T_{C} of about 500 K.

The calculations with the use of the above Hamiltonian are performed self-consistently adjusting a value of n, for the given set of CEF parameters, that reproduces the value of the magnetic temperature. Such calculations are performed in two stages — at first we derived self-consistently CEF parameters remembering about the proper ground state that can reproduce the experimentally-observed magnetic moment at the ordered state. Later the value of n is adjusted to the existing T_0 that has to reproduce the real value of the ordered magnetic moment as well as its direction within the elementary cell. Exemplary results of these calculations have been shown in Fig. 3 for $\mathrm{ErNi_5}$. All thermodynamics is performed similarly to that discussed earlier for $\mathrm{PrNi_5}$ but now the levels are temperature dependent what makes the calculations much more sophisticated.

4. Spin and orbital moments

The total moment is composed from the spin and orbital parts. In case of a system with the good quantum number J as is the case of rare-earth ions the spin $S = (g_L - 1)J$ and the orbital quantum number $L = (2 - g_L)J$. The associated spin moment in the z-direction amounts to $\mu_s = 2(g_L - 1)J_z$ (in μ_{B}) and the orbital moment $\mu_0 = (2 - g_L)J_z$. In case of, for instance, the $\mathrm{Nd}^{3+}/\mathrm{U}^{3+}$ ion in a $|JJ_z\rangle$ state the orbital moment amounts to $\mu_0 = (14/11)\,J_z$ and the spin moment $\mu_s = (-6/11)\,J_z$. The total moment is $\mu = \mu_0 + \mu_s = (8/11)\,J_z$ as should be. (8/11 is the Lande factor for the $\mathrm{Nd}^{3+}/\mathrm{U}^{3+}$ ion.) For the Er^{3+} ion $\mu_0 = +0.8\,J_z$, $\mu_s = +0.4\,J_z$.

The ratio of the spin and orbital moments sometimes discussed amounts to $\mu_s/\mu_0 = 2(g_L - 1)/(2 - g_L)$ whereas $\mu_s/\mu = 2(g_L - 1)/g_L$.

For the Nd^{3+} (Er^{3+}) ion it equals $-3/7$ ($+0.5$) and $-3/4$ ($+1/3$), respectively. One sees that *(i)* the orbital moment is very large and that *(ii)* the spin moment is opposite to the orbital moment for light RE ions and parallel for the heavy RE ions. These facts are in agreement with the 3rd Hund's rule.

5. The crystal-field in heavy-fermion systems

An interesting situation is realized in the case of compounds containing atomic Kramers systems, when the ground-state doublet is only slightly split. It will result in a large heat capacity at low temperatures. Such a situation is thought to occur for the heavy-fermion (h-f) compounds that exhibit enormous low-temperature heat capacity. It is worth to note that the Kramers degeneracy has to be always removed before the absolute zero temperature is reached. Otherwise the 3^{rd} law of thermodynamic would be violated. In this model the f electrons are localized but spin-like excitations can propagate.

The splitting of the Kramers ground doublet of so small value as 0.4 meV has been recently revealed by high-resolution inelastic-neutron-scattering (INS) experiments in $\mathrm{Nd_2CuO_4}$ [8,9]. These results confirm the earlier theoretical prediction on basis of temperature dependence of the heat capacity [10]. In case of $\mathrm{ErNi_5}$ the splitting of the ground doublet is 1.5 meV at zero temperature. This gap closes with temperature at T_{C} (T_{N}). Such the behaviour is typical for the Kramers system. To make it clear, the CEF provides the Kramers doublets on individual atoms. These doublets can interact via spin-spin interactions. These interactions can be quite complex.

6. Magnetism and electronic structure of $\mathrm{LaCoO_3}$

One of the very intriguing property of $\mathrm{LaCoO_3}$ is related with its diamagnetic state at zero temperature [11]. The diamagnetic state is a surprise as most of Co compounds are strongly magnetic. CoO, for instance, is antiferromagnetic below 291 K. In the insulating state $\mathrm{LaCoO_3}$ the cobalt atoms are in the trivalent state as is seen from the compensated valences $\mathrm{La^{3+}Co^{3+}O_3^{2-}}$. $\mathrm{LaCoO_3}$ crystallizes in the perovskite-like structure where the $\mathrm{Co^{3+}}$ ions are situated in the octahedral surrounding of the oxygen ions. The $\mathrm{Co^{3+}}$ ion has 6 d-electrons in the incomplete outer shell *and here they will be treated as forming the highly-correlated electron system* $3d^n$. In a zero-order approximation these electron correlations within the incomplete $3d$ shell are accounted for by the two phenomenological Hund's rules. They yield for $3d^6$ electron configuration the term ^5D with $S = 2$ and $L = 2$ as the ground term, Fig. 8. Under the action of the dominant cubic crystal field, the ^5D term splits into the orbital triplet $^5T_{2g}$ and the orbital doublet ^5E_g. For the $3d^6$ configuration the orbital triplet $^5T_{2g}$ is lower.

