Formation, structure and magnetic properties of $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds

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Abstract

Single-phase $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds with $\text{Nd}_3(\text{Fe,Ti})_{29}$ -type structure have been synthesized successfully for $x = 0$ –12; and their structures and magnetic properties were investigated by x-ray diffraction and magnetic measurements. The Curie temperature increases drastically with increasing Co content from 500 K for $x = 0$ –847 K for $x = 12$. All the compounds show a spin reorientation transition as temperature decreases. Spin reorientation temperature T_{sr} shows an increasing tendency with the exception of a minimum at around $x = 6$. Saturation magnetization increases monotonically with increasing Co content, which can be understood in terms of a rigid band model. The anisotropy field at 5 K decreases with increasing Co content. All the compounds show easy-plane-type anisotropy at room temperature and the series of the compounds is not suitable for permanent materials.

1. Introduction

Since a novel phase of $\text{Nd}_2(\text{Fe,Ti})_{19}$, which is located at the iron-rich corner of the rare earth–iron–titanium (R–Fe–Ti) phase diagram and stabilized by a third element Ti, was discovered by Collocott *et al* [1], much attention has been attracted to this new compound system. Later, the crystal structure of the novel phase was identified to be of the $\text{Nd}_3(\text{Fe,Ti})_{29}$ -type based on x-ray diffraction (XRD) [2] and neutron diffraction [3]. Recently, a series of ternary iron-rich rare earth–transition metal intermetallic compounds with stoichiometric composition $\text{R}_3(\text{Fe,T})_{29}$ were synthesized for $\text{R} = \text{Nd, Ce, Pr, Sm, Gd, Tb and Dy}$, and $\text{T} = \text{Ti, V, Cr, Mo, Mn, etc}$ [4–9]. Yang *et al* [10] have synthesized $\text{Sm}_3(\text{Fe,Ti})_{29}\text{N}_y$ compounds that exhibit outstanding intrinsic permanent magnetic properties. Subsequently, Yang *et al* [11] and Wang *et al* [12] have synthesized $\text{Gd}_3\text{Fe}_{29-x-y}\text{Co}_x\text{Cr}_y$ compounds with the substitution of Co for Fe and found that $\text{Gd}_3(\text{Fe}_{1-x}\text{Co}_x)_{25}\text{Cr}_4$ compounds show a room temperature uniaxial magnetocrystalline anisotropy for $x \geq 0.4$, which is important for application as permanent materials. These results indicated a prospective application of the non-interstitial $\text{R}_3\text{M}_{29-x}\text{T}_x$ compounds as permanent magnetic

materials. However, $\text{Gd}_3(\text{Fe}_{1-x}\text{Co}_x)_{25}\text{Cr}_4$ compounds cannot be directly used as permanent magnetic materials because of their small saturation magnetization due to the antiferromagnetic coupling between the heavy rare earth element Gd moments and the transition metal moments. In order to obtain larger saturation magnetizations, light rare earth elements are suitable, because the moments of the light rare earth elements have ferromagnetic coupling with the transition metal moments. Meanwhile, in order to investigate further the effect of substitution of Co for Fe on the magnetic properties of $\text{Nd}_3(\text{Fe,Ti})_{29}$ -type compounds, a Nd-based $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compound system with substitution of Co for Fe have been synthesized. In this paper, a study of the formation, structure and magnetic properties of a Co substituted $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compound is presented.

2. Experiment methods

Ingots with the composition $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ ($0 \leq x \leq 15$) were prepared by arc-melting the constituent elements with a purity of at least 99.9% in argon atmosphere. All the ingots were melted at least four times to ensure homogenization. In

order to compensate for the loss of Nd during melting and annealing, a 5% excessive amount of Nd relative to the stoichiometric composition $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ was added. Then, the ingots were sealed in a quartz tube and annealed in argon atmosphere at 1398 K for 72 h, followed by quenching in water. XRD and thermomagnetic analysis were employed to check the phase characteristics. The thermomagnetic curves were measured by a vibrating sample magnetometer (VSM) from room temperature to above the Curie temperature, and by a superconducting quantum interference device (SQUID) magnetometer from 5 K to room temperature at a low field of 0.05 T. The Curie temperatures were derived from the M^2 - T curves and by extrapolating M^2 to zero. The magnetization curves were measured at 5 K by means of a SQUID magnetometer with external magnetic fields up to 5 T. The saturation magnetizations M_s were obtained by plotting M - $1/B$ curves and by extrapolating $1/B$ to zero.

