Research Article

Introduction to rare-earth compounds.
Magnetism and electronic structure
of $PrNi_5$ and $ErNi_5$

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

The basic concepts of the crystal-field theory and its application to rare-earth compounds have been presented. Very consistent physical understanding of electronic, magnetic and spectroscopic properties of $PrNi_5$ and $ErNi_5$ has been obtained treating the RE atoms as highly-correlated electron systems. 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 pointed out that significant successes of the crystal-field theory indicate on the substantial preservation of the atomic-like structure of the open-shell atoms even when they become the part of a solid. An extension of the CEF theory to a quantum atomistic solid-state theory is proposed.

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

I. INTRODUCTION

Rare earth systems are a subject of very intensive studies, both experimental and theoretical [1, 2]. Most of them exhibit properties of industrial applications. Let mention, 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 neodym or erbium laser, where RE atoms are introduced as impurities to a transparent matrix (e.g. CaF_2, $CaWO_4$, YAG-$Y_3Al_5O_{12}$, ...) or are the part of a solid like in $PrCl_3$. $RECu_2O_4$- and $REBa_2Cu_3O_7$- based compounds exhibit high-temperature superconductivity [3, 4].

From theoretical point of view there is the continuous 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 land-mark of exotic and scientifically intriguing phenomena. The discovery of heavy-fermion phenomena in so-called low-carriers systems like Yb_4S_3 has shown that the heavy-fermion behaviour is not related with the metallic systems and a large number of electronic carriers. In the mixed-valence and hybridization theories the significant delocalization of the f electrons, leading to a non-integer value of f electrons, plays the crucial role. In the same time there is growing number of rare-earth compounds describable within the crystal-field (CEF) model. In the CEF model the f electrons are treated as fully localized and the RE ions show the integer valence.

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}, $REAl_2$... Compounds of the second group are insulators - here can be mentioned RE_2O_3, $PrCl_3$, NdF_3. The aim of this paper is to present the consistent physical model for the understanding of electronic and magnetic (e-m) as well as spectroscopic properties of rare-earth systems. For this the knowledge of low-energy part of the electronic structure is essentially important. We extend the CEF theory to the quantum atomistic solid-state theory (QUASST) that points out the existence of the discrete atomic-like energy states in systems containing $4f$, $5f$ and $3d$ open-shell atoms.

In order to focus our interest let concentrate on $ErNi_5$, an exemplary compound that belong to the wide class of $RENi_5$ 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
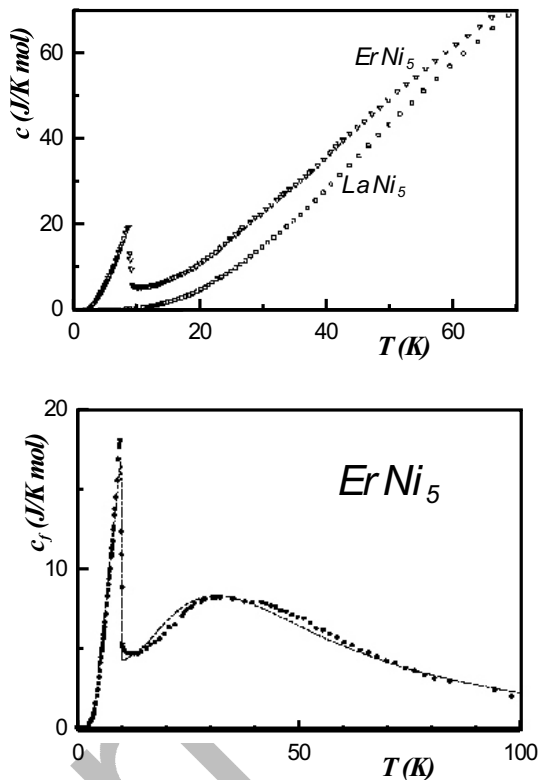
FIG. 1: a) Temperature dependence of the heat capacity of single crystalline ErNi$_5$ and LaNi$_5$ (experiment). b) Temperature variation of the contribution of the f subsystem to the heat capacity of ErNi$_5$ derived as the difference of the molar specific heat of ErNi$_5$ and LaNi$_5$. The dotted line 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].

