Structure and magnetic properties of \((\text{Nd}_{1-x}\text{Ho}_x)_{3}\text{Fe}_{23-y}\text{Co}_6\text{V}_y\) compounds

B. D. Liu, a) W. X. Li, J. L. Wang, G. H. Wu, and F. M. Yang
State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, 100080 Beijing, China
Y. X. Li
School of Material Sciences and Engineering, Hebei University of Technology, 300130, Tianjin, China
(Presented on 12 November 2002)

The Ho-substituted \((\text{Nd}_{1-x}\text{Ho}_x)_{3}\text{Fe}_{23-y}\text{Co}_6\text{V}_y\) compounds with \(x=0–0.9\) have been synthesized and their structure and intrinsic magnetic properties have been investigated by x-ray diffraction and magnetic measurements. It is found that all the investigated compounds crystallize in the \(\text{Nd}_3(\text{Fe},\text{Ti})_{29}\) type structure with monoclinic symmetry and \(A_{2/m}\) space group. The unit-cell volume \(V\) shows a decreasing tendency with increasing Ho content, reflecting the lanthanum contraction. All the compounds show easy-plane type anisotropy at room temperature. The Curie temperatures \(T_C\) are almost independent of the Ho content and the spin reorientation temperature, \(T_{\text{ar}}\), decreases with increasing Ho content from 266 K for \(x=0\) to 127 K for \(x=0.7\). No spin reorientation occurs for \(x=0.9\). The saturation magnetization \(M_s\) decreases linearly with increasing Ho content due to the antiferromagnetic coupling between Ho and Nd moments. The anisotropy field \(B_a\) increases first, going through a maximum at \(x=0.5, y=2.0\), and then decreases with increasing Ho content. © 2003 American Institute of Physics. [DOI: 10.1063/1.1544492]

INTRODUCTION

The discovery of \(\text{Nd}_3(\text{Fe},\text{Ti})_{19}\) compound by Collocott et al.\(^1\) which was later indexed to be \(\text{Nd}_3(\text{Fe},\text{Ti})_{29}\) with monoclinic structure and \(A_{2/M}\) space group has attracted much interest to the study of the rare-earth transition intermetallic compounds. Recently, the \(R_3(\text{Fe},\text{M})_{29}\) compounds with \(R=\text{Sm}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Y}, \text{Gd}, \text{Tb}, \text{Co}, \text{Cr}, \text{Nb}, \text{Mn}\) were measured \(2–8\) have been investigated. However, up to now, the study of \(R_3(\text{Fe},\text{M})_{29}\) with \(R=\text{the heavier rare-earth elements than Tb}\) was rarely reported due to the difficult synthesis, \(8\) reported the \((\text{Nd}_{1-x}\text{Er}_x)_3(\text{Fe},\text{Ti})_{29}\) compounds with \(x=0–0.6\), Liu et al.\(^9\) increased the Er content to \(x=0.8\) in \((\text{Nd}_{1-x}\text{Er}_x)_3\text{Fe}_{19}\text{Co}_{6}\text{Cr}_5\) compounds, and no structure transition was observed in the two series compounds. But the study on Ho-based 3:29 compounds has never been reported, so it is interesting to investigate the structure and magnetic properties of Ho-based compounds. In this article, on the basis of our previous work on \(\text{Nd}_3(\text{Fe},\text{Co},\text{V})_{29}\) compounds, a study of structure and magnetic properties of the Ho-substituted \((\text{Nd}_{1-x}\text{Ho}_x)_3\text{Fe}_{23-y}\text{Co}_6\text{V}_y\) compounds was presented.

EXPERIMENT

Ingots with composition \(\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_6\text{V}_y\) were prepared by arc melting the constituent elements with a purity of at least 99.9% in an argon atmosphere. All the ingots were remelted at least four times to ensure homogenization. An excessive amount of Nd and Ho were added to compensate for the loss of Nd and Ho during melting and annealing. Then the alloys were sealed in a quartz tube and annealed under protection of argon atmosphere at 1398 K for 72 h, followed by quenching in water. X-ray diffraction (XRD) patterns and thermomagnetic analysis were employed to check the phase homogeneity. The thermomagnetic curves were measured in a vibrating sample magnetometer from room temperature to above the Curie temperature. The Curie temperatures were derived by plotting \(M_s^2\) vs \(T\) and extrapolating the steep part of the curve to \(M_s^2=0\). The isotherms were measured at 5 K in superconducting quantum interference device magnetometer in magnetic fields up to 5 T. Saturation magnetization \(M_s\) were obtained by plotting \(M-1/B\) and extrapolating the straight line part of the curve to \(1/B=0\), using the saturated part of the magnetization curves.

