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Model based on single-ion theory: Preferential substitution at different rare-earth sites in quasiternary (Nd,Pr)₂Fe₁₄B compounds

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A model based on single-ion theory has been presented and is shown to be applicable for quasiternary compounds. The model allows one to obtain from the experimental data information about the contributions to the magnetic properties originating from rare-earth ions at different crystallographic sites as well as on the preferential substitution of rare-earth ions for (Nd,Pr)₂Fe₁₄B compounds.

I. INTRODUCTION

The magnetocrystalline anisotropy in R₂Fe₁₄B can be understood through the study of contributions to the anisotropy originating from the R sublattice and the T sublattice. In this type of study, however, an evaluation of the exchange field plays a decisive role. The T sublattice can be treated phenomenologically in first approximation because of the equal order of magnitude of all terms in the Hamiltonian \mathcal{H}_T . The Hamiltonian \mathcal{H}_R for the R sublattice can be written in an explicit form in which the spin-orbit interaction, the R-T exchange interaction, the crystalline-electric field (CEF), the Zeeman magnetostatic energy of the magnetic moment in an external magnetic field B, and the R-R exchange interaction have been taken into account. For most of the 4f ions, the crystal-field and exchange interactions are much smaller than the spin-orbit coupling. As a consequence, they play the role of a perturbation energy acting on the spin-orbit Hamiltonian.

For a 4f ion, the CEF Hamiltonian is usually expressed in terms of the equivalent operators O_n^m .¹ It is common practice to determine the B_n^m (and thus A_n^m) as empirical parameters. By fitting experimental magnetization curves for a single crystal the CEF parameters can, in general, be obtained.²⁻⁵ The experimental data, in which any transition is of crucial importance, have to be reproduced by self-consistent adjusting of the values of the CEF parameters and the molecular-field coefficient. For the complicated Nd₂Fe₁₄B-type structure (tetragonal, space group $P4_2/mnm$), the Hamiltonian to describe the whole system can be written by considering different inequivalent sites in the form^{6,7}

$$\mathcal{H} = \sum_{i=1}^4 \mathcal{H}_R(i) + 28K_0(T)\sin^2\theta - 28m_0(T)B, \quad (1.1)$$

$$\mathcal{H}_R = \mathcal{H}_{CF}(i) + 2(g_J - 1)\mu_B JB_m + g_J\mu_B JB, \quad (1.2)$$

where $m_0(T)$ is the magnetic moment per Fe ion at temperature T, $K_0(T)$ the uniaxial anisotropy energy per Fe ion, θ the angle between m_0 and the [001] direction, B the external magnetic field, and B_m the molecular field acting on the reference R ion with J and g_J . This field couples antiparallel to m_0 due to the R-Fe exchange interactions. In the limiting case of extremely large R-T exchange interaction, the fitting procedure can also be performed with the anisotropy energy expressed in terms of the anisotropy constants $\{K_i\}$. Considering the transformation properties of the Stevens operators O_n^m , the transformation relations between the anisotropy constants $\{K_i\}$ and the CEF parameters B_n^m can be deduced.^{4,8}

After systematic studies of the magnetic properties of single crystals of simple ternary compounds, one becomes interested in investigating complicated quasiternaries.⁹⁻¹¹ Here the situation is much more complex as single-crystalline samples are usually not available. A model has been developed for the quasiternary powder materials in which the effect of misalignment of grains was taken into account.¹⁰ Having in mind the difficulty of the fitting procedure for the polycrystalline samples in which the effects of misalignment of grains must be taken into account, we consider the phenomenological expression of the anisotropy energy neglecting the terms of the inplane anisotropy.^{10,11} The expression can also be written in the form²

$$E_{an} = \kappa_2^0 P_2^0 + \kappa_4^0 P_4^0 + \kappa_6^0 P_6^0, \quad (1.3)$$

where P_n^m are Legendre functions¹ and k_n^m are the corresponding anisotropy coefficients. Replacing the anisotropy energy expression by Eq. (1.3) in the model proposed by Huang *et al.*¹⁰ for magnetically aligned samples one can obtain the magnetocrystalline-anisotropy coefficients k_n^m which can be transformed directly to the crystal-field coefficients.¹²

It is now necessary to establish a model in order to extract more information regarding the intrinsic properties of the rare-earth ions from the experimental data. To identify the contribution to the anisotropy from the rare-earth ions at different crystallographic sites we developed a single-ion model (see Sec. II). In this description the preferential-site substitution of the rare-earth ions in a quasiternary compound as well as the different contributions to the total magnetocrystalline anisotropy originating from different nonequivalent rare-earth sites have been taken into account. In Sec. III the model is applied to the quasiternary $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ system.

