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STARK AND ZEEMAN EFFECTS IN $Nd_2Fe_{14}B$ AND $Pr_2Fe_{14}B$ INTERMETALLICS

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The energy level scheme of the Nd^{3+} and Pr^{3+} ions in ferromagnetic $Nd_2Fe_{14}B$ and $Pr_2Fe_{14}B$ intermetallic compounds was evaluated on the basis of all known experiments. In calculations the effect of charge (Stark effect) and spin-dependent (Zeeman effect) interactions were taken into account by means of the crystal-field and molecular-field approximation, respectively. The derived energy level scheme is associated with the removal of the degeneracy of the lowest multiplet given by Hund's rules, i.e. $^4I_{9/2}$ (Nd^{3+}) and $^3H_4$ (Pr^{3+}). The revealed low-energy electronic structure (< 25 meV $=$ 200 cm^{-1}) is associated with many-electron states of the RE^{3+} ions. Magnetic and electronic properties resulting from this fine structure are compared with all known experimental results. The localized crystal electric field levels exist also in Nd_2CuO_4, an ionic compound which by doping with Ce becomes high-T_c superconductor, indicating the formation of crystal electric field states independently on the metallic or ionic state.

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1. Introduction

Electronic structure of the RE^{3+} ions can be studied by different experimental techniques. Applied techniques depend on the studied energy scale which subsequently depends on the electronic structure to be investigated. In this paper we are interested in the fine electronic structure and involved transitions have energies below 25 meV. This energy is equivalent to the thermal energy of $T = 300$ K. These low-energy transitions are of great importance in solid-state physics. In this energy region experimental techniques like inelastic neutron scattering, specific heat, magnetic measurements are of great importance. As all of these techniques have some advantages and disadvantages, the most proper way to evaluate the electronic structure goes via self-consistent analysis of different experimental results. It is, however, very troublesome procedure, but there is no other way to get *a consistent description* of magnetic and electronic (m-e) properties. It turns out that m-e properties of an intermetallic compound containing rare-earth elements are largely determined by properties of the unfilled *f*-shell electrons.

Two systems, $Pr_2Fe_{14}B$ and $Nd_2Fe_{14}B$, were chosen, as Pr^{3+} and Nd^{3+} ions behave differently under the action of crystal field, as they are non-Kramers and Kramers ions, respectively. The aim of this contribution is to present electronic structures of the trivalent *f* ions which have been derived from a consistent theoretical analysis of different experimental results.

2. Experimental results for $Pr_2Fe_{14}B$ and $Nd_2Fe_{14}B$ — an overview

$Pr_2Fe_{14}B$ and $Nd_2Fe_{14}B$ are examples of intermetallic compounds formed by rare-earth metals with 3*d* transition metals. They crystallize in a tetragonal structure and exhibit a ferromagnetic magnetic ordering below 565 and 592 K, respectively. This ordering is due to Fe–Fe interactions. The magnetization curves measured on single-crystalline sample in high magnetic fields up to 40 T are presented in Figs. 1 and 2. These measurements reveal in both compounds large anisotropy of magnetic properties and complex magnetic-field dependence [1, 2]. The most remarkable feature of $Pr_2Fe_{14}B$ is the steep, but smooth, increase in the magnetization at fields of 13.2 T and 17.1 T applied along the [100] and [110] direction, respectively. The saturation magnetization M_s amounts to $37.0\mu_B$/f.u. and is directed along the tetragonal axis.

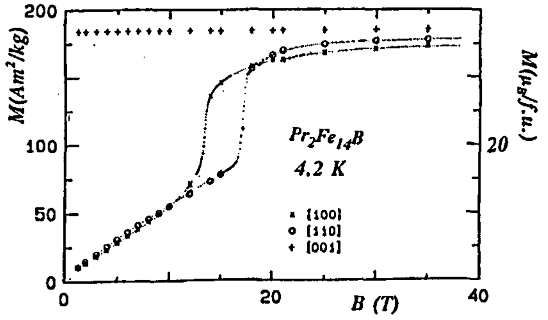

Fig. 1. Magnetization curves measured at 4.2 K on single-crystalline $Pr_2Fe_{14}B$ along main crystallographic directions of the tetragonal unit cell. After Ref. [1].