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 (EMD). 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 (HMD). In this case, the values of the anisotropy field B_a were obtained from ΔM - H ($\Delta M = M_{\perp} - M_{\parallel}$) plots by extrapolating the straight line parts to zero.

3. Results and discussion

Both the XRD patterns and thermomagnetic curves indicate that $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds with x ranging from 0 to 12 are essentially single phase and crystallize in the $\text{Nd}_3(\text{Fe}, \text{Ti})_{29}$ -type structure with monoclinic symmetry and space group $A_{2/m}$. When x exceeds 12, for example $x = 14$, we changed the content of V from 1.6 to 2.8 and the annealing temperature from 1378 to 1428 K and found that for the several annealing temperatures selected, the compounds consist of 3:29 and 1:12 phases for larger V content and 3:29 and 2:17 phases for a smaller V content, respectively. A single phase of 3:29 could not be obtained under the conditions mentioned above. This situation is different from the case of $\text{Gd}_3(\text{Fe}_{1-x}\text{Co}_x)_{29-y}\text{Cr}_y$ compounds, where 3:29-type compounds have been obtained in the whole Co composition region. This seems to be related to the atomic radius of the stabilizing element.

As an example, figure 1 shows the XRD pattern of the powder sample of $\text{Nd}_3\text{Fe}_{20.8}\text{Co}_6\text{V}_{2.2}$, which was quite well indexed on the basis of the $\text{Nd}_3(\text{Fe}, \text{Ti})_{29}$ -type structure with monoclinic symmetry and space group $A_{2/m}$. The lattice parameters have been derived from the XRD patterns and are listed in table 1. It can be seen that the lattice parameters a , b , c and the unit cell volume V have no obvious change with increasing Co content in the Co range investigated.

In order to investigate the room temperature magnetocrystalline anisotropy of the compounds, the XRD patterns of

Figure 1. XRD patterns of (a) randomly oriented, (b) normally aligned and (c) rotation-aligned powder samples of $\text{Nd}_3\text{Fe}_{20.8}\text{Co}_6\text{V}_{2.2}$.

Table 1. Lattice constants a , b , c , β and volume V of $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds.

x	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
0	10.594	8.563	9.734	96.725	876.698
3	10.607	8.569	9.737	96.664	879.068
6	10.556	8.539	9.707	96.607	869.156
9	10.567	8.542	9.718	96.640	871.393
12	10.558	8.525	9.700	96.725	867.044

magnetically aligned powder samples were measured. As an example, figure 1(b) shows the XRD pattern of the normally magnetically aligned powder sample for $\text{Nd}_3\text{Fe}_{20.8}\text{Co}_6\text{V}_{2.2}$. It can be seen that the (23-1), (40-2) and (040) peaks are strongly strengthened and the (30-4) peak is weakened, whereas other peaks have almost disappeared, compared with the XRD patterns of the random-oriented sample with the same composition, as shown in figure 1(a). This indicates that $\text{Nd}_3\text{Fe}_{20.8}\text{Co}_6\text{V}_{2.2}$ is of easy-plane-type anisotropy at room temperature. Figure 1(c) shows the XRD pattern of the rotation-aligned powder sample of $\text{Nd}_3\text{Fe}_{20.8}\text{Co}_6\text{V}_{2.2}$. It can be seen that only the (204) peak remains after rotation alignment and the other peaks have almost disappeared. This further confirms that the EMD of these compounds is in the plane perpendicular to the [204] direction and the HMD can be obtained by the rotation alignment method. All the investigated $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds with $x \leq 12$ are of easy-plane-type anisotropy at room temperature, which is different from $\text{Gd}_3\text{Fe}_{25-x}\text{Co}_x\text{Cr}_4$ compounds [11, 12], where the anisotropy at room temperature is dependent on the content of Co and has an easy-axis-type anisotropy for $x \geq 10$.

Figure 2 shows the thermomagnetic curves of $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds measured from 5 K to above the Curie temperature in a low magnetic field of 0.05 T. The values of T_c are shown in figure 3 and are listed in table 2. It can be seen that the substitution of Co for Fe leads to a nearly linear

Figure 2. Thermomagnetic curves for $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds measured in a low field of 0.05 T in the temperature range from 5 K to above the Curie temperature.

Figure 3. Composition dependence of Curie temperature T_c and spin reorientation temperature T_{sr} of $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds.