but also for the whole series. Thanks it the transformation, suggested by the crystal-field theory, of the CEF parameters from one compound to another can be tested. The RENi$_5$ compounds with magnetic rare-earth elements i.e. from Ce to Tm are magnetic except 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 a magnetic state (de Gennes factor S(S+1) is the largest for the Gd^{3+} ion). The nickel ions
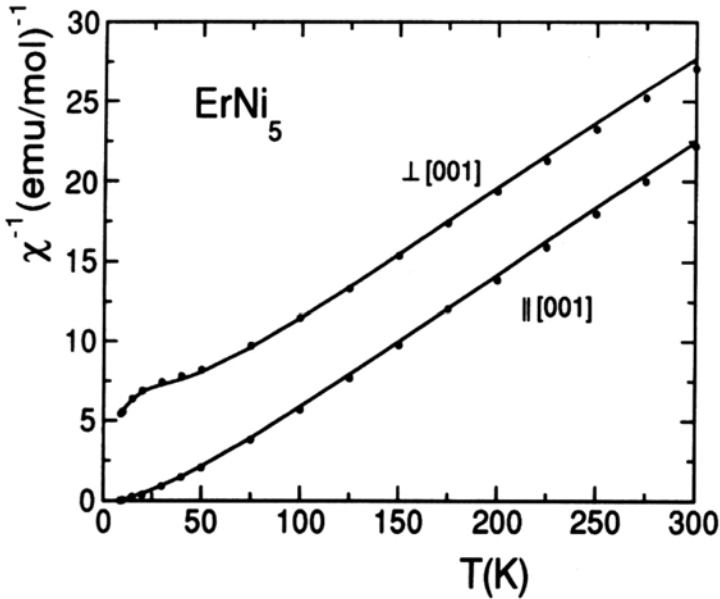
FIG. 2: Temperature dependence of the paramagnetic susceptibility along the principal directions of the hexagonal ErNi$_5$. The calculated results (lines) fully reproduce experimental data (closed circles). Violation of the Curie-Weiss law should be noticed at low temperatures [5].

are non-magnetic as we can infer from YNi$_5$ and LaNi$_5$. They both are Pauli paramagnets though with the exchange-enhanced susceptibility.

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. We would like to know ... - there are really a lot of interesting questions in rare-earth compounds.
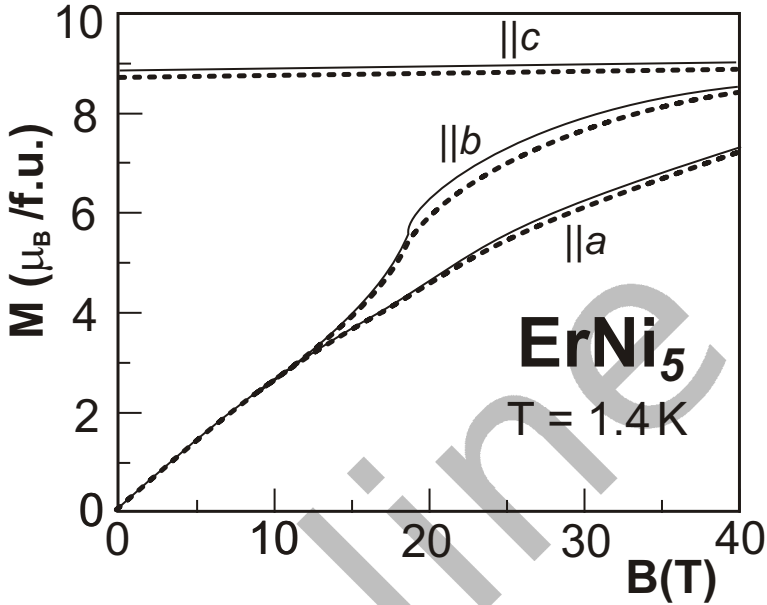
FIG. 3: The high-field magnetization curves at 1.5 K for single crystalline ErNi5 measured along the main hexagonal directions. The calculated results (lines) fully reproduce experimental data [5].

