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THE EFFECT OF SUBSTITUTION IN Nd$_2$Fe$_{14-x}$Z$_x$B (Z = Al, Si, Ga, Co, Ni) COMPOUNDS

R. Grössinger (1), X. C. Chou (2), R. Krewenka (1), G. Wiesinger (1), R. Eibler (1), X. K. Sun (2) and Y. C. Chuang (2)

(1) Inst. F. Experimentalphysik, Techn. Univ. Vienna, Austria
(2) Inst. of Metal Research, Academia Sinica, Shenyang, China

Abstract. - Almost every element substituting Fe in Nd$_2$Fe$_{14}$B lowers the magnetocrystalline anisotropy. The effect on the ordering temperature $T_c$ is different: in particular Al and Ni reduce $T_c$, whereas Si, Ga and Co increase $T_c$. Mössbauer experiments show that the Fe atoms are substituted in a non random manner. This is supported by the different magnetic properties due to the various substituents.

Introduction

Since the discovery of Nd$_2$Fe$_{14}$B in 1983 by Sagawa et al. [1], great efforts have been undertaken in order to understand the physical origin of its high coercivity [2], but also to further improve the properties of magnets based on this compound [3]. The main disadvantage of Nd$_2$Fe$_{14}$B is its rather low Curie temperature of 580 K which results in an upper limit of 100 °C for efficient operation of Nd-Fe-B magnets. Therefore attempts to improve the temperature behaviour have been made by substituting various elements. Co and Si were found to increase $T_c$, but to decrease the saturation magnetization [4, 5]; Mn, Ru and Al lower the ordering temperature [6-8]. Nevertheless, magnets with small amounts of Al exhibit a remarkable higher coercivity field $H_C$ [9] compared to the pure ternary compound. A similar effect was found by substituting small amounts of Ga [10]. In order to clarify the role of the different substituents, we systematically investigated samples of the composition Nd$_2$Fe$_{14-x}$Z$_x$B (Z = Al, Si, Ga, Co, Ni) in the present work.

Experimental procedure

The samples were prepared from 99.9 % pure starting materials under purified argon gas in an arc furnace. Subsequently they were annealed for three weeks at 900 °C under vacuum. The spin reorientation temperature $T_{sr}$ was deduced from the temperature dependence of the initial susceptibility $x_i(T)$. The anisotropy field was determined by applying the SPD-method (Singular Point Detection) in a pulsed field system [11]. The $^{57}$Fe Mössbauer spectra were recorded at room temperature.

Results and discussion

In the systems R$_2$Fe$_{14-x}$Ga$_x$B (R = Nd, Pr, Gd, Y) the magnetic ordering temperature $T_c$ increases along with $x$ ($x < 1$) up to about 30 K. A similar behaviour is found for Si substitution which is remarkable, since Ga and Si are nonmagnetic substituents. In the case of Si this finding was explained by a preferential substitution of Fe by Si [12].

Nd$_2$Fe$_{14}$B exhibits a spin reorientation at about 135 K [13]. This fact is generally explained by competing terms of the Nd-sublattice crystal field. The substitution of Fe commonly causes a reduction of $T_{sr}$ up to 30 K as shown in table I.

Table I. - Spin reorientation temperature $T_{sr}$ and anisotropy field $\mu_0 H_A$ at room temperature (22 ± 0.5 °C) of Nd$_2$Fe$_{14}$ZB.