$Nd_2Fe_{14}B$ undergoes a metamagnetic first-order transition at 18 T for the [100] direction. There exists at 4.2 K a tilted magnetic structure, tilted 30° from the *c* axis, as non-zero magnetization is found along three main crystallographic directions. In this tilted structure magnetic moments of Fe and Nd are directed 30° with respect to the tetragonal *c* axis. (In fact, there is some spread in direction of the Nd and Fe moments by about 4° — this detail, related with complex crystallographic structure, will not be discussed here.) This tilted magnetic structure vanishes with temperature and disappears at 135 K. M_s amounts to $37.2\mu_B$/f.u. Inelastic-neutron-scattering experiments of Loewenhaupt et al. [3] reveal local excitations with energies of 22 and 36 meV providing strong argument

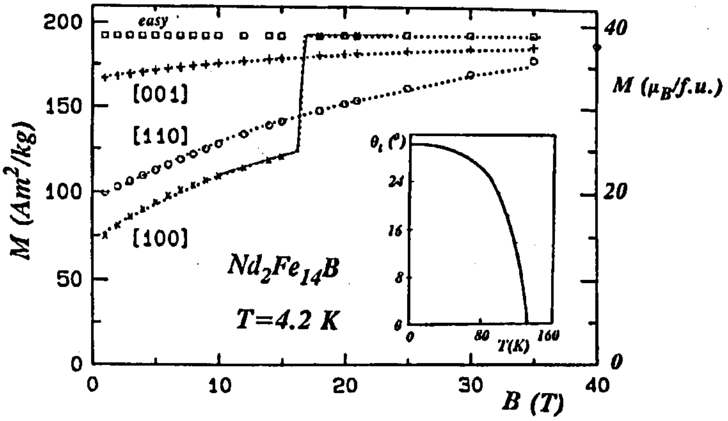

Fig. 2. Magnetization curves measured at 4.2 K on single-crystalline $Nd_2Fe_{14}B$ along main crystallographic directions of the tetragonal unit cell [1]. There are two important features: (i) the abrupt metamagnetic transition at 17.1 T for the [100] direction and (ii) that the magnetic moment does not lie along any main crystallographic direction as the magnetization does not start from zero for all curves. Data denoted by squares were obtained for the single-crystalline sample which was free-to-rotate under the action of the applied field. Its value is equal to the spontaneous moment though the direction is not determined in the experiment.

for the existence of the localized crystal electric field (CEF)-like levels. In advance we can say that the present calculations are able to account very well for the observed phenomena yielding the absolute-zero temperature values for the magnetocrystalline-anisotropy energy, and the magnetic moment as well as their temperature dependences, in good agreement with experimental data.

3. Analysis and discussion

It turns out that electronic and magnetic properties of great number of rare-earth intermetallics are very well understood within the individualized-electron model for rare-earth compounds [4, 5]. According to this model f electrons keep their individuality also being placed into intermetallic and ionic compounds. In intermetallics there are also itinerant electrons originating from outer electrons of all constituting elements. Thus in intermetallics there coexists a few (here only 2 are specified) physically important electronic subsystems: f electronic subsystem(s) and conduction-electron subsystem [6, 7]. These two subsystems are described by completely different theoretical approaches: localized-electron and itinerant-electron models. The f electron subsystem exhibits a discrete energy spectrum associated with bound states of the highly-correlated electron system f^n whereas conduction electrons form a band. The interaction between them goes basically via the spin polarization [4].