These are some example questions that we put on in the discussion of rare-earth compounds.

II.   QUANTUM ATOMISTIC SOLID-STATE THEORY (QUASST) - AN EXTENSION OF THE CEF THEORY

The basic ideas of the CEF theory - the existence of the discrete energy states for the paramagnetic open-shell $4f$ ions and the importance of the local symmetry - have been taken as the main ingredients in the construction of the more general theory for the solids - the quantum atomistic solid-state theory (QUASST). The basic idea of QUASST is that the paramagnetic atoms preserve much of their atomic properties also becoming the part of a solid. In short - atoms exist also in a solid. The novelty of this simple idea can be understood if one remembers that
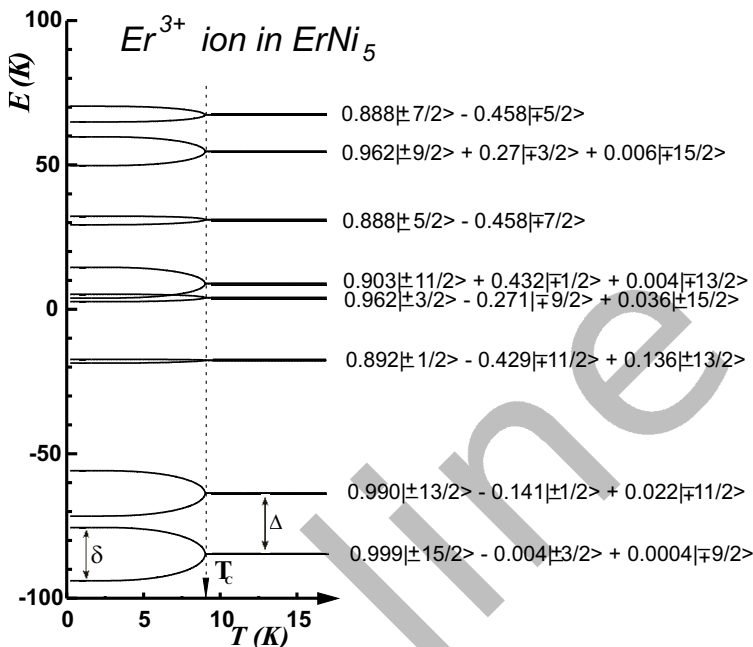
FIG. 4: The energy level scheme of the Er^{3+} ion in the hexagonal $ErNi_5$ under the action of the CEF interactions. All the levels are doublets as the Er^{3+} ion with J = 15/2 is a Kramers ion. These doublet states are split in the magnetically ordered state, below T_C of 9.2 K [5].

in the presently-in-fashion modern theories of solids atoms somewhere disappear. It is clearly visible in the band theories, more often recently used for the description of systems with open-shell atoms, which yield the continuous energy spectrum. We should explain 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. 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 electronic spectra has formulated 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 the total spin S and ii) the maximal possible value of the total orbital quantum number L provided the 1st condition is fulfilled. For the case of the Pr^{3+} ion with 2 f electrons we have S=1 (=1/2+1/2) and L=5 (3+2) and the ground term is denoted as ^3H. The ground terms of all rare-earth ions are collected in text books (e.g. C. Kittel, Introduction to Solid State Physics, ch. 14).

As we see for the case of the Pr^{3+} ion we have still the problem of the 33-fold degeneracy of the ^3H 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 introduction.

The separation between multiplets depends on the strength of the intra-atomic spin-orbit (s-o) coupling. RE atoms are characterized by 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) experiments 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 orbital 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.

III.   EXAMPLES

A.   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 different 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 $|J J_z\rangle$ with J_z different by 6. Having the eigenvalues E_i (= energies) and the eigenfunctions $|\Gamma_i\rangle$ we can calculate thermodynamics, i.e. temperature dependence 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 magnetisation and its temperature dependence. Having available energies we can calculate the canonical partition function.

