Calculated and Experimental Magnetic Phase Diagrams for $(Nd,Y)_2(Fe,Co)_{14}B$ Systems.

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Spin reorientation transitions in $(Nd_xY_{1-x})_2(Fe_yCo_{1-y})_{14}B$ diluted systems are decribed based on free energy calculations for the model of two coupled sublattices (rare earth metals sublattice and 3d metals sublattice). Spin reorientation temperatures are calculated, the temperature dependence of the tilting angle (between c-axis and magnetization vector) is determined and spin phase diagrams are established. The obtained theoretical values are compared with the existing experimental data, showing a good agreement. The used method is very useful in constructing the magnetic phase diagrams for the diluted ternary and quaternary systems.

Introduction.

The $R_2(Fe,Co)_{14}B$ systems (R = rare earth) exhibit many interesting properties which are important both for fundamental and for applied research. After extensive studies of these systems, the large amount of measured data has been accumulated [1-3]. However, the description of the complex spin reorientation phenomena – which appear in these compounds very often - is still far from being complete. Only non-diluted, parent compounds have been treated using CEF calculations and semi-phenomenological approach [4-6].

The high magnetocrystalline anisotropy of the R- and 3d- metal sublattices and their different behaviour with temperature are the reasons for the two types of spin reorientation transitions observed in 2:14:1 compounds: (1) a cone (or planar)-to-axis transition at low temperature, T_{SR1}, and (2) an axis-to-plane transition at high temperature, T_{SR2} . During these transitions the tilting angle, Θ, between c-crystallographic axis and the direction of the magnetization vector is changing. For the axial arrangement of spins (along c-axis) this angle equals zero, for planar arrangement (spins in basal plane) the angle is 90^0, for conical arrangement $0^0 < \Theta < 90^0$.

Based on free energy calculations and using the model of the two coupled sublattices [4,5] we made an attempt to extend this method to more complicated (ternary and quaternary) systems and to describe one aspect of the spin reorientation phenomena in diluted $(Nd_xY_{1-x})_2(Fe_yCo_{1-y})_{14}B$ system , namely the temperature dependence of the tilting angle and the spin reorientation temperature dependence on composition. The values

obtained from the calculations were used to construct the spin phase diagrams, which were confronted with the available experimental data.

Model description.

We used a simplified model [4,5] in which the magnetic atoms are separated into two coupled sublattices (R- rare earth sublattice and 3d– metal sublattice). Each sublattice is treated in a different way.

(1) The magnetic interaction between rare-earth atoms (R-R interaction) is neglected against the 3d-3d and R-3d interactions. This assumption enables to treat the rare-earth sublattice as an assembly of isolated atoms, the magnetic free energy of which can be easily calculated from the energy levels corresponding to a particular set of crystal electric field (CEF) parameters. These parameters can be obtained from neutron spectroscopy. If an external field, B, is present a Zeeman term should be added.

$$\hat{H}_{CEF}(i) = \sum_{n,m} B_n^m(i) O_n^m \tag{1}$$

$$\hat{H}_{Zee} = \mu_B g_J \mathbf{J} \cdot \mathbf{B} \tag{2}$$

where $B_n^m(i)$ are the crystal field parameters of the rare-earth atom at site i, O_n^m are Steven operators, J is the angular momentum and g_J is the Landé factor.

(2) The previous assumption is inapplicable to the 3d sublattice. In this case, instead of tackling the difficult approach of energy bands, this sublattice is introduced in a phenomenological way: the magnetic anisotropy energy is transferred from the anisotropy constant K_1 of a similar compound with a non magnetic rare-earth or the yttrium compound with a convenient temperature scaling to have the Curie temperature of the studied magnetic rare-earth compound at the right position. This anisotropy energy is not a free energy, but it is expected that the entropy term is negligible. An external field will contribute to the energy with a term –$\mathbf{M} \bullet \mathbf{B}$, and in this case we also need the magnetization of the 3d sublattice, which is obtained from the yttrium compound with a convenient scaling [7].