As far as the spontaneous magnetization is concerned the magnetization of $Pr_2Fe_{14}B$ and $Nd_2Fe_{14}B$ is formed both by iron ions ($2.2\mu_B$) and RE ions (3.2 and $3.27\mu_B$ for the Pr and Nd ions). The observation of the iron moment exactly of this value in $Y_2Fe_{14}B$ makes the analysis complete. Moreover, as $Y_2Fe_{14}B$ shows simple magnetization curves, with the spontaneous magnetization of $30.6\mu_B$/f.u. and the anisotropy field of 5 T, the complex magnetic behavior in $Pr_2Fe_{14}B$ and $Nd_2Fe_{14}B$ must be attributed to the presence of the f electrons. In fact, this complex behaviour allows for evaluation of the electric and magnetic fields acting on the Pr^{3+} ion in $Pr_2Fe_{14}B$ and on the Nd^{3+} ion in $Nd_2Fe_{14}B$ [8].

In Fig. 3 the energy level scheme of the Pr^{3+} ion in $Pr_2Fe_{14}B$ is presented. It contains 5 singlets and 2 doublets as one expects for the action of the tetragonal CEF interactions. The 9-fold degeneracy of the ground multiplet is fully removed as the ground state is a singlet. The CEF Hamiltonian for the tetragonal symmetry has the form

$$H_{\mathrm{CF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4 + B_6^4 O_6^4. \qquad (1)$$

Off-diagonal terms B_4^4 and B_6^4 cause the mixture of J_z states that differ by 4 as one can see inspecting the shape of the eigenfunctions. One should note that the whole CEF effect is comprised in energy to 50 meV. It is much lower than the separation to the first excited multiplet which is expected to lie at 261 meV as it is in the Pr element [9]. It causes that there is no influence of higher multiplets on the magnetic and electronic properties at temperatures up to room temperature. Although the charge-formed ground state is a non-magnetic singlet, the magnetic moment can be induced by magnetic fields. Effect of the magnetic field has been simulated in Fig. 4. Fields larger than 20 T substantially modify the energy level scheme producing finally the magnetic state. Namely, the field of 35 T applied along the tetragonal axis induces the magnetic ground state with the full Pr magnetic moment, see Fig. 5. Such field, even much larger, is set up in $Pr_2Fe_{14}B$ by the ordered Fe moments. From analysis it follows that the Fe moments produce the molecular

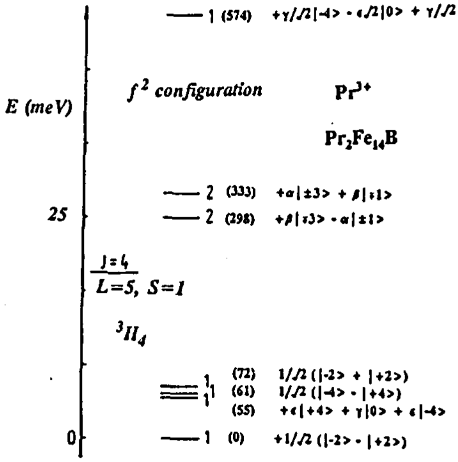

Fig. 3. Energy level scheme of the Pr^{3+} ion in $Pr_2Fe_{14}B$. Under the action of the tetragonal CEF interactions the 9-fold degenerate ground multiplet is split into 5 singlets and 2 doublets. The charge-formed ground state is a non-magnetic singlet.

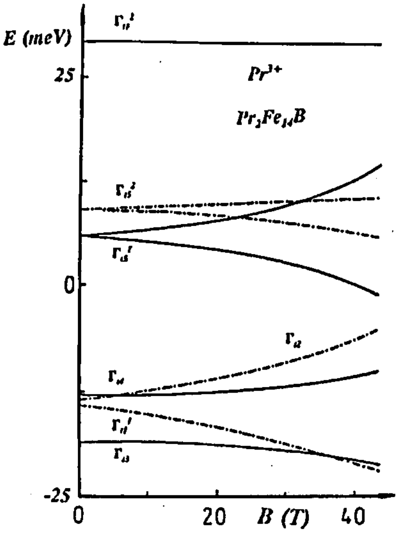

Fig. 4. Field dependence of the energy level scheme of the Pr^{3+} ion in $Pr_2Fe_{14}B$. The first excited level is much more magnetic state and this state becomes the ground state in fields above 35 T.