<table>
<thead>
<tr>
<th>Element</th>
<th>$T_{sr}$ (K)</th>
<th>$\mu_0 H_A$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>135</td>
<td>6.99</td>
</tr>
<tr>
<td>Co</td>
<td>133.5</td>
<td>6.88</td>
</tr>
<tr>
<td>Ni</td>
<td>115.5</td>
<td>7.04</td>
</tr>
<tr>
<td>Si</td>
<td>112.5</td>
<td>7.33</td>
</tr>
<tr>
<td>Al</td>
<td>105.5</td>
<td>6.32</td>
</tr>
<tr>
<td>Ga</td>
<td>110.5</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Fig. 1. - Mössbauer spectrum of Nd$_2$Fe$_{13}$SiB recorded at room temperature; (× × × × ×) - experimental points, (-----) computer fit.
The effect of different substitutions on the anisotropy field is also summarised in Table I. Due to uncertainties in the demagnetizing field the error in $H_A$ is ±0.1 T. Consequently $H_A$ for the samples with $Z = \text{Fe, Co, Ni}$ is equal within the experimental error. Al causes a drop in $H_A$, whereas Si and Ga lead to an increase. The rise in $H_C$ for which Al and Ga substituted magnets is more than 50% compared to pure Nd-Fe-B cannot be explained by such small changes of the anisotropy. It is therefore supposed to be of metallurgical origin (pinning effects).

In order to clarify the role of the different substituents, systematic $^{57}\text{Fe}$ Mössbauer studies were carried out. In figure 1 Nd$_2$Fe$_{13}$SiB is shown as a typical spectrum. The bars on the top of the spectrum indicate the line positions. The two uppermost represent an impurity ferromagnetic phase (presumably binary Fe-Si) and a nonmagnetic one (Nd$_{1.1}$Fe$_4$Ba). The binary precipitations are larger for Z$_{\text{comp}}$ than 4%, for the remainder they occur to an amount less than 4%. The Nd-rich phase remains below 3%.

In Table II the results of a least square analysis of the spectra are summarised.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$j_1$</th>
<th>$j_2$</th>
<th>$B_{eff}$(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$<em>2$Fe$</em>{13}$B</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{13}$CoB</td>
<td>1.05</td>
<td>0.95</td>
<td>0.5</td>
<td>0.55</td>
<td>29.4</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{13}$NiB</td>
<td>0.85</td>
<td>0.85</td>
<td>0.55</td>
<td>0.55</td>
<td>27.9</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{13}$SiB</td>
<td>0.9</td>
<td>0.8</td>
<td>0.65</td>
<td>0.65</td>
<td>24.3</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{13}$AlB</td>
<td>1.1</td>
<td>0.9</td>
<td>0.55</td>
<td>0.45</td>
<td>24.8</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{13}$GaB</td>
<td>1.1</td>
<td>0.6</td>
<td>0.75</td>
<td>0.55</td>
<td>26.4</td>
</tr>
</tbody>
</table>

Considering the analysis of the Mössbauer pattern with respect to a deviation from a random Fe substitution, attention is focused to those subspectra arising from the lattice sites with the largest occupation numbers, i.e. $k_1$, $k_2$, $j_1$, $j_2$. As can be seen from Table II for the $k$ and $j$ sites a strong preference in either direction can be found; in any case the $k_1$ site is preferably occupied by Fe, the $k_2$ site by the substituent. As a whole the $k$ sites are preferred by the substituent; in the case of $Z = \text{Ni, Si}$ a preference of Fe for the $j$ sites is found. A distinct difference between the $j$-sites is obtained for $Z = \text{Al and Ga}$ (Fe prefers the $j_1$ site, Z the $j_2$ site).

In the case of Co substitution a deviation from random occupation has already been found by neutron diffraction experiments of Herbst and Yelon [14], their results agreeing sufficiently well with the present one. Further evidence in this direction has been given by van Noort and Buschow [15].

The above discussion shows that just a preferential occupation cannot cause the different effects of the substitution of Fe on $T_c$ and $H_A$. Other physical properties, such as the electronic structure or the local interatomic distances might be the reason for the specific role of substituents.

Comparing tables I and II a hint may be obtained for the enhancement of the anisotropy field: a preference of the substituent for the $k$ sites and a preference of Fe for the $j$ sites favours larger $H_A$ values.

Careful lattice parameter determination and further theoretical calculations [16] would be most helpful in improving the understanding of this complex substitution process.