$$E_a = K_1(T')\sin^2\vartheta \quad ; \quad T' = \frac{T_c(\mathrm{Y}_2\mathrm{Fe}_{14}\mathrm{B})}{T_c(\mathrm{R}_2\mathrm{Fe}_{14}\mathrm{B})} T \tag{3}$$

$$E_H = -\mathbf{M}_{3d} \cdot \mathbf{B} \tag{4}$$

(3) The two magnetic sublattices are coupled with an associated exchange energy of the molecular magnetic field, B_{mol}, of the magnetization of the 3d-sublattice, M_{3d}, acting on the magnetization of the rare-earth sublattice:

$$\mathbf{B}_{mol} = n_{RFe}\mathbf{M}_{Fe} \tag{5}$$

studied compound from the Curie temperature with the same assumption of negligible R-R interaction [4]. The molecular field is related to the exchange fields, B_{ex}, between magnetic moments For this part of the energy we need the magnetization of the 3d sublattice, which is obtained from the yttrium compound, and the coupling constant, n_{RFe}. This can be deduced for the as

$$B_{mol} = 2\frac{\left|g_J - 1\right|}{g_J} B_{ex} = \gamma B_{ex} \tag{6}$$

The hamiltonian is

$$\hat{H}_{ex} = 2\mu_B(g_J - 1)\mathbf{J} \cdot \mathbf{B}_{ex} \tag{7}$$

where the temperature dependence of B_{ex} is assumed to be that of the magnetization

$$B_{ex}(T) = B_{ex}(0)\frac{M(T')}{M(0)} \tag{8}$$

Finally, the total free energy is

$$F(T) = \sum_{i=1}^{4}\left\{-k_B T \ln Z(i)\right\} + 28 K_1(T)\sin^2\vartheta - 2\mathbf{M} \cdot \mathbf{H} \tag{9}$$

where the partition function Z(i) contains the contributions from (1), (2) and (7) four different sites for CEF calculations and the numerical factors appear because K_1 is used in units per 3d atom, while M is used in units per formula unit.

In the calculation the free energy function (or as pointed out above an approximate free energy function) is minimized with respect to Θ, with a given set of CEF parameters, magnetization and anisotropy constant of the yttrium compound and the coupling constant of the studied compound. This has been done in various instances for $R_2Fe_{14}B$ with good results, that is, the input data obtained from independent experiments produce magnetization curves (temperature and field dependence) and spin reorientation temperatures correctly.

We have applied the above procedure to substitution compounds where one of the rare-earth atoms is yttrium; $(Nd,Y)_2(Fe,Co)_{14}B$. Here we have to deal with various problems:

(1) CEF parameters are only available for non-substituted compounds and therefore a procedure to estimate them for a particular substitution is needed. Both the (Nd,Y) and (Fe,Co) substitutions can affect the values of the CEF parameters. We will treat these substitutions in a different way. Since the R-R interaction is negligible, we will consider the contribution of each type of rare-earth separately (in this particular case this is more simple since Y is non magnetic); for each rare-earth the CEF-different site (four in the $R_2Fe_{14}B$ structure) the partition function and free energy are computed and a concentration averaged is calculated. The effect of the (Fe,Co) substitution is introduced on the CEF parameters:

for each rare-earth a Co concentration average is calculated form the CEF parameters of $R_2Fe_{14}B$ and $R_2Co_{14}B$.

(2)   The magnetic anisotropy of the (Fe,Co) substitutions have to be introduced both with the concentration and the temperature dependence. This is done from data on $Y_2(Fe,Co)_{14}B$ compounds. Since the available data correspond to a few given temperatures (usually room, liquid nitrogen and liquid helium), we have fitted the available data [7-11] with polynomials.

(3)   Also the concentration and temperature dependence of the magnetization of the yttrium compounds $Y_2(Fe,Co)_{14}B$ is required for the exchange energy term and for the external field contribution to the free energy in the 3d sublattice. The same procedure was applied with available data in the literature [10-14].

(4)   Concerning the coupling constant, what is actually required is $B_{ex}(0)$. For substitution $Nd_xY_{2-x}Fe_{14}B$, this value is constant within 1% for x=2 to x=1.2 and then decreases [15]. Values for $Nd_2Fe_{14}B$ and $Nd_2Co_{14}B$ can be found in [3,6,16]

Calculation results.

The formative tests of the program were performed on the $Nd_2Fe_{14}B$ and $Nd_2Co_{14}B$ compounds. The Fe-based compound exhibits only one transition (cone-to-axis), at the temperature T_{SR1} = 136 K (Fig.1.). The temperature dependence of the tilting angle Θ,
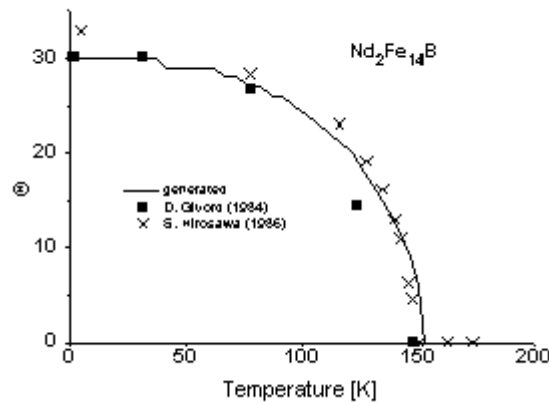

Fig.1 The temperature dependence of the tilting angle for $Nd_2Fe_{14}B$

generated from the calculations , was compared with the literature data [7,18]. This test showed a good agreement between the calculated and experimental data.