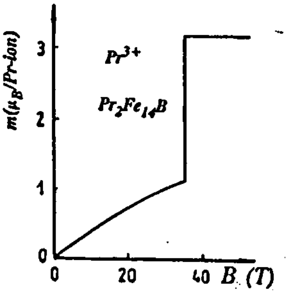

Fig. 5. Field dependence of the induced magnetic moment of the Pr^{3+} ion. The field is directed along the tetragonal axis. The jump at 35 T is related with the crossing of CEF levels. After the crossing the full Pr^{3+} ion moment of $3.2\mu_B$ is obtained. The Pr ion in $Pr_2Fe_{14}B$ experiences a molecular field of about 230 T originating from the ordered Fe sublattice and thus its moment in this compound exhibits the full trivalent-ion value.

field at the Pr site of 240 T [10]. For full clarity it is necessary to add that there is no direct correlation between the metamagnetic field in which the full Pr moment is induced and the metamagnetic transitions observed in the magnetization curves in Fig. 1. These latter transitions are associated with some peculiarities in the angular dependence of the magnetocrystalline anisotropy during the rotation of the full Pr moment towards the field direction. These peculiarities are, of course, produced by CEF interactions, the same which are responsible for the energy level scheme. In formation of these peculiarities the higher order CEF parameters play

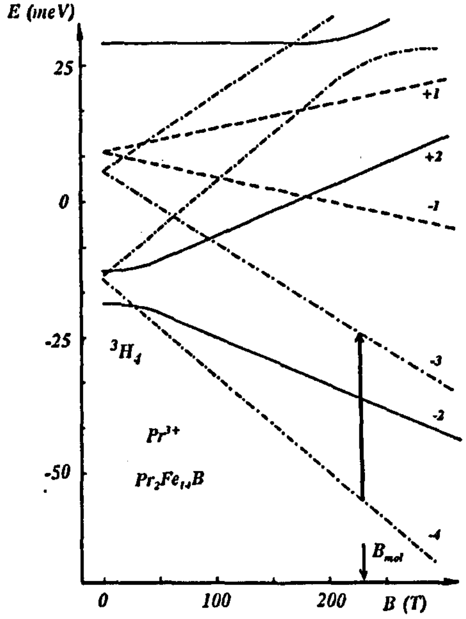

Fig. 6. Dependence of the energy level scheme of the Pr^{3+} ion in $Pr_2Fe_{14}B$ on the applied magnetic field of values comparable with those realized in the crystal. In $Pr_2Fe_{14}B$ the Pr ion experiences a field of 240 T originating from the Fe moments. The levels are labelled with value of J_z which becomes at these fields already quite close to the integer values. Note that for large fields energy level scheme becomes more and more determined by molecular-field interactions.

decisive role. The CEF interactions are 2 times weaker than the molecular field interactions. The overall CEF splitting amounts to 50 meV whereas the effect of molecular field $2\mu_B J \cdot B_{\text{mol}}$ amounts to 90 meV. From Fig. 6 one can see that the energy levels are not at all equally separated as one expects in the absence of the CEF interactions. Moreover, the energy levels are still not in good order i.e. they are not ordered according to the increasing number of the z-component $\langle J_z \rangle$ though the ground level is already described by the $J_z = J$ as should be in case of the large molecular-field limit. This energy level scheme, derived from analysis of high-field magnetization curves, has been confirmed by inelastic-neutron-scattering (INS) studies [3]. These studies have revealed CEF excitations with energy of 32 meV which is identified with the excitation to the second excited level. The observation of the excitation to the second level instead to the first is in agreement with theoretical predictions for the matrix elements for the transition probability. This INS result is of unvaluable importance as high-field magnetization and INS experiments probe the energy level scheme in completely different ways. Thus, such agreement gives large confidence to the obtained energy level scheme. The energy level scheme for the Nd^{3+} ion in $Nd_2Fe_{14}B$ is presented in Fig. 7. It has been derived by the analysis of magnetization curves presented in Fig. 2. Details