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 all Pr ions exhibit practically the same energy level splitting. It is remarkable - but it is done in a crystal by the translational symmetry.

Inspecting Fig. 6 one can find there the Schottky-type heat capacity named in the memory of Schottky who was the first to study 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
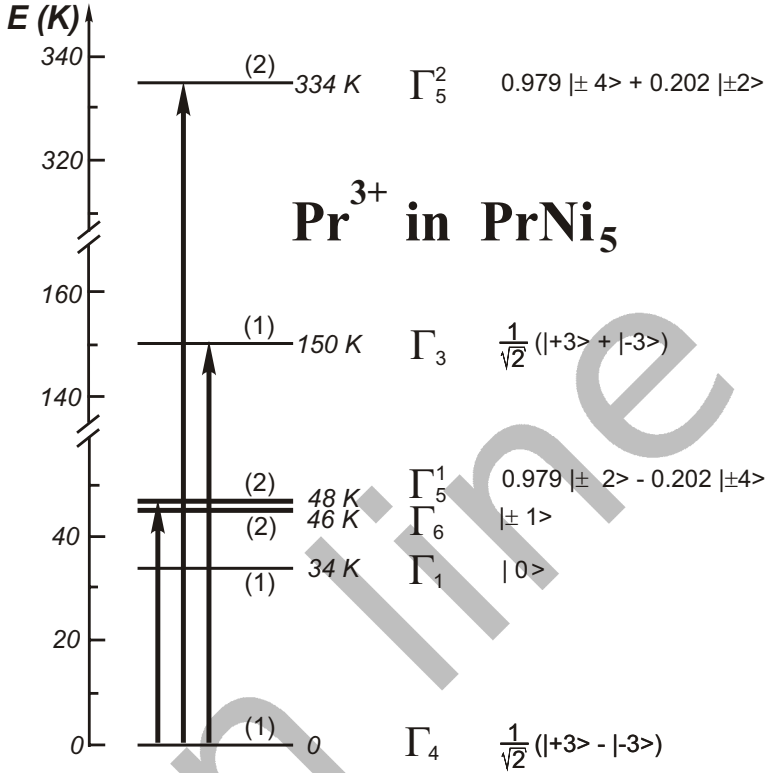
FIG. 5: The energy level scheme of the Pr^{3+} ion in the hexagonal non-magnetic compound $PrNi_5$ under the action of the CEF interactions [7]. Arrows indicate the transitions observed in the INS spectroscopy.

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/Kmol. In case of $PrNi_5$ the maximal heat reaches almost 3 times more (≈ 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).

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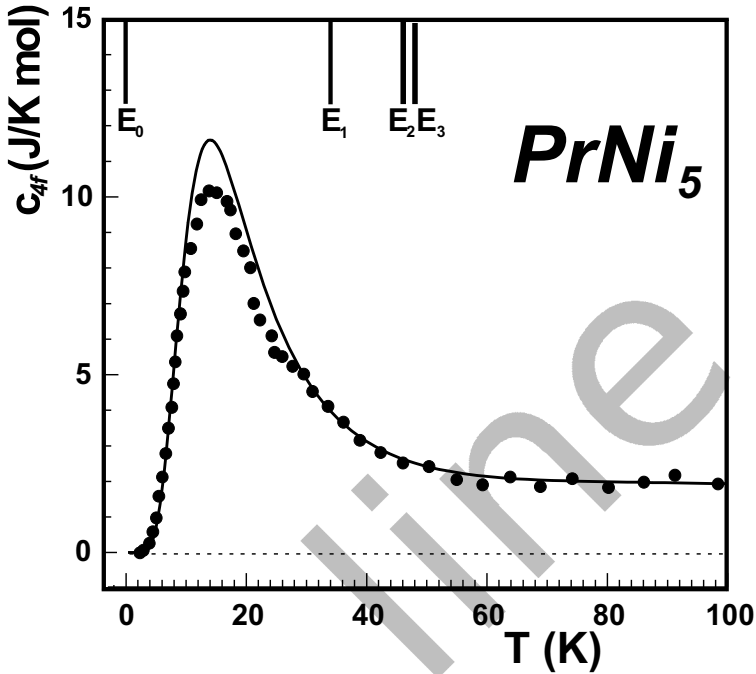
FIG. 6: Experimentally derived temperature dependence of the f-heat capacity of $PrNi_5$ together with calculations for the atomic-like discrete energy spectrum of the Pr^{3+} ions [7]. On the top the energy position of the CEF states are shown.