The fine electronic structure can be calculated from the Hamiltonian [12]

$$H_d = H_{\mathrm{CF}}^{\mathrm{cub}} + k\lambda_0 \vec{L}\cdot\vec{S} + B_2^0 O_2^0 + \mu_{\mathrm{B}}(\vec{L} + g_e\vec{S})\cdot\vec{B}_{\mathrm{ext}} (3)\,.$$

The crystal-field interactions have been divided into the cubic (dominant) and the leading axial term $B_2^0 O_2^0$. The second term is the intra-atomic spin-orbit (S-O) coupling where k denotes the change of the S-O coupling in a solid compared to the free-ion value. These terms are written in the decreasing energy sequence though we proceed calculations treating all terms on the same foot in the same diagonalization procedure. The results are shown in Figs 8 and 9.

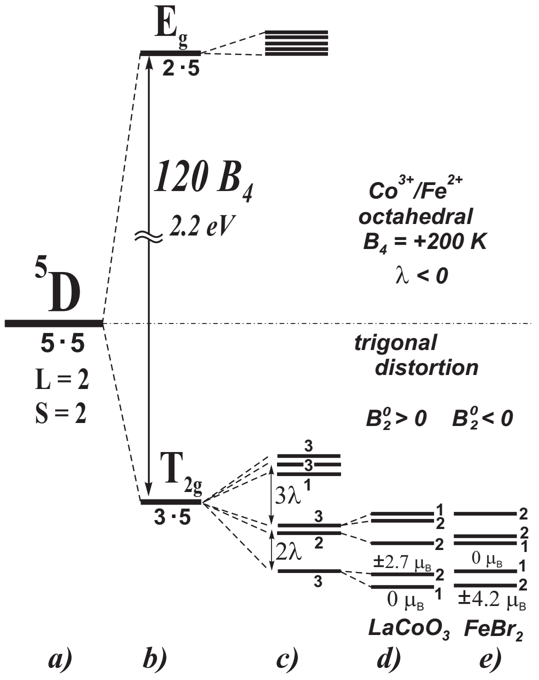

Fig. 8. The fine electronic structure produced by the cubic CEF in the presence of the spin-orbit coupling for the Co^{3+} ($3d^6$) ions. The 25-fold degeneracy of the ^5D ground term in the spin-orbital space is removed by the octahedral CEF, the S-O coupling and the trigonal distortion.

The results are quite peculiar. The low-energy electronic structure has *(i)* a non-magnetic singlet ground state and *(ii)* highly-magnetic excited doublet states ($\pm 2.32\ \mu_B$ and $\pm 3.66\ \mu_B$). The size of the lowest splitting depends on the value of the trigonal-distortion parameter B_2^0. The singlet-doublet sequence with the non-magnetic ground state, of Fig. 8(d), is the realization of the Jahn–Teller theorem.

The calculated temperature dependence of the paramagnetic susceptibility exhibits the low-temperature non-magnetic state, the pronounced maximum at 90 K and the Curie–Weiss law at temperatures above 150 K [12]. The change of the effective moment, calculated from the slope of χ^{-1} *vs* T curve, is seen at about 300 K. Such behaviour of χ *vs* T is quite general for

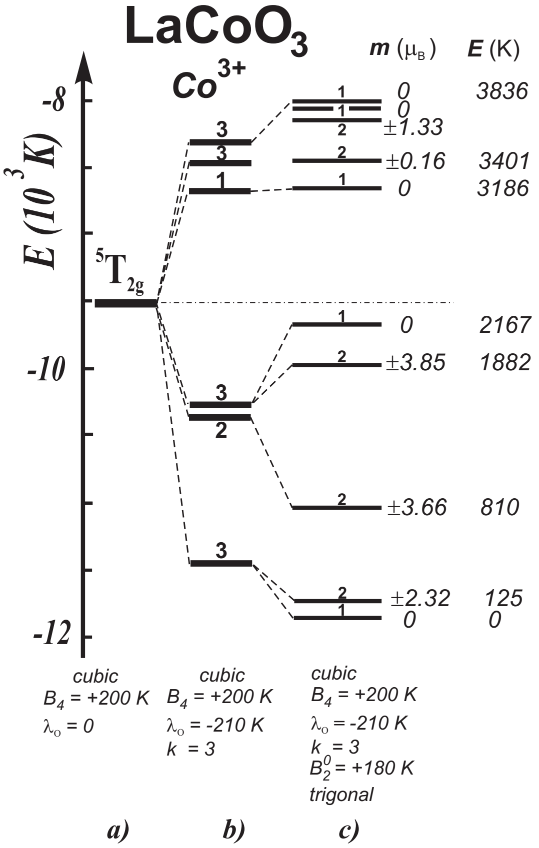

Fig. 9. The detailed low-energy electronic structure of the Co^{3+} ion in $LaCoO_3$ related with the splitting of the ${}^5T_{2g}$ cubic subterm.