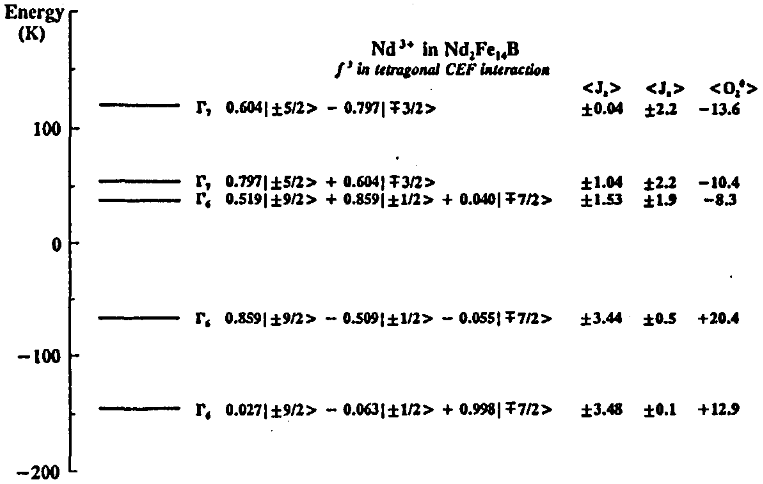

Fig. 7. The energy level scheme of the Nd^{3+} ion in $Nd_2Fe_{14}B$ together with eigenfunctions. Under the action of the tetragonal CEF interactions the 10-fold degenerate ground multiplet $^4I_{9/2}$ is split into 5 Kramers doublets. Magnetic characteristics of the CEF levels are also shown. For the ground state they are much smaller than the value of 9/2 existing for the free ion.

of analysis of magnetization curves have been presented in Ref. [11]. The scheme contains 5 doublets as the Nd^{3+} ion having 3 f electrons is the Kramers ion. All doublets are the Kramers doublets with magnetic characteristics given as $\langle J_z \rangle$ and $\langle J_x \rangle$. All CEF effect on the lowest multiplet is within 24 meV. It is 10 times smaller than the separation to the first excited multiplet which is expected to be at about 237 meV as has been observed for the Nd element [9]. Despite of this "weakness" of CEF interactions they determine the m-e properties of $Nd_2Fe_{14}B$ up to, at least, room temperature.

All the experimental curves are very well described as the rotation of two magnetizations, formed by the Fe and Nd ions, towards the field direction overcoming the magnetocrystalline anisotropy of the Fe and Nd ions [11]. The used description is the same as applied earlier to $Pr_2Fe_{14}B$. It turns out that the magnetocrystalline anisotropy of the Nd ion is of the single-ion origin being determined by the CEF interactions. The Nd ion experiences molecular field of 350 T originating from the Fe sublattice magnetization. As the action of the Fe-produced molecular field is isotropic, the calculations of the energy level scheme were performed for different directions of the internal molecular field. Figure 8 displays the energy level scheme of the Nd^{3+} ion as the function of the direction of the molecular field measured by the angle θ with respect to the tetragonal axis. The minimum of the free energy of the Nd^{3+} ion, which is at $T = 0$ K equal to the energy of the ground state, occurs for $\theta = 30°$. In this way experimental observation about the tilted magnetic structure is correctly reproduced. With temperature this angle decreases as the minimum of the free energy shifts with temperature to lower value of 0. It

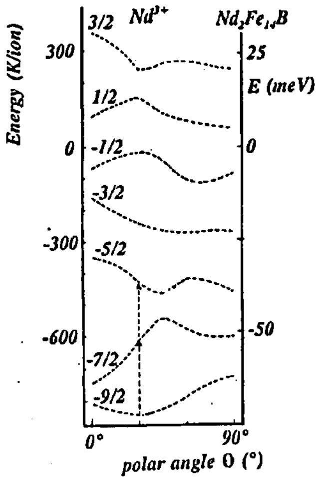

Fig. 8. The energy level scheme of the Nd^{3+} ion in $Nd_2Fe_{14}B$ for different directions of the molecular field as derived from the analysis of high-field magnetization measurements of Fig. 2. The direction is given by the polar angle of the field with respect to the tetragonal axis. The molecular field amounts to 350 T. The minimum energy of the ground state indicates the preferred direction of the Nd moment — it is 30° from the c axis in agreement with experimental observation. Two arrows indicate the allowed INS excitations which were indeed measured.