ions we have to take into account the Pauli-like (= temperature independent) susceptibility χ_0 of $4 \cdot 10^{-3}$ μ_B/Tf.u. originating from the conduction electrons according to the formulae: $\chi_{exp} = \chi_{CF} + \chi_0$. 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. 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 derived the value of the effective moment in μ_B as $p_{eff}^2 = 3k_B \Delta T/\Delta \chi^{-1})$. 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_{eff}^2(free ion) $= g^2 \mu_B^2 J(J+1)$.

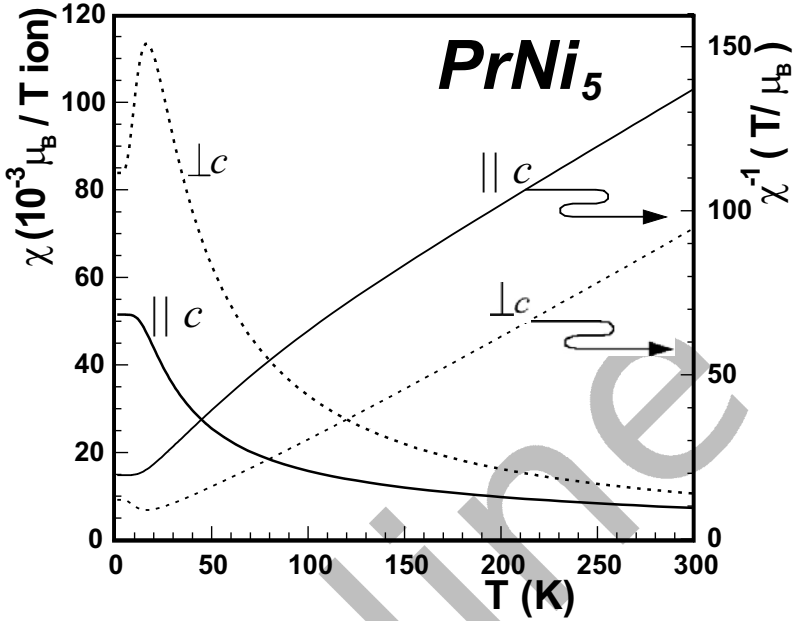These calculations reproduce also the low-temperature susceptibility.

FIG. 7: Temperature dependence of the paramagnetic suscepti-bility 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 $\chi_0 = 4\cdot10^{-3}$ μ_B/T-ion is taken into account. The violation of the Curie-Weiss law should be noticed at low temperatures [7].

Hence one can say that the reason for the departure from the Curie (Curie-Weiss) law at low temperatures is the existence of the fine electronic structure related with the Pr^{3+} ions.

B. 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 $^4I_{15/2}$ with J = 15/2, S = 3/2 and L = 6 and the Lande factor $g_L = 6/5$. The overall degeneracy is 16. The energy level scheme of the f^{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-)

11

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 approximation and by considering the RE moments. It is justified as when J is the good quantum number then the magnetic moment ($\mu = -g_L\mu_B J$) 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 [3–5]:

$$H = H_f + H_{f-f} =$$

$$\sum_n \sum_m B_n^m \hat{O}_n^m + n g_L^2 \mu_B^2 \left(-J\langle J \rangle + \frac{1}{2}\langle J \rangle^2 \right) + g_L \mu_B J \cdot B_{ext}$$