The $Nd_2Co_{14}B$ compound exhibits two transitions (at low temperature ,T_{SR1}, cone to axis transition and at high temperature ,T_{SR2}, an axis to plane transition). The results of this test are shown in Fig.2. Two reorientations are reproduced in the temperature regions 30-60 K (cone to axis) and 425-440 K (axis to plane), in good agreement with the experimentally obtained data [1].
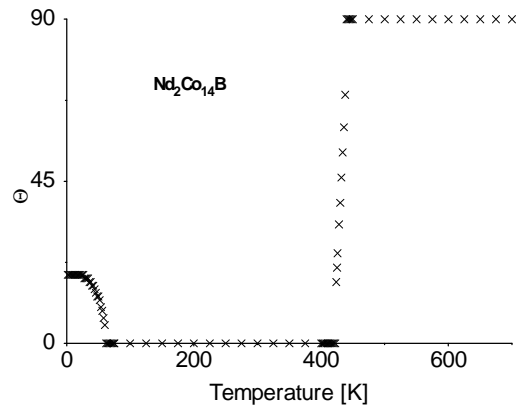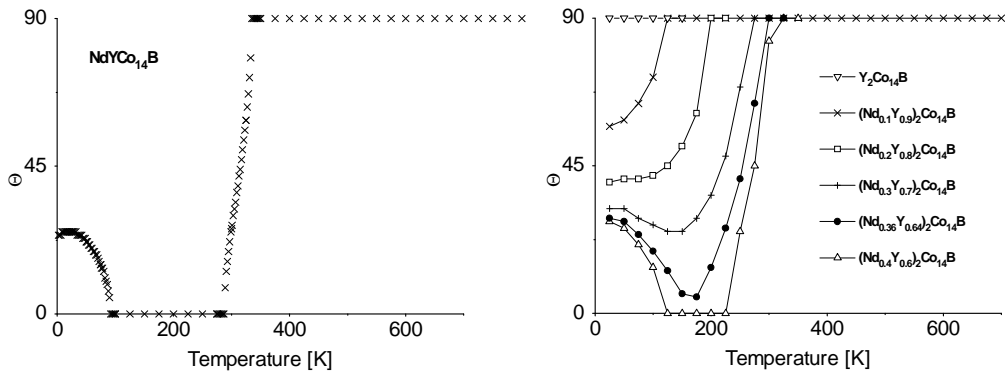

Fig.2 The teperature dependence of the tilting angle for $Nd_2Co_{14}B$ obtained from calculations.

After the above tests, the substitution of Y in place of Nd was studied . It was obvious that Y addition into R– sublattice should decrease the temperature region of axial arrangement. This is indeed clearly shown in Figs 3 and 4. For Y concentration larger than 0.64 , the axial arrangement vanishes completely giving way to conical arrangement only. Finally the tilting angle reaches 90^0 for $Y_2Co_{14}B$ and only the planar arrangement is shown , as experimentally observed for this compound .

Figs. 3 and 4. The calculated temperature dependencies of the tilting angle for $(Nd_xY_{1-x})_2Co_{14}B$ system.

When Fe is introduced into $Nd_2Co_{14}B$, the T_{SR1} increases rapidly (Fig. 5) and for Fe concentration y> 0.408 the planar arrangement disappears. This is illustrated better on the temperature vs composition phase diagram (Fig.6). The available experimental points [19] (black dots) follow the calculated line quite reasonably, especially for the low temperature transition.
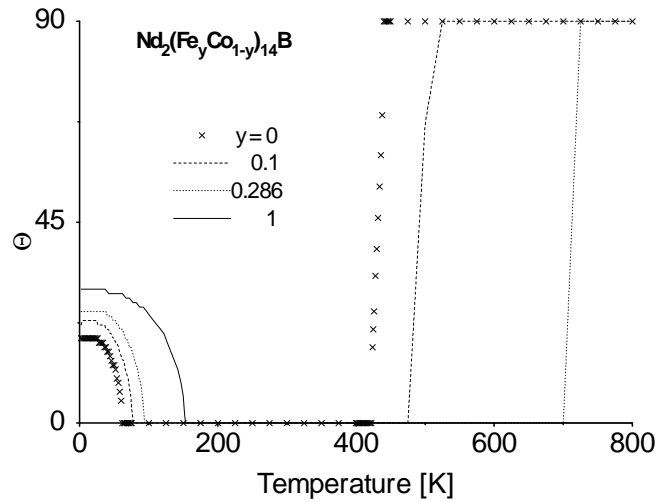