II. THEORETICAL OUTLINE

At first we study a simple case of a quasiternary system in which there are two boundary ternary compounds, A and B , which have the same crystalline structure with two different rare-earth sites. We assume that the rare-earth ions obey a single-ion model. This means that the characteristic magnetic parameters like the anisotropy coefficients $\{k_n^m\}$, describing the contribution from the ions at the different sites are independent of each other and can be represented by the following expressions:

$$K_{iA} = A_{i1} + A_{i2} \quad (i=1, \dots, I, \text{ where } I=3), \quad (2.1)$$

$$K_{iB} = B_{i1} + B_{i2} \quad (i=1, \dots, I, \text{ where } I=3),$$

where K_{iA} and K_{iB} are measurable parameters of the A and B compounds, respectively. A_{i1} (B_{i1}) and A_{i2} (B_{i2}) represent the contributions from ions at site 1 and site 2 in the A (B) compound. In order to get a better understanding of the properties of the quasiternary compounds we select four compositions a_j of the B substitution for A , which are expressed by the equations

$$2a_j = x_{1j} + x_{2j} \quad (j=1, \dots, J, \text{ where } J=4), \quad (2.2)$$

where x_{1j} and x_{2j} are the concentrations of the B ions which occupy site 1 and site 2, respectively. The factor 2 before the a_j means that there are two different crystallographic sites. Then, the parameters K_{ij} of the compound with concentration a_j can be expressed as

$$K_{ij} = \sum_{k=1}^2 [(1-x_{kj})A_{ik} + x_{kj}B_{ik}] \quad (i=1, \dots, I=3; \quad j=1, \dots, J=4). \quad (2.3)$$

There are three groups of equations which include a number of unknown parameters. For solving these groups of equations we should consider the number of equations and unknowns. The condition for solution of the equations is that the total number of the equations in the three equation groups, Eqs. (2.1), (2.2), and (2.3), is not less than that of the unknowns. The following condition for the solution of the equation groups can be derived:

$$J \geq 2I/(I-1) \quad \text{with } I > 1. \quad (2.4)$$

It is possible to obtain a solution if the condition of Eq. (2.4) is satisfied. It means that we can solve the equation

group if $I > 1$ if we select a sufficient number of compositions. It is impossible to solve the equation group if $I=1$ because then the number of the unknowns becomes infinite. By solving the equation group one simultaneously derives the preferential substitution and the properties contributed by the different sites.

III. RESULTS AND DISCUSSION

The magnetic isotherms at 4.2 K of magnetically aligned $(\text{Nd}_{1-x}\text{Pr}_x)_2\text{Fe}_{14}\text{B}$ compounds have been reported in Ref. 13. The anisotropy coefficients k_n^m in the $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ series, derived by fitting magnetization curves (as mentioned above), do not depend linearly on the Pr concentration (see Fig. 1). Because in $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ both the Nd and Pr ions experience the crystalline-electric field, the values for the anisotropy coefficients cannot be transferred directly to the crystal-field parameters. The nonlinear variation of the anisotropy coefficients in this series might be due to strong local-environment effects at the different crystallographic sites or/and to the presence of the preferential occupation of the rare-earth sites in this series. In the following part of this paper we shall try to apply the model described above to explain the crystal-field phenomena in this pseudoternary system.