Table 2. The magnetic parameters of $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds.

x	T_c (K)	T_{sr} (K)	M_s (5 K) (μ_B/fu)	μ_{3d} (μ_B/fu)	H_A (5 K) (T)
0	467	284	44.75	1.27	13.5
3	590	303	45.38	1.29	13.3
6	705	266	46.40	1.33	12.8
9	752	377	48.43	1.40	12.7
12	836	382	50.47	1.48	12.5

increase of T_c of $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds with a rate of 30 K per Co atom. It is well known that in the R-T compounds there exist three exchange interactions: the R-R interactions between the R magnetic moments within the R sublattice, the T-T exchange interactions between the T magnetic moments within the T sublattice and the R-T interactions between the R moments and T moments. Among them, the T-T exchange interaction is the strongest and dominates the magnetically ordering temperature, while the R-R interaction is the weakest and usually neglected. It has been found that the exchange interactions between the Co-Co pairs and the Fe-Co pairs are

stronger than those of the Fe-Fe pairs in $\text{Y}(\text{Fe}, \text{Co})_{10}\text{Si}_2$ [14] and the exchange interaction between Co-Co is about twice that of Fe-Fe in the $\text{Ho}_2\text{Co}_{17}$ and $\text{Ho}_2\text{Fe}_{17}$ compounds [15]. This may be the same in $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds. Based on the molecular field model, the Curie temperature can be expressed as follows:

$$3T_C = a_{TT} + a_{RR} + [(a_{TT} - a_{RR})^2 + 4a_{RT}a_{TR}]^{1/2} \quad (1)$$

where a_{TT} , a_{RR} and $a_{RT}(=a_{TR})$ are the interaction coefficients of T-T, R-R and R-T, respectively. When the T sublattice consists of Co and Fe atoms, there exist six interactions in the R-T intermetallics: Nd-Nd, Nd-Fe, Nd-Co, Fe-Fe, Fe-Co and Co-Co. The contribution to the Curie temperature comes mainly from the Fe-Fe, Fe-Co and Co-Co interactions. On increasing the substitution of Co for Fe, the number of Co-Co pairs and Co-Fe pairs, which have relatively strong exchange interaction, increases, while the number of Fe-Fe pairs, which have relatively weak interaction, decreases. Therefore, the total exchange interaction within the T sublattice increases with increasing Co content. As a result, the substitution of Co for Fe leads to the increase of the Curie temperature of $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds.

In the thermomagnetic curves for $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds shown in figure 2, an anomaly can be seen at certain temperatures for all the compounds, which corresponds to a spin reorientation, as reported for $\text{Nd}_3(\text{Fe}, \text{Ti})_{29}$ compounds [13]. The spin reorientation temperatures T_{sr} at which the spin reorientation occurs have been derived from the peak position in the thermomagnetic curves and are shown in figure 3 as a function of Co content; it can be seen that T_{sr} shows an increasing tendency with the exception of a minimum around $x = 6$, which can be related to the preferential occupation of V atom in different sites.

It is found that in $\text{Nd}_3(\text{Fe}, \text{Ti})_{29}$ -type compounds the magnetocrystalline anisotropy contribution resulting from the Fe-sublattice is along the $[40-2]$ direction ($[110]$ direction in 1:5 structure), the contribution resulting from Nd is along the $[040]$ direction ($[1-10]$ direction in 1:5 structure) [16] and the contribution resulting from Co is along the $[204]$ direction ($[001]$ direction in 1:5 structure) [12]. On increasing the content of Co the easy-plane-type anisotropy resulting from the Fe-sublattice decreases, which leads to an increase in T_{sr} . The appearance of the minimum in the Co content dependence of T_{sr} may result from the preferential occupation of Co atoms in certain T sites, which leads to an increase of the total contribution in the $[40-2]$ direction.

It is noteworthy that in contrast to the usual magnetization behaviour of the R-T intermetallic compound with ferromagnetic coupling between the R and T magnetic moments the magnetization decreases gradually on increasing temperature from low temperature to Curie temperature; the magnetization of $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds increases gradually on increasing the temperature from 4.2 K to around room temperature in a low field of 0.05 T. This phenomenon was reported for $\text{Nd}_3\text{Fe}_{24.5}\text{Cr}_{4.5}$ and $\text{Sm}_3\text{Fe}_{24}\text{Cr}_5$ compounds [17] and was explained as the magnetohistory effect, which can be described based on the presence of narrow Bloch walls [18, 19]. The presence of the narrow Bloch walls requires a large ratio of anisotropy energy to exchange energy. The large anisotropy fields B_a at 4.2 K and the low

Figure 4. Temperature dependence of the magnetization for $\text{Nd}_3\text{Fe}_{20.8}\text{Co}_6\text{V}_{2.2}$ after ZFC or FC.