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 Bext. The internal molecular field amounts to $B_{mol} = n\mu$. This field produces the splitting of the charge-formed Kramers-doublet ground state at each f site in the magnetically-ordered state as is shown in Fig 4. This field has been calculated to be 1.5 T at 0 K for $ErNi_5$ [5]. A field of 350 T, for example, has been evaluated to be in $Nd_2Fe_{14}B$. $Nd_2Fe_{14}B$ 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 a given set of CEF

parameters, that reproduces the value of the magnetic temperature. These 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. Examplary results of these calculations have been shown in Fig. 3 for ErNi$_5$. All thermodynamics is performed similarly to that discussed earlier for PrNi$_5$ but now the levels are temperature dependent what makes the calculations much more sophisticated.

IV.   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 $S=(g_L-1)\cdot J$ and the orbital quantum number $L = (2 - g_L)\cdot J$ are determined by J. The associated spin moment in the z-direction amounts to $\mu_s = 2\cdot (g_L-1)\cdot J_z$ (in μ_B) and the orbital moment $\mu_o = (2-g_L)\cdot J_z$. In case of, for instance, the Nd^{3+} ion in a $|JJ_z\rangle$ state the orbital moment amounts to $\mu_o=14/11\cdot J_z$ and the spin moment $\mu_s = -6/11\cdot J_z$. The total moment is $\mu = \mu_o + \mu_s = 8/11\cdot J_z$ as should be. (8/11 is the Lande factor for the Nd^{3+} ion). One sees that i) the orbital moment is very large and that ii) the spin moment is opposite to the orbital moment. This latter fact is the effect of the 3rd Hund's rule. For the heavy RE the spin and orbital moments are parallel. For the Er^{3+} ion $\mu_o=+0.8\cdot J_z$, $\mu_s = +0.4\cdot J_z$.

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

V.   CRYSTAL-FIELD ORIGIN OF THE HEAVY-FERMION PHENOMENA

The splitting of the lowest doublet produces, in case of the well-defined long-range magnetic structure, the λ type of peak in temperature dependence of the heat capacity as is seen for ErNi$_5$ in Fig. 1. From this figure one can see that the mean-field approximation describes surprisingly well the transition peak. It means that in heat-capacity experiments, even at lowest temperatures, even in the intermetallic compound,

many-electron excitations of the f subsystem over the fine energy level scheme are superimposed on single-electron excitations, associated with conduction electrons, at the Fermi level. In case of the Kramers system the localized conjugate state can lie very closely to the ground state. In case of ErNi$_5$ it is 1.5 meV at zero temperature (the splitting of the ground doublet). This gap closes with temperature at T_C (T_N). Such the behaviour is typical for the Kramers system. It can be, in principle, shifted down to much lower temperatures as the low-temperature heat capacity depends on the energy distance to the first excited level(s). In case of the Kramers system the splitting of the doublet depends on the strength of the spin interactions. They can be sometimes quite small and produce the very small splitting, of 0.1 meV (=1.2 K) only. It will result in a large heat capacity at low temperatures. Such the situation occurs for the heavy-fermion (h-f) compounds that exhibit enormous low-temperature heat capacity. In the CEF-like picture the f count is integer and h-f particles are associated with the local neutral spin-like excitation. These excitations can easily propagate from site to site in the crystal. It is worth to note that the Kramers degeneracy has to be always removed before the absolute zero temperature is reached - otherwise the 3rd thermodynamic law would be violated. In this model the f electrons are localized. This starting point is in contrary to presently-in-fashion theories that point out the delocalization of f electrons, so f deviates from an integer number, as the origin of heavy-fermion phenomena.

The splitting of the Kramers ground doublet of so small value as 0.4 meV has been recently revealed by high-resolution INS in Nd$_2$CuO$_4$ [8, 9]. These results confirm the earlier theoretical evaluations on basis of temperature dependence of the heat capacity [10].

To make clear for the understanding - the CEF provides the Kramers doublet for the action of spin interactions. Also the fine electronic structure can differ from site to site. The lowering symmetry at low temperatures breaks the translational symmetry.

