Structure and magnetic properties of R(FeVB)12 compounds


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Structure and magnetic properties of $R(FeVB)_{12}$ compounds

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Abstract

Stable $R(FeVB)_{12}$ compounds ($R=$Nd, Sm, Y) with the ThMn$_{12}$-type tetragonal structure have been prepared. The Curie temperatures of these compounds are enhanced compared with the boron-free compounds. In some of these compounds the saturation magnetization at 4.2 K is also increased. A spin reorientation is observed at 130 K in Nd(FeVB)$_{12}$. FOMP transitions occur at 4.2 K in both Sm(FeVB)$_{12}$ and Nd(FeVB)$_{12}$ compounds, with onset fields of 11.5 T and 2.2 T, respectively.

Keywords: Magnetic properties; Permanent-magnet applications

1. Introduction

The structure and magnetic properties of ternary compounds of the type $RFe_{12-x}M_x$ ($R=$ rare earth; $M=$ Ti, V, Cr, Mo, W, etc.) have been studied by numerous investigators [1–6]. These compounds crystallize in the tetragonal ThMn$_{12}$ structure in which there is only one crystallographic site for the rare earth and three nonequivalent sites for the $M$ and Fe atoms. High Curie temperatures and high uniaxial anisotropy near room temperature make these systems promising starting materials for permanent-magnet applications [7,8].

The effect of carbon on the structure and magnetic properties of these ThMn$_{12}$-type rare-earth–transition-metal intermetallics has been investigated recently [9]. Certain carbides of these novel intermetallics were found to exist. Some interesting magnetic phase transitions are observed in these compounds. In the carbide Nd(FeMoC)$_{12}$ a spin reorientation occurs at 70 K. A first-order magnetization process (FOMP) was observed in Sm(FeVC)$_{12}$ at 4.2 K. It was found that addition of an appropriate amount of carbon enhances the $T$–$T$ exchange interaction whereas the $R$–$T$ exchange interaction is substantially reduced. However, as far as the authors are aware, no work has ever been published concerning the effect of boron addition on the structure and the magnetic properties of these 1:12 compounds. In the present investigation, an attempt has been made to prepare stable isostructural borides of the $RFe_{10}V_2$ compounds with $R=$ Nd, Sm and Y. The magnetic properties have been studied by a.c. initial susceptibility measurements from 4.2 K to room temperature as well as by high-field magnetization measurements at 4.2 K.

2. Experimental details

Polycrystalline samples with the nominal composition $RFe_{10}V_2B_{0.5}$ ($R=$ Nd, Sm and Y) were prepared by arc melting. Boron was added in the form of Fe-B alloy containing 20% boron. The as-cast samples were annealed at 950 °C for 3 weeks and checked by X-ray diffraction. The main phase possesses the ThMn$_{12}$-type tetragonal structure, and the second phase is $\alpha$-Fe.

X-ray diffraction patterns of random powders and magnetically aligned powders (with incident X-ray beam perpendicular to alignment direction) were used to determine the easy direction of the magnetization at room temperature.

The Curie temperatures were determined by a.c. initial-susceptibility measurements from room temperature up to 600 °C. Spin-reorientation transitions in these compounds at low temperature were studied through a.c. initial-susceptibility measurements from 4.2 K to room temperature.

High-field magnetization measurements up to 35 T were performed at 4.2 K in the High Field Installation at the University of Amsterdam. Powdered samples of cylindrical shape were obtained by aligning the powders at room temperature parallel and perpendicular to the cylinder axis in a magnetic field of 1 T and by fixing...
the direction with epoxy resin. The high-field isotherms at 4.2 K were recorded with the external field either parallel or perpendicular to the alignment field. The anisotropy fields $B_A$ were derived from the intersection points of the extrapolated magnetization curves of the parallel and perpendicular aligned materials. Values for the saturation magnetization $M_s$ were derived from the high-field part of the magnetization curves by extrapolation to zero field.

### 3. Experimental results and discussion

The lattice parameters of these borides are little changed compared with those of the corresponding boron-free compounds. Fig. 1 shows the X-ray diffraction patterns at room temperature of random powders and magnetically aligned powders (X-ray beam perpendicular to the alignment direction) of NdFe$_{10}$V$_2$B$_{0.5}$ and SmFe$_{10}$V$_2$B$_{0.5}$ alloys, respectively. The X-ray diffraction patterns of random powders of NdFe$_{10}$V$_2$B$_{0.5}$ and SmFe$_{10}$V$_2$B$_{0.5}$ show reflections of the main phase characteristic of the body-centered tetragonal structure. This is in agreement with the neutron-diffraction result of another alloy, YFe$_{11}$TiB, which was prepared in the same way [10]. The neutron diffraction result indicates that boron atoms prefer to occupy the substitution sites and that the real composition of the main phase is Y(FeTiB)$_{12}$, suggesting that the main phase obtained in the present work could be identified as R(FeVB)$_{12}$. Although there is the possibility of the formation of small amounts of the relatively stable V$_2$B$_3$ phase, along with the corresponding shift in composition of REF$_{10}$V$_2$B$_{0.5}$ to higher Fe concentrations than REF$_{10}$V$_2$, we choose to interpret our data, in view of pending neutron diffraction data and the electron probe microanalysis results, as obtained on real B-substituted compounds.