In order to measure the magnetocrystalline anisotropy field, fine-powdered particles were mixed with epoxy resin and packed in a plastic tube of cylindrical shape. For normal magnetic alignment, the epoxy was allowed to harden while the plastic tube was positioned in an applied magnetic field of about 1 T with the cylinder axis parallel to the field direction, so that the cylinder axis becomes the easy magnetization direction. In the case of rotation alignment, the epoxy hardened while the plastic tube rotated around its cylinder axis in a magnetic field that was applied perpendicular to the axis, so that the cylinder axis corresponds to the hard magnetization direction.

RESULTS AND DISCUSSION

X-ray diffraction patterns and the thermomagnetic curves show that all the compounds with \(x=0–0.9\) are of single phase and crystallize in \(\text{Nd}_3(\text{Fe},\text{Ti})_{29}\) type structure. As an example, Fig. 1(a) shows the XRD pattern of a random oriented powdered sample of the \(\text{Nd}_{0.6}\text{Ho}_{2.4}\text{Fe}_{27}\text{Co}_6\text{V}_2\) compound, which was quite well indexed based on the \(\text{Nd}_3(\text{Fe},\text{Ti})_{29}\) type structure with monoclinic symmetry and \(A_{2/M}\) space group. The experimental results imply that the...
In order to investigate the anisotropy of the compounds at room temperature, x-ray diffraction pattern of the normally aligned sample was measured as shown in Fig. 1(b). It can be seen that the (23-1), (40-2), (040), and (30-4) reflections are enhanced or remained unchanged, and the other reflections have become disappeared or much weakened after the alignment compared with those of the XRD pattern of randomly oriented powder sample of the corresponding compound shown in Fig. 1(a). This suggests that the \((\text{Nd}_{1-x}\text{Ho}_x)\text{Fe}_{23-y}\text{Co}_y\text{V}_y\) compounds are of easy plane type of anisotropy at room temperature in the investigated Ho and V content range. Figure 1(c) is the XRD pattern of the rotation-oriented sample, it can be seen that only the (204) reflection is maintained and enhanced and other reflections have become disappeared or much weakened. This suggested that the easy magnetization direction is in the plane perpendicular to the [204] direction, and therefore the [204] direction is the hard magnetization direction as obtained by rotation alignment.

Figure 2 shows the thermomagnetic curves for the \((\text{Nd}_{1-x}\text{Ho}_x)\text{Fe}_{23-y}\text{Co}_y\text{V}_y\) compounds measured in a low field of 0.05 T in temperature range from 5 K or liquid nitrogen temperature to room temperature. It can be seen that there is a sharp peak in the curves with \(x = 0.7\). The peak indicates a spin reorientation transition as observed in the \(\text{Nd}_3(\text{Fe},\text{V})_{29}\) compounds.\(^{12}\) The spin reorientation temperature \(T_{sr}\) at which the spin reorientation occurs, was derived from the peak position in the thermomagnetic curves, is listed in Table I. It can be seen that \(T_{sr}\) decreases drastically with increasing Ho content from 266 K for \(x = 0\) to 127 K for \(x = 0.7\). It is well known that the spin reorientation transition results from the competition between the different magnetic sublattice anisotropies, which have different types and show different temperature dependencies. It is found that in the \(\text{Nd}_3(\text{Fe},\text{Co},\text{V})_{29}\) compounds the contribution to the magnetocrystalline anisotropy resulting from Fe sublattice is along the [40-2] direction,\(^{13}\) the contribution from Co sublattice is along the [204] direction,\(^{14}\) and the contribution from Nd sublattice is along the [040] direction.\(^{13}\) Due to the negative Stevens factor \(\alpha_f\) of Ho, as same as Nd, it is well accepted

![FIG. 1. XRD patterns of (a) randomly oriented, (b) normally aligned, and (c) rotation-aligned powder samples of \((\text{Nd}_{1-x}\text{Ho}_x)\text{Fe}_{23-y}\text{Co}_y\text{V}_y\) compounds.](image1)

![FIG. 2. Thermomagnetic curves for \((\text{Nd}_{1-x}\text{Ho}_x)\text{Fe}_{23-y}\text{Co}_y\text{V}_y\) compounds measured in a low field of 0.05 T in the temperature range from 5 K or liquid nitrogen temperature to room temperature.](image2)

TABLE I. The unit-cell constants and magnetic parameters of \((\text{Nd}_{1-x}\text{Ho}_x)\text{Fe}_{23-y}\text{Co}_y\text{V}_y\) compounds.