positive values of B_2^0 as then always the ground state is singlet. The position of the maximum depends on value of the energy gap that depends on B_2^0 and λ ($k\lambda_0$). In order to reproduce the behaviour for $LaCoO_3$, the maximum at 90 K, we have performed computations for the parameters $B_4 = +17$ meV, $\lambda_0 = -20$ meV, $k = +2.7$ and $B_2^0 = +15.5$ meV that yields the spin gap of 11 meV. The E_g sub-term lies 2 eV above the ground state ($= 120\,B_4$) in agreement with optical data. In the electronic structure presented in Fig. 9 one can find the single-ion microscopic base for the low-, intermediate- and high-spin states postulated in theoretical discussions [13].

Thus, the non-magnetic state of $LaCoO_3$ is associated with the non-magnetic singlet ground state of the Co^{3+} ion formed by the slight trigonal distortion of the octahedral crystal field in $LaCoO_3$. One can say that this non-magnetic singlet state is the physical realization of the Jahn–Teller theorem. Our atomic-like model explains in very natural way the insulating state of $LaCoO_3$ — in fact, $LaCoO_3$ is one of the best insulators (ρ at 77 K amounts to 10^7 $\Omega\,$m). These calculations prove the importance of the quasi-atomic fine electronic structure resulting from the crystal-field and S-O interactions for description of low-temperature properties of compounds containing $3d$ ions. In magnetic Co^{3+} and Fe^{2+}-ion compounds the doublet magnetic ground state is realized, see Fig. 8(e). Detailed analysis performed by us for $FeBr_2$ provides very consistent description of its magnetic and electronic properties [14].

7. CEF states in UPd_2Al_3

The scientific interest in UPd_2Al_3 is related with the coexistence of the h-f phenomena and the large magnetic moment of about $1.5\mu_B$ ($T_N = 14\,K$). Moreover, UPd_2Al_3 exhibits superconductivity below 2 K [15]. The search for the crystal-field excitations in UPd_2Al_3 has been undertaken by the group of Steglich [16] with the purpose to verify the U^{4+} states proposed in Ref. [17]. The inelastic-neutron-scattering experiments [16] have revealed at 25 K the existence of the crystal-field excitations with energies of 7 and 23.4 meV. This experiment at 150 K has revealed further excitations at 3 and 14 meV at the energy-loss side and at 7 meV at the energy-gain side.

The observation of CEF excitations as well as their energies are in good agreement with those predicted on basis of the specific-heat analysis, but performed with the U^{3+} configuration [18]. This specific-heat analysis has yielded the energy levels at 0, 100, 150, 350 and 600 K, *i.e.* at 0, 8.6, 12.9, 30.1 and 51.7 meV, Fig. 10. All of them are Kramers doublet owing to the assumed U^{3+} configuration. The observed transitions are marked on this energy level scheme [19]. The analysis of other electronic and magnetic properties has been performed within the same Hamiltonian as presented for $ErNi_5$ but with the ground multiplet J value of 9/2. The hexagonal symmetry CEF parameters amount to $B_2^0 = +\,7.5$ K, $B_4^0 = +\,60$ mK, $B_6^0 = +\,0.07$ mK and $B_6^6 = -\,32$ mK. The crystal field in UPd_2Al_3 is more than two times bigger than in $NdNi_5$ (the overall splitting amounts to 54 and 21 meV, respectively). The CEF parameters for $NdNi_5$ of $B_2^0 = +3.35$ K, $B_4^0 = +14.5$ mK, $B_6^0 = -0.35$ mK and $B_6^6 = -13.5$ mK are quite similar to that of UPd_2Al_3 what is very nice owing to the same hexagonal crystallographic structure. In fact, the electronic structure the U^{3+} ion found in UPd_2Al_3 is very similar to that found for the Nd^{3+}-ion $NdNi_5$ [20]. Moreover in both compounds the magnetic moment is directed perpendicular to the hexagonal c-axis. Value of their magnetic moment is largely reduced, compared to the free-ion value, due to the crystal field.