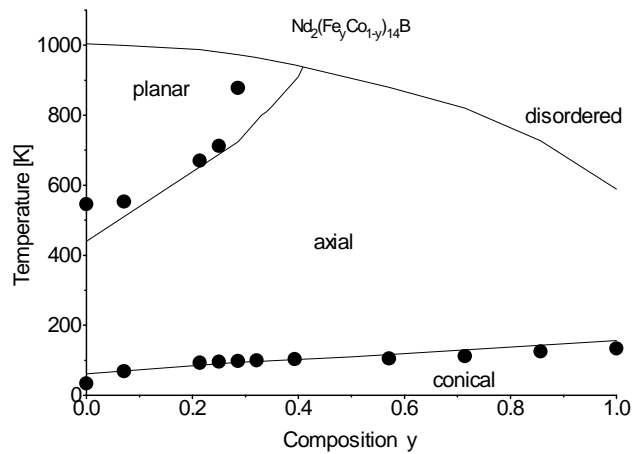Fig.5.The calculated temperature dependencies of the tilting angle for $Nd_2(Fe_yCo_{1-y})_{14}B$ system.

Fig.6. The calculated (solid line) and experimental (full circles) [19] spin phase diagram for $Nd_2(Fe_yCo_{1-y})_{14}B$ system.

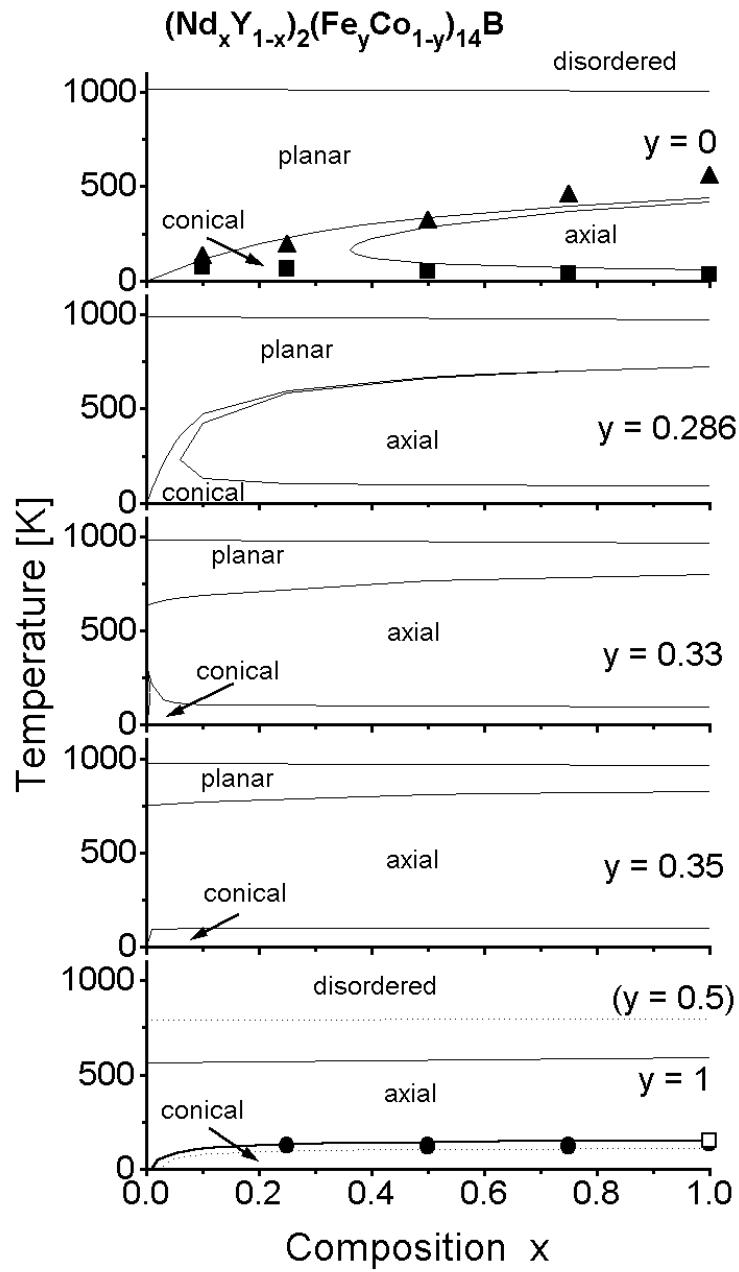Fig.7.The combined calculated (solid lines) and experimental [8,20-22] spin phase diagram for $(Nd_xY_{1-x})_2(Fe_yCo_{1-y})_{14}B$. Dotted line corresponds to y=0.5.