<table>
<thead>
<tr>
<th>((x,y))</th>
<th>(a (\text{Å}))</th>
<th>(b (\text{Å}))</th>
<th>(c (\text{Å}))</th>
<th>(\beta (\text{deg}))</th>
<th>(V (\text{Å}^3))</th>
<th>(T_s (\text{K}))</th>
<th>(T_{sr} (\text{K}))</th>
<th>(M_{5K}(\mu_B/\text{f.u.}))</th>
<th>(B_{5K} (\text{T}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,2.2)</td>
<td>10.556</td>
<td>8.539</td>
<td>9.707</td>
<td>96.607</td>
<td>869.156</td>
<td>694</td>
<td>266</td>
<td>47.2</td>
<td>12.5</td>
</tr>
<tr>
<td>(0,1.2)</td>
<td>10.556</td>
<td>8.514</td>
<td>9.685</td>
<td>96.582</td>
<td>865.148</td>
<td>692</td>
<td>227</td>
<td>49.3</td>
<td>13.0</td>
</tr>
<tr>
<td>(0.3,2)</td>
<td>10.542</td>
<td>8.522</td>
<td>9.690</td>
<td>96.696</td>
<td>863.051</td>
<td>698</td>
<td>213</td>
<td>36</td>
<td>13.2</td>
</tr>
<tr>
<td>(0.5,2)</td>
<td>10.554</td>
<td>8.488</td>
<td>9.667</td>
<td>96.736</td>
<td>860.046</td>
<td>693</td>
<td>154</td>
<td>35.8</td>
<td>13.3</td>
</tr>
<tr>
<td>(0.7,2)</td>
<td>10.526</td>
<td>8.477</td>
<td>9.655</td>
<td>96.9</td>
<td>855.274</td>
<td>679</td>
<td>127</td>
<td>29.2</td>
<td>12.6</td>
</tr>
<tr>
<td>(0.9,1.8)</td>
<td>10.494</td>
<td>8.443</td>
<td>9.629</td>
<td>96.649</td>
<td>847.334</td>
<td>711</td>
<td>…</td>
<td>28.4</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Downloaded 07 Oct 2009 to 159.226.35.191. Redistribution subject to AIP license or copyright; see http://jap.aip.org/jap/copyright.jsp
that the contribution from the Ho sublattice is also along the [040] direction. Therefore, it is easy to understand that the easy magnetization direction at room temperature has deviated from the [40-2] direction and achieved a certain direction \( \phi_1 \) in the plane perpendicular to the [204] direction. With increasing Ho content, the easy magnetization direction changes from the \( \phi_1 \) direction toward the [40-2] direction, this may result from the smaller anisotropy of the Ho sublattice compared with that of the Nd sublattice. For \((\text{Nd}_{0.1}\text{Ho}_{0.9})_3\text{Fe}_{21.2}\text{Co}_6\text{V}_{1.8}\) because the contribution resulting from the rare earth sublattice becomes too small compared with that resulting from the transition metal sublattice, so no spin reorientation transition occurs.

The thermomagnetic curves for all the compounds were plotted in Fig. 3. Curie temperature \( T_c \) of the \((\text{Nd}_{1-x}\text{Ho}_x)_3\text{Fe}_{23-y}\text{Co}_y\text{V}_y \) compounds were derived and listed in Table I. It can be seen that the Curie temperature are almost independent of the Ho content. In the \( R-T \) intermetallic compounds, there exist three exchange interactions: the \( T-T \) exchange interaction between the \( T \) magnetic moments, the \( R-T \) exchange interactions between the \( R \) and the \( T \) moments and the \( R-R \) exchange interaction between the \( R \) moments. Among them, the \( T-T \) exchange interaction is the strongest while the \( R-R \) interaction is the weakest, and the latter is usually neglected. The Curie temperature is mainly determined by \( T-T \) interaction. In the \((\text{Nd}_{1-x}\text{Ho}_x)_3\text{Fe}_{23-y}\text{Co}_y\text{V}_y \) compounds, the number of the transition metals almost keep fixed, so the Curie temperature is almost independent of the Ho content.

Magnetization curves of the \((\text{Nd}_{1-x}\text{Ho}_x)_3\text{Fe}_{23-y}\text{Co}_y\text{V}_y \) compounds measured at 5 K in fields up to 5 T are shown in Fig. 4. The saturation magnetization \( M_s \) was obtained by plotting \( M/B \) and extrapolating \( M^2 \) to zero along the easy direction magnetization curve as listed in Table I. It can be seen that the \( M_s \) decreases with increasing Ho content. In the \((\text{Nd}_{1-x}\text{Ho}_x)_3\text{Fe}_{23-y}\text{Co}_y\text{V}_y \) compounds, the content of transition metals Fe and Co keeps nearly fixed, the decrease of \( M_s \) mainly comes from rare earth sublattice contribution to the magnetization. In the present case, the decrease of \( M_s \) upon the substitution of Ho for Nd results from the antiferromagnetic coupling between Ho and Nd moments. The anisotropy field \( B_a \) were derived from the \( \Delta M - H \) plots by extrapolating the straight line parts to zero, where \( \Delta M = M_1 - M_2 \). \( M_1 \) and \( M_2 \) are the magnetization measured in the easy and hard magnetization direction, respectively. The values of the \( B_a \) are listed in Table I. It can be seen that the \( B_a \) increases first from \( x = 0 \) to 0.5, going through a maximum at \( x = 0.5 \), then decreases with further increasing Ho content.

**ACKNOWLEDGMENT**

This work is supported by State Key Project of Fundamental Research Grant. No. G2000067106.