Curie temperature T_c show the presence of large anisotropy energy and small exchange energy of $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds. The propagation of the narrow Bloch walls needs thermal activation. The energy required for the latter becomes available when the temperature is increased from 4.2 K to room temperature, which corresponds to the increasing values of $M(T)$. On the other hand, it is well known that the anisotropy energy decreases quickly as temperature increases due to the strong temperature dependence of the rare earth ion anisotropy. When the temperature reached a certain value, the ratio of anisotropy energy to exchange interaction energy becomes small and no longer satisfies the condition of the presence of a Bloch wall. So, when temperature exceeds a certain value, the magnetohistory effect does not exist.

In order to investigate further the magnetohistory effect, as an example, we measured the temperature dependence of the magnetization of $\text{Nd}_3\text{Fe}_{20.8}\text{Co}_6\text{V}_{2.2}$ after zero-field cooling (ZFC) and field cooling (FC), as shown in figure 4. The ZFC curves were obtained by cooling the sample from room temperature to 5 K in zero applied field and then measured at 0.1 T, whereas the FC curves were obtained by cooling the sample from room temperature to 5 K in various applied fields as shown in figure 4 and then measured at 0.1 T. It can be seen that the ZFC and FC curves exhibit a remarkable irreversible behaviour. However, the FC (0.5 T) and FC (1.0 T) curves coincide completely, suggesting that the pinning field of the Bloch walls is smaller than 0.5 T.

Figure 5 shows the magnetization curves for $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds. The values of the saturation magnetization M_s are listed in table 2. It can be seen that M_s increases monotonically with increasing Co content. In general, in rare earth transition metal intermetallic compounds the light rare-earth moments have a ferromagnetic coupling with the transition metal moments. Assuming that the moment of Nd is completely parallel to those of Fe and Co at 5 K, and their values are all independent of the V content, then the saturation magnetization M_s of $\text{Nd}_3(\text{Fe}_{1-x}\text{Co}_x)_{26.8}\text{V}_{2.2}$ compounds at 5 K

Figure 5. Magnetization curves in EMD and HMD at 5 K for $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds.

can be calculated by the following equation:

$$M_s = 3\mu_{\text{Nd}} + 26.8\mu_{3d} \quad (2)$$

where μ_{Nd} is the average magnetic moment of Nd atoms and is assumed to be $3.62\mu_B$, the same as that of the free Nd atom, while μ_{3d} is the average magnetic moment of 3d atoms including Fe and Co. The values of μ_{3d} were derived according to equation (2), as listed in table 2. It can be seen that the value of μ_{3d} increases monotonically with increasing Co content, which is similar to the Fe–Co binary alloy in the Fe-rich region. It has been explained in terms of the rigid band model [20]; however, in our experiment results, the continuous increase of μ_{3d} results from the fact that the Co content in $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds can only be up to 12.

The anisotropy field B_a were obtained from $\Delta M-H$ plots by extrapolating the straight line parts to zero, where $\Delta M = M_{\perp} - M_{\parallel}$, where $M_{\perp}$ and $M_{\parallel}$ are the magnetizations measured in the EMD and HMD, respectively. The anisotropy values are listed in table 2. It can be seen that the anisotropy field B_a decreases monotonically with increasing Co content.

4. Conclusion

The $\text{Nd}_3\text{Fe}_{26.8-x}\text{Co}_x\text{V}_{2.2}$ compounds with $\text{Nd}_3(\text{Fe,Ti})_{29}$ -type structure were synthesized for x up to 12. When the V content is kept fixed, substitution of Co for Fe leads to an increase of the Curie temperature at a rate of 30 K/Co with increasing Co content. All the compounds show a spin reorientation as temperature decreases and the spin reorientation temperature T_{sr} shows an increasing tendency with the exception of a minimum at around $x = 6$ with increasing Co content. The saturation magnetization increases with increasing Co content, which can be understood in terms of the rigid band model. The anisotropy field at 5 K decreases with increasing Co content. All the compounds show easy-plane-type anisotropy at room temperature and the series of the compounds is not suitable for permanent materials.

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