In the patterns of the aligned NdFe$_{10}$V$_2$B$_{0.5}$ and SmFe$_{10}$V$_2$B$_{0.5}$ powders, only reflections from the (h00) planes are prominent, indicating that the EMD is along the c-axis at room temperature. The Curie temperatures of the borides and the virgin compounds have been determined and are listed in Table 1. The observed Curie temperatures of the virgin compounds are comparable with the values reported in literature [1,9]. From Table 1, it can be seen that the Curie temperatures of the RFe$_{10}$V$_2$ compounds are substantially increased by the incorporation of 0.5 boron atom per formula unit.

Results of the high-field magnetization measurements on 4.2 K of the R(FeVB)$_{12}$ compounds are shown in Figs. 2, 3 and 4. Figs. 2(a) and 2(b) show the high-field magnetization at 4.2 K of Y(FeVB)$_{12}$ and YFe$_{10}$V$_2$ compounds. In both compounds, the anisotropy field is slightly above 4 T, which is close to the earlier reported value for YFe$_{10}$V$_2$ [1]. The magnetization of YFe$_{10}$V$_2$ at 4.2 K is slightly enhanced by the incorporation of boron.

In Nd(FeVB)$_{12}$ and NdFe$_{10}$V$_2$ (Figs. 3(a) and 3(b)), the curves for parallel and perpendicular alignment almost coincide, indicating the the magnetocrystalline anisotropy in these compounds is small. FOMP transitions are observed in the high-field magnetization at 4.2 K. Fig. 4(a) shows the field dependence of the magnetization of Sm(FeVB)$_{12}$ for the field applied parallel and perpendicular to the alignment direction. For comparison, the high-field magnetization of SmFe$_{10}$V$_2$ at 4.2 K is also shown in Fig. 4(b). It is interesting to note that though the Curie temperature

### Table 1

Curie temperatures of R(FeVB)$_{12}$ and RF$_{10}$V$_2$ compounds with R = Y, Nd, Sm

<table>
<thead>
<tr>
<th>R</th>
<th>Compound</th>
<th>$T_c$ (K)</th>
<th>$\Delta T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Y(FeVB)$_{12}$</td>
<td>568</td>
<td>34</td>
</tr>
<tr>
<td>Y</td>
<td>YFe$_{10}$V$_2$</td>
<td>534</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>Nd(FeVB)$_{12}$</td>
<td>607</td>
<td>30</td>
</tr>
<tr>
<td>Nd</td>
<td>NdFe$_{10}$V$_2$</td>
<td>577</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>Sm(FeVB)$_{12}$</td>
<td>632</td>
<td>29</td>
</tr>
<tr>
<td>Sm</td>
<td>SmFe$_{10}$V$_2$</td>
<td>603</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. X-ray diffraction patterns of random and magnetically aligned powders of Nd(FeVB)$_{12}$ and Sm(FeVB)$_{12}$. In aligned samples the X-ray beam was directed perpendicular to the alignment direction.
is increased substantially with addition of boron (Table 1), the saturation magnetization appears little improved. In the magnetic isotherms for both Sm(FeVB)₁₂ and SmFe₁₀V₂ at 4.2 K, a slight upward curvature of the magnetization is found for the hard direction, indicating that these compounds exhibit a first-order magnetization process (FOMP). The critical fields for these FOMPs, identified by the peaks in the corresponding dM/dB vs. B curves, are 11.5 T and 11.0 T, respectively.

The magnetic characteristics are summarized in Table 2. The Nd-containing boride has the highest saturation magnetization (22.9 μB/f.u.) at 4.2 K. The anisotropy field found for Y(FeVB)₁₂ (4.2 T) is comparable with the value reported for YFe₁₀V₂ in the literature [1].

The temperature dependence of the a.c. initial susceptibility of R(FeVB)₁₂ measured from 4.2 K to room temperature is shown in Fig. 5(a). The curve for Nd(FeVB)₁₂ exhibits a peak at approximately 130 K indicating the occurrence of a spin reorientation. NdFe₁₀V₂ undergoes a spin-reorientation transition at 159 K (Fig. 5(b)), which differs from the value (Tₛᵣ = 112 K) reported by Arnold et al. [3], while the value of Curie temperature agrees well with that reported in Ref. [1].