We also constructed the combined phase diagrams in T vs x (Nd - composition) plane for different y (Fe - composition) values . These are shown in Fig.7. The available experimental points [8,20,21] (indicated by black symbols) confirm that the calculated curves reflect the trend quite well.

From the above results we conclude that the used method of calculations (although simplified and based on approximations) is indeed able to describe the macroscopic anisotropy behaviour for the diluted ternary and quaternary $(Nd,Y)_2(Fe,Co)_{14}B$ systems. The calculations proved to be useful in constructing the magnetic phase diagrams.

References:

[1] K.H.J. Buschow, *Rep. Prog. Phys*. **54** (1991)1123.

[2] J.F. Herbst, *Rev. Mod. Phys.*, **63** (1991), 819.

[3] J.J.M. Franse & R.J. Radwanski in *Rare-earth Iron Permanent Magnets*, Ed- J.M.D. Coey. Clarendon Press. Oxford (1996).

[4] C.D. Fuerst, J.F. Herbst & E.A. Alison, *J. Mag. Mag. Mat.*, **54-57** (1986), 567.

[5] M. Yamada, H. Kato, H. Yamamoto & Y. Nakagawa, *Phys. Rev. B*, **38** (1988), 620.

[6] H.S. Li, J.P. Gavigan, J.M. Cadogan, D. Givord & J.M.D. Coey, *J. Mag. Mag. Mat.*, **72** (1988), L241.

[7] C. Pique, R. Burriel & J. Bartolome*, J. Mag. Mag. Mat*. **154** (1996) 71.

[8] S. Hirosawa, Y. Matsuura, H. Yamamoto, S. Fujimura, M. Sagawa & H. Yamauchi, *J. Appl. Phys.*, **59** (1986), 873.

[9] F. Bolzoni, J.M.D. Coey, J. Gavigan, D. Givord, O. Moze, K. Pareti & T. Viadieu, *J. Mag. Mag. Mat.*, **65** (1987), 123.

[10] M. J. Bartashevich, N.V. Kudrevatykh, A.V. Andreev & A. Reiner, *Sov. Phys. JEPT*, **70** (1990), 1122.

[11] L. Pareti, M. Solzi, F. Bolzoni, O. Moze & R. Panizzieri, *Solid St. Comm.*, **61** (1987), 761.

[12] A.V. Andreev, M.I. Bartashevich, T. Goto & S.M. Zadvorkin*, J. Alloys and Compounds* **262-263** (1997) 467.

[13] E. Burzo, N. Plugaru, V. Pop, L. Stamciu & W.E. Wallace, *Solid. St. Comm.*, **58** (1986), 803.

[14] M.Q. Huang, E. B. Boltich, W.E. Wallace & E. Oswald, *J. Mag. Mag. Mat.*, **60** (1986), 270.

[15] F. Bolzoni, F. Leccabue, O. Moze, L. Pareti, M. Solzi & A. Deriu, *J. Appl. Phys.*, **61** (1987), 5369.

[16] Y. Yu, Z. Tiesong & J. Hanmin, *J. Phys.: Condens. Matter*, **3** (1991), 195.

[17] M. Loewenhaupt, I. Sosnowska & B. Frick, *Phys. Rev. B*, **42** (1990), 3866.

[18] D. Givord, H.S. Li & R. Perrier de la Bäthie*, Solid State Comm*. **51** (1984) 857.

[19] A.T.Pedziwiatr & W.E Wallace, *J .Mag. Mag. Mat.* **65** (1987) 139.

[20] A.T.Pedziwiatr, H.Y. Chen, W.E. Wallace & S.K. Malik, *JEEE Trans. on Magnetics, Mag*.**23** (1987) 2717 .

[21] Y.B. Kim, M.J. Kim, S.G. Kim, M.S. Song, J. Hur, Jin Hun-min & T.K. Kim*, J.Magn.Soc.Japan* **23** (1999) 498.

[22] A.T. Pedziwiatr, M. Artigas, B.F. Bogacz, R. Wielgosz, J. Rubin, J. Bartolome. C. Rillo & J. Fernandez, *J. Mag. Mag. Mat.* **196-197** (1999) 639.