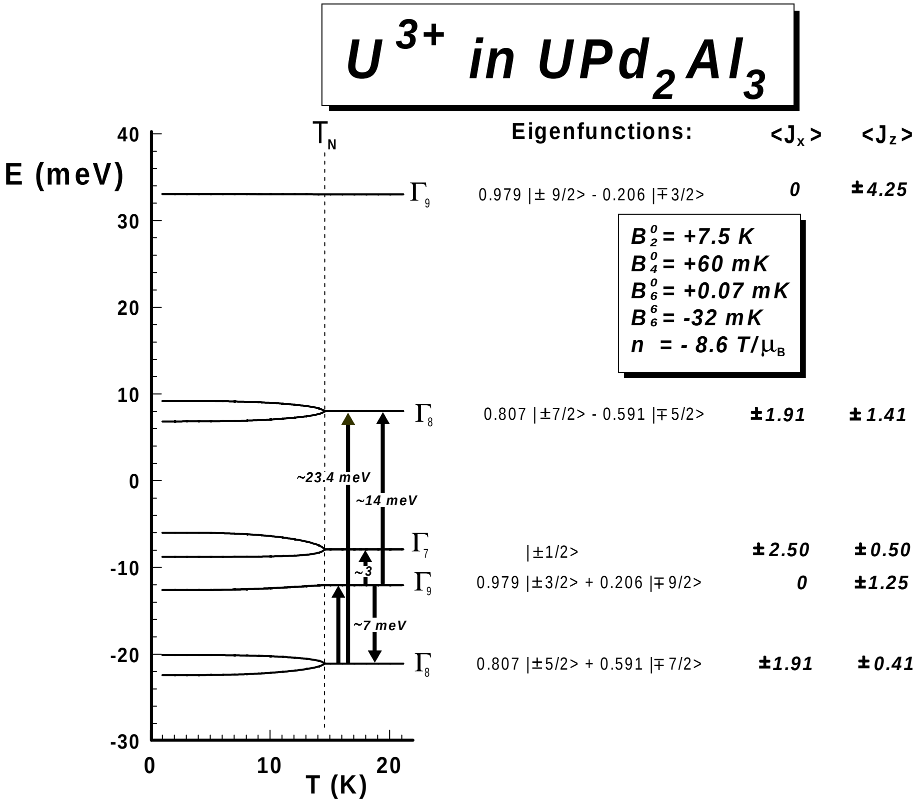

Fig. 10. Energy level scheme of the U^{3+} ion in UPd_2Al_3.The arrows indicate CEF transitions revealed by inelastic-neutron-scattering experiments [19].

Such good agreement with predictions derived for the U^{3+} ion in UPd_2Al_3 on basis of completely different experiments indicate the large physical adequacy of the derived fine energy level scheme and of the U^{3+} state. We would like to point out that the existence of the localized *f* electrons may not contradict the formation of the cooperative phenomena like magnetism or superconductivity. In system like UPd_2Al_3 the metallic properties are assured by conduction electrons made by, among others, three outer uranium electrons. Within the individualized-electron model, in intermetallics there coexists a few electronic subsystems, conduction-electron and *f*-electron system, that strongly interacts but without the charge exchange between them.

The observation of the localized states by such different techniques and their consistency provides strong argument for the applicability of the CEF model to (at least some) actinide compounds like it was found for UGa_2 [20] and $NpGa_2$ [21].

8. Concluding remarks

The basic concepts of the CEF model have been presented with the applications to electronic, magnetic and spectroscopic properties. The very consistent physical understanding of properties for $PrNi_5$ and $ErNi_5$ intermetallics has been obtained treating the f electrons as highly-correlated electron systems $4f^n$. The fine electronic structure, related with the atomic-like states and determined by the crystal-field and spin-orbit interactions, has been evaluated. These discrete energy states are within the meV range and their number agrees with that derived from atomic physics. We pointed out that significant successes of the crystal-field theory indicate the persistence of the atomic-like structure of the open-shell atoms even when they become a part of solid. The analysis of experimental results for $RE\,Ni_5$ series reveal the importance of the higher-order charge multipolar interactions for the fine electronic structure and for the realized ground state. There is very strong interplay of the magnetic state of a paramagnetic ion and the electric field produced by surrounding charges. The well-known example is the Pr^{3+} ion in $PrNi_5$. Similar situation takes place for the Co^{3+} ion is non-magnetic in $LaCoO_3$. It is the local symmetry of the crystal field that produces the non-magnetic state of the paramagnetic ion. These non-magnetic states are the manifestation of the Jahn–Teller effect. We would like to stress that the non-magnetic state in $LaCoO_3$ is produced by the local trigonal off-cubic distortion provided the intra-atomic spin-orbit coupling is taken into account.

Finally we should mention about very good description of electronic, magnetic and spectroscopic properties of UPd_2Al_3, UGa_2 and $NpGa_2$ within the CEF theory with the trivalent state. It indicates the existence of the discrete energy states and the substantial applicability of the CEF theory to (at least some) actinide compounds. In the CEF-like picture the number of f electrons is integer and excitations are the local neutral spin-like excitations. The same holds for excitations to the conjugate Kramers-doublet state, which in case of small splitting can be gapless.

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