To simplify the computation process we consider the case, in contrast to the actual four magnetic sites in $R_2\text{Fe}_{14}\text{B}$ structure, in which only two sites, denoted as R(I) and R(II), are taken into account. In that case the equation group can be directly taken from that described above that includes three subequation groups, Eqs. (2.1), (2.2), and (2.3). In Eq. (2.1), K_{iA} and K_{iB} refer to the measured anisotropy coefficients k_2^0 , k_4^0 , and k_6^0 of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Pr}_2\text{Fe}_{14}\text{B}$ compounds, respectively. In ac-

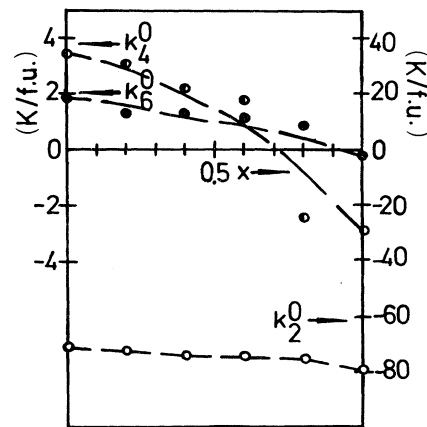


FIG. 1. Composition dependence of the anisotropy coefficients k_2^0 , k_4^0 , and k_6^0 at 4.2 K of $(\text{Nd}_{1-x}\text{Pr}_x)_2\text{Fe}_{14}\text{B}$. The dashed lines represent the values determined by the least-square procedure as well as these derived by combining occupation of the rare-earth ions at different sites for $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ compounds with contributions of the Nd and Pr ions at different sites to the anisotropy coefficients obtained in $(\text{Nd,Gd})_2\text{Fe}_{14}\text{B}$ and $(\text{Pr,Gd})_2\text{Fe}_{14}\text{B}$, respectively (see text).

cordance with $I=3$ and $J=4$, the total number of the equations in the three equation groups amounts to 22, whereas the number of the unknowns is 20. According to the condition of Eq. (2.4) for solving the equation group, it is possible to obtain nonunique solutions of the equation group because only in the ideal case the number of the equations is equal to the number of unknowns the equation group has a unique solution. If the number of the equations is taken larger than that of the unknowns, no unique solution for the equation group is found. Fortunately, the occurrence of such a nonunique solution is due to the experimental errors. One may average the values of the different solutions to obtain a unique solution. Then, one obtains a set of anisotropy coefficients by adjusting the anisotropy coefficients by a least-squares procedure. This set of anisotropy coefficients will be unique.

To find the solution of the equation group, one may divide it into two parts. As the first step one can get a subequation group which only includes the unknowns related with the occupation of rare-earth sites by canceling the unknowns related to the different anisotropy contributions of the rare-earth ions at different sites. As mentioned above we find three different solutions for the atomic occupation. These nonunique solutions depend on the experimental data for the anisotropy coefficients. However, the variation between them is not so large so that we can take their average as the unique solution. The derived occupation by the rare-earth ions of the different sites in $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ is collected in Table I. The deviation of the adjusted values for the anisotropy coefficients from the experimental values, shown in Fig. 1, indicates the satisfactory results of applying the model. Moreover, it is obvious that in the case of data on single crystals the experimental errors are much smaller than for the present polycrystalline samples. Unfortunately, due to difficulties with growing of single crystals for quasiternaries, up to now, experimental data on single crystals are hardly available.

The values shown in Table I indicate a strong preferential occupation of the rare-earth ions in this series. Such preferential substitution can partly explain the nonlinear concentration dependence of the anisotropy coefficients observed in the $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ series. It proves that a simple dilution model, as used for the interpretation of the magnetic properties of the Gd-containing compounds,¹⁴¹ does not hold in this case. This is possibly due to the large contribution of both Nd and Pr ions to the anisotropy. It is quite understandable that the rare-earths with different atomic volume and different contribution to anisotropy would segregate so as to minimize the free energy, especially if there are inequivalent sites in the structure. As the next step the solution obtained above can be taken as a known condition to put into the equation group. Now the problem is to solve the group of linear equations, Eq. (2.3), in which only the contributions of the rare-earth ions at different sites to the anisotropy coefficients remain as the unknowns. Unfortunately, in this system, it is very difficult to determine accurately the contributions to the anisotropy from the Nd and Pr ions at the different sites because both contribu-

TABLE I. Calculated occupation of the rare-earth ions at different sites for $(\text{Nd}_{1-x}\text{Pr}_x)_2\text{Fe}_{14}\text{B}$ compounds. The values collected in this table are averages of the three different solutions of the equation group.