VI.   CONCLUSIONS

The basic concepts of the CEF theory have been presented with the illustration of the calculations of electronic, magnetic and spectroscopic properties of RENi$_5$ intermetallic compounds. The very consistent physical understanding of properties for PrNi$_5$ and ErNi$_5$ intermetallics has been obtained treating the RE atoms as highly-correlated electron systems. The fine electronic structure, related to the atomic-like states

and determined by the crystal-field and spin-orbit interactions has been evaluated.

We pointed out that significant successes of the crystal-field theory indicate on the preservation of the atomic-like structure of the open-shell atoms even when they become the part of a solid. The analysis of experimental results for $RENi_5$ series reveal the importance of the higher-order charge multipolar interactions for the fine electronic structure and for the ground state. An extension of the CEF theory to the quantum atomistic solid-state theory (QUASST) is proposed, that points out the existence of the discrete energy spectrum in $4f$-, $5f$- and $3d$-atom containing compounds.

QUASST points out the importance of the intra-atomic s-o coupling and the atomic scale symmetry in the description of electronic and magnetic properties macroscopically observed. This atomic symmetry is related to the symmetry of the local crystal field rather than of the lattice point-symmetry. QUASST points out the 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 $PrNi_5$. It is the local symmetry of the crystal field that produces the non-magnetic state of the paramagnetic ion. Within the CEF community this effect is discussed in the connection to the Kramers and the Jahn-Teller theorem. The CEF interactions can substantially reduce the local magnetic moment also in case of the Kramers ions. It has been found that the hexagonal symmetry CEF can produce a non-magnetic Kramers-doublet ground state [11].

Finally we should mention about very good description of electronic, magnetic and spectroscopic properties of UPd_2Al_3 [12, 13], UGa_2 [13] and $NpGa_2$ [14] within the CEF theory with the trivalent state. It indicates substantial applicability of the CEF theory to (some) actinide compounds.

[1] J. J. M. Franse and R. J. Radwanski, in: *Handbook of Magnetic Materials*, K. H. J. Buschow, ed. (North-Holland, 1993) **7**, 307 (1993).

[2] O. Moze, in: *Handbook of Magnetic Materials*, K. H. J. Buschow, ed. (North Holland 1998) **11**, 493 (1998); P. Fulde, Physica B **230-232**, 1 (1997).

[3] A. Furrer, P. Bruesch, and P. Unternahrer, Phys. Rev. B **38**, 4616 (1988).

[4] J. Mesot and A. Furrer, J. of Superconductivity, **10**, 623 (1997).

[5] R. J. Radwanski, N. H. Kim-Ngan, F. E. Kayzel, J. J. M. Franse, D. Gignoux, D. Schmitt, and F. Y. Zhang, J. Phys.: Condens. Matter **4**,

8853 (1992).

[6] M. Guillaume, W. Henggeler, A. Furrer, R. S. Eccleston and V. Trounov, Phys. Rev. Lett. **74**, 3423 (1995).

[7] N. H . Kim-Ngan, R. J. Radwanski, F. E. Kayzel, and J. J. M. Franse, J. Magn. Magn. Mater. **140-144**, 863 (1995).

[8] A. Furrer and H-U. Gudel, Phys. Rev. B **56**, 5062 (1997).

[9] W. Henggeler, B. Roessli, A. Furrer, P. Vorderwisch, and T. Chatterji, Phys. Rev. Lett. **80**, 1300 (1998).

[10] R. J. Radwanski, Solid State Commun. **99**, 981 (1996); Acta Physica **1**, 15 (2006).

[11] R. J. Radwanski, Physica B **182**, 209 (1992).

[12] R. J. Radwanski and J. J. M. Franse, in *Physics of Transition Metals*, P. M. Oppenner and J. Kubler, eds (World Scientific 1993) p. 38 (1993).

[13] R. J. Radwanski and N. H. Kim-Ngan, J. Alloys and Compounds **219**, 260 (1995).

[14] R. J. Radwanski, J. Phys.: Condens. Matter **8**, 10467 (1996).