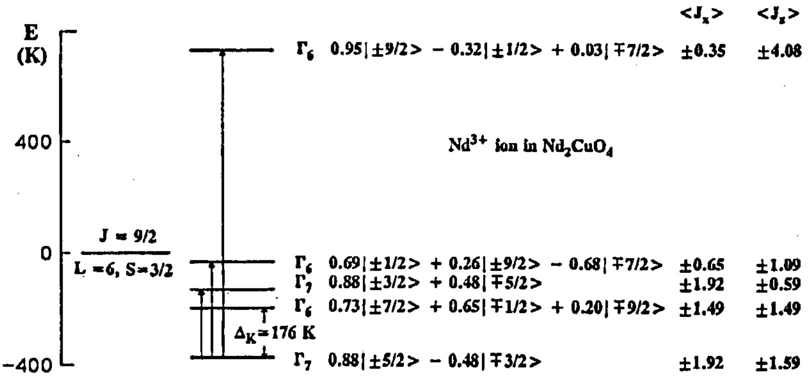

Fig. 9. The energy level scheme of the Nd^{3+} ion in tetragonal Nd_2CuO_4 together with eigenfunctions. It contains 5 Kramers doublets. Magnetic characteristics of the CEF levels are also shown. For the ground state they are much smaller than the value of 9/2 existing for the free ion.

can be understood knowing that the minimum of free energy shifts in the direction in which the excited level is closer.

These calculations allow for evaluation of the magnetic moment (in this case it takes the maximal value of $3.27\mu_B$ at $T = 0$ K), the magnetocrystalline energy and its angular dependence as well as their temperature dependences. The energy level scheme derived from the analysis of high-field magnetization studies was verified by INS experiments. In these experiments performed at helium temperature two CEF excitations were observed at 22 and 36 meV. Two CEF excitations are due to the peculiarities of CEF interactions which produce the preferred moment direction tilted from the tetragonal axis. In case of the molecular-field determined energy level scheme only transitions to the subsequent levels are allowed. It is worth noting that the minimum at 30° of the ground state is produced by higher-order CEF interactions. It shows that for the physically proper analysis of m-e properties of a rare-earth compound all CEF terms, relevant for the given symmetry, have to be taken into account.

We applied the same procedure to Nd_2CuO_4, a compound which by doping with Ce becomes high-T_c superconductor. The energy-level scheme of the Nd^{3+} in Nd_2CuO_4, presented in Fig. 9, is predominantly determined by CEF interactions as the molecular field acting on the Nd ion is very small [12]. It is due to the antiferromagnetic ordering of the Cu ions which causes that the molecular field originating from different Cu ions largely cancels each other.

4. Conclusions

The energy level scheme of the Pr^{3+} and Nd^{3+} ions in $Pr_2Fe_{14}B$, $Nd_2Fe_{14}B$ and Nd_2CuO_4 was constructed on the basis of all known experimental data. The energy level scheme results from the interplay of the charge and spin interactions. Approximation of these interactions by CEF and molecular-field approaches gives a surprisingly good description of the observed phenomena. It turns out that for a quantitative description of magnetic and electronic properties all CEF terms relevant to the ion point-symmetry have to be taken into account. It has been shown that higher-order CEF terms produce very remarkable effects like substantial reduction of the magnetic moment or tilted magnetic structures. Localized CEF states are detected both in the metallic, ionic or superconducting state. It is worth making a remark that the CEF approach, often considered as too simple, is a semi-relativistic approach as it takes into account the spin–orbit interactions, which are of the relativistic origin. This fact seems to be important as most of the present band-structure calculations are not able to take this effect into account yielding only the spin moment.

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