x	$x_{\text{Nd}}(\text{I})$	$x_{\text{Pr}}(\text{I})$	$x_{\text{Nd}}(\text{II})$	$x_{\text{Pr}}(\text{II})$
0.0	1	0	1	0
0.2	0.701	0.299	0.899	0.101
0.4	0.540	0.460	0.660	0.340
0.6	0.198	0.802	0.602	0.398
0.8	0.057	0.943	0.343	0.657
1.0	0	1	0	1

tions are of similar size. Nevertheless, the values for the contributions of Nd and Pr ions obtained in the Gd-substituted series¹⁴ can be taken to combine with the values listed in Table I to reproduce concentration dependence of the anisotropy coefficients of the $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ compounds (see also the dashed lines in Fig. 1). The results obtained in the Gd-containing series¹⁴ demonstrate the strong local-environment effects at different rare-earth sites, which are in good agreement with the feature revealed by neutron diffraction¹⁵ and inelastic-neutron-scattering experiments.¹⁶

The phenomenological expressions of the anisotropy energy are often used to interpret experimental results. They are correct only in the limiting case of a large molecular field B_m . Fortunately, for reproducing the observed spin-reorientation temperature T_{SR} of $\text{Nd}_2\text{Fe}_{14}\text{B}$, a much larger value for the molecular field is necessary.⁴ Previous analyses by various authors^{2,4,8} have shown that in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type compounds the R - T exchange interaction is much stronger than the crystal-field interaction. This suggests that the influence of external fields on the internal magnetic structure is not too large. Actually, this effect does not strongly affect the anisotropy parameters for the compounds with light rare-earth elements in which the magnetizations of the two sublattices are parallel to each other. In the present examples the phenomenological expression Eq. (1.3) with neglecting of the basal-plane anisotropy is used due to the fitting procedure to determine the anisotropy coefficients, in which the effects of misalignment of domain grains must be taken into account. The values $B_2^0 = -2.0$ K/ion, $B_4^0 = 9.1 \times 10^{-3}$ K/ion, and $B_6^0 = 9.4 \times 10^{-4}$ K/ion for $\text{Nd}_2\text{Fe}_{14}\text{B}$ in the present work are in good agreement with those shown in Ref. 17 although we have used a smaller number of CEF parameters and, what is more important is that data on polycrystalline samples were used. Our crystal-field parameters yield $A_2^0 = +278$ K a_0^{-2} , $A_4^0 = -11$ K a_0^{-4} and $A_6^0 = -1.7$ K a_0^{-6} . These values are quite close to the values $A_2^0 = +304$ (+308) K a_0^{-2} , $A_4^0 = -15$ (-13) K a_0^{-4} , and $A_6^0 = -2$ (-2) K a_0^{-6} for the $4f$ (4g) site in $\text{Nd}_2\text{Fe}_{14}\text{B}$ calculated in Ref. 8. The crystal-field parameters obtained by the method developed by Huang *et al.*¹⁰ on the polycrystalline samples are very similar to these obtained by the fitting procedure on single crystals, meaning that this method can be used to a certain extent. It suggests that although the

planar anisotropy in $R_2Fe_{14}B$ is certainly different from zero, the expression for the anisotropy energy with only the axial anisotropy parameters is quite useful in order to understand the origin of phenomena like, for instance the FOMP's in $Nd_2Fe_{14}B$ and $Pr_2Fe_{14}B$.

IV. CONCLUSION

In conclusion, a model based on the single-ion theory, has been presented and is shown to be applicable for quasiternary compounds. The model allows one to obtain from the experimental data information regarding the intrinsic characteristics of the rare-earth ions and distinguishes the contribution to the anisotropy from rare-earth ions at different crystallographic sites. The total contribution of rare-earth ions to magnetic properties (like, for instance, anisotropy coefficients) is simply determined as the sum of the contributions from the rare-earth

ions at the different sites. According to this model, one can obtain information about the preferential substitution of the rare-earth ions at the different sites and the different contribution to properties from the rare-earth ions if only the condition given in Eq. (2.4) is satisfied. This can be done by selecting the relevant number of compositions for experimental investigations or inserting enough compositions between experimental data.

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