It is known that in the RFe₁₂₋ₓTₓ tetragonal structure the crystalline electric field (CEF) at the R site tends to align the R magnetic moment along the c-axis for rare-earth ions such as Sm, Er, Tm or Yb which have a positive second-order Stevens coefficient (α₂ > 0), whereas it tends to align the R moment in the basal plane for rare-earth ions with α₂ < 0 (e.g. Nd, Tb, Dy etc.). In RFe₁₀V₂, the Fe-sublattice contribution is represented by YFe₁₀V₂ in which the EMD is along the c-axis in the temperature range from 4.2 to 300 K. One can infer from this result that in NdFe₁₀V₂ and Nd(FeVB)₁₂, the Nd and Fe contributions to the magnetocrystalline anisotropy have opposite sign and a competition between them appears. At low temperature, the planar anisotropy of the R ion with α₂ < 0 will dominate the uniaxial anisotropy of the Fe sublattice but the R-ion anisotropy rapidly decreases with increasing temperature. At higher temperature, the contribution of the Nd sublattice to the anisotropy will

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Fig. 2. High-field magnetic isotherms of (a) Y(FeVB)₁₂ and (b) YFe₁₀V₂ compounds at 4.2 K. O, M₁; ●, M₂.

Fig. 3. High-field magnetic isotherms of (a) Nd(FeVB)₁₂ and (b) NdFe₁₀V₂ compounds at 4.2 K. O, M₁; ●, M₂. Insets: dM/dB vs. B curve, Bc indicated by arrow.
Fig. 4. High-field magnetic isotherms of (a) Sm(FeVB)_{12} and (b) SmFe_{10}V_{2} compounds at 4.2 K. O, M; ●, M±. Insets: dM/dB vs. B curve, B_{z} indicated by arrow.

Table 2
Magnetic characteristics of R(FeVB)_{12} and RFe_{10}V_{2} at 4.2 K

<table>
<thead>
<tr>
<th></th>
<th>M_{s} (μ_{B}/f.u.)</th>
<th>μ_{B}</th>
<th>μ_{Fe}</th>
<th>μ_{Sm}</th>
<th>μ_{Fe}/μ_{Sm}</th>
<th>B_{COMP} (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(FeVB)_{12}</td>
<td>22.9</td>
<td>3.3</td>
<td>1.96</td>
<td>1.64</td>
<td>1.64</td>
<td>2.2</td>
</tr>
<tr>
<td>NdFe_{10}V_{2}</td>
<td>18.5</td>
<td>3.3</td>
<td>1.52</td>
<td>1.26</td>
<td>1.52</td>
<td>2.3</td>
</tr>
<tr>
<td>Sm(FeVB)_{12}</td>
<td>19.2</td>
<td>0.7</td>
<td>1.85</td>
<td>1.54</td>
<td>1.28</td>
<td>11.5</td>
</tr>
<tr>
<td>SmFe_{10}V_{2}</td>
<td>19.2</td>
<td>0.7</td>
<td>1.85</td>
<td>1.54</td>
<td>1.18</td>
<td>11.0</td>
</tr>
<tr>
<td>Y(FeVB)_{12}</td>
<td>16.9</td>
<td>0</td>
<td>1.69</td>
<td>1.4</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>YFe_{10}V_{2}</td>
<td>15.9</td>
<td>0</td>
<td>1.59</td>
<td>1.3</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

surpass that of the Fe sublattice and consequently a spin reorientation will take place. Arnold et al. [3] found that the spin actually rotates from the basal plane to a cone during this transition. This has been explained by considering higher-order CEF terms. In the case of Sm(FeVB)_{12} with a Sm ion with α_{2} > 0, the Sm anisotropy will reinforce the axial 3d magnetic anisotropy and consequently no SR transition will occur.

It has been reported that the EMD of NdFe_{12−x}M_{x} (M = V, Ti and Mo) compounds at 4.2 K changes from basal plane to c-axis upon incorporation of nitrogen because the second-order crystal field coefficient A_{20} has different signs before and after nitrogenation [11,12]. The results of the present work show that addition of B does not alter the anisotropy of NdFe_{10}V_{2} very much. The decrease of the SR temperature indicates that the planar anisotropy of the Nd sublattice decreases with the B addition.

4. Concluding remarks

In recent years, the search for new permanent-magnet materials has been focussed on the ternary compounds RFe_{12−x}M_{x} (R = rare earth, M = Ti, V, Cr, Si, Mo, W etc.) which crystallize in the tetragonal ThMn_{12} structure. The effect of B on the structure and magnetic properties of the R(Fe,M)_{12} compounds has never been reported. Our present investigation shows that with proper processing such as adequate control of rare-earth losses in the course of preparation, optimizing annealing procedures followed by rapid cooling, stable R(Fe,M)_{12} boride can be prepared. A number of R(FeVB)_{12} borides have been prepared with the required ThMn_{12}-type structure. Boron atoms prefer to
occupy substitutional sites in the ThMn$_{12}$-type compounds.

The Curie temperatures of the R(FeVB)$_{12}$ (R = Nd, Sm, Y) are substantially enhanced compared with the B-free compounds. The saturation magnetization of Nd(FeVB)$_{12}$ at 4.2 K is increased. In Nd(FeVB)$_{12}$ a spin reorientation was observed at 130 K and at 4.2 K a FOMP transition takes place at $B_c = 2.2$ T. A FOMP transition also occurs in Sm(FeVB)$_{12}$ at 4.2 K with a FOMP onset field at 11.5 T.

Acknowledgements

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References