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W F Liu[1,3]**, G H Rao**[1]**, Z W Ouyang**[1]**, G Y Liu**[1]**, X M Feng**[1]**, S Y Wang**[1] **and J K Liang**[1,2]

[1] Institute of Physics and Centre for Condensed Matter Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, People's Republic of China
[2] International Centre for Materials Physics, Academia Sinica, Shenyang 110015, People's Republic of China

E-mail: wfliu@aphy.iphy.ac.cn

Abstract

The Nd$_{1-x}$Y$_x$Co$_{9.5}$V$_{2.5}$ compounds with $x = 0$–1 crystallize in the tetragonal ThMn$_{12}$ structure. The lattice parameters a, c and the cell volume V decrease with increasing Y content. The Curie temperature increases for $x \leqslant 0.2$, then decreases with increase of the Y content. The exchange field coefficient n_{RCo} was derived from the Curie temperature and follows the general trend of rare-earth–3d intermetallic interaction exchange. The high field saturation magnetization decreases with increase of the Y content. A domain wall pinning phenomenon was observed in all of the compounds and the substitution of Y for Nd makes this phenomenon less obvious. High field measurements of the magnetization show a field induced metamagnetic transition in each compound and the critical field H_{crit}^{H} decreases with increase of the Y content.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Intermetallic compounds based on rare earths (R) and the late 3d transition (T) metals form a very important class of materials that find numerous applications in e.g. permanent magnets, magnetostrictive devices and magneto-optical recording [1]. In these compounds, the 3d–3d interaction is the strongest, which essentially determines the Curie temperature. The 4f–3d interaction, although much weaker than the 3d–3d interaction, is of special importance since it is by this interaction that the strongly anisotropic R-sublattice magnetization is coupled to the less anisotropic T-sublattice magnetization. Among these systems, the R(Co, M)$_{12}$ compounds crystallizing in the tetragonal ThMn$_{12}$ structure with space group $I4/mmm$ have

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[3] Author to whom any correspondence should be addressed.

attracted considerable attention. It is found as a rule [2] that 4f–3d spin–spin coupling is antiferromagnetic, leading to a parallel alignment of the 3d and 4f moments in the light lanthanide compounds and an antiparallel alignment in the heavy lanthanide compounds. Recently, our investigation on $Nd(Co, V)_{12}$ revealed a metamagnetization transition when a higher field up to 140 kOe was applied, accompanied by an increase of the magnetization of about 3.1 μ_B per formula for $NdCo_{9.5}V_{2.5}$, whereas the magnetization of $NdCo_{12-x}V_x$ in a field of 50 kOe is almost the same as that reported for $YCo_{12-x}V_x$ [3]. It seems that the Nd moment makes no contribution to the total moment of the compound at 50 kOe. Later, we noticed that Fe substitution for Co in $NdCo_{9.5}V_{2.5}$ could result in a shift of the critical field required for the metamagnetic transition, which may be understood by considering the effects of the exchange coupling parameter J_{RT} (between R and T atoms) and the T-sublattice moment μ_T [4]. As a continuation of the systematic research on the compound $NdCo_{9.5}V_{2.5}$, in this paper we report the structural and magnetic properties of $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$. Since Y is a nonmagnetic element, the substitution of Y for Nd provides a unique opportunity for obtaining a deeper understanding of the magnetic properties of the compounds.

2. Experimental details

Samples of $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$ with $x = 0, 0.1, 0.2, 0.3, \ldots, 0.9, 1$ were prepared by arc melting stoichiometric amounts of the constitutive metal elements Nd, Y, Co and V with purity better than 99.9% under a high purity argon atmosphere. Appropriate excess amounts of Nd and Y were added to compensate for the weight loss during arc melting and subsequent heat treatment. The ingots were wrapped in Ta foil and sealed in an evacuated quartz tube and homogenized at 1373 K for ten days. To avoid possible phase transitions during cooling, the samples were water quenched.

X-ray powder diffraction (XRD) experiments were performed by using a Rigaku D/max 2500 diffractometer with Cu Kα radiation (40 kV $\times$ 300 mA) and a graphite monochromator. A step-scan mode was adopted with a sampling time of 1 s and a step width of $2\theta = 0.02°$. The temperature dependence of the ac susceptibility of the samples was measured by a mutual inductance method with a fixed frequency of 240 Hz. Curves of magnetization versus temperature (M–T) for the samples were measured by a SQUID magnetometer in a field of 500 Oe. The field dependence of the magnetization (M–H) at 5 K of the fine powder, which was used for XRD analysis, was measured using a PPMS.

3. Results and discussion

3.1. Crystallographic properties

The phase purity of the prepared $(Nd_{1-x}Y_x)Co_{9.5}V_{2.5}$ was examined by XRD and thermomagnetic analysis. All the samples are single phase with the expected tetragonal $ThMn_{12}$ structure as shown in figure 1. The unit-cell parameters a, c and unit-cell volume V based on the Rietveld refinement of the XRD pattern [5, 6] are shown in figure 2 and listed in table 1. The values of a, c and V for $x = 1$ agree well with those reported in [7, 8]. Because the atomic radius of Y is smaller than that of Nd, the unit-cell volume V for $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$ ($x = 0$–1) compounds decreases slightly with increase of the Y content.

3.2. The Curie temperature and exchange interaction

Figure 3 shows the temperature dependence of the ac susceptibility χ_{ac} of $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$. It exhibits a distinct susceptibility peak near the Curie temperature. With increasing Y content, the

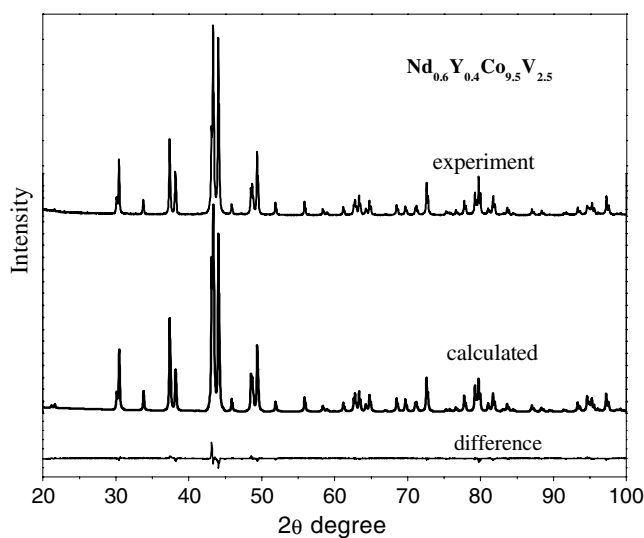**Figure 1.** The experimental and the calculated XRD patterns of Nd$_{0.6}$Y$_{0.4}$Co$_{9.5}$V$_{2.5}$; the lowest curve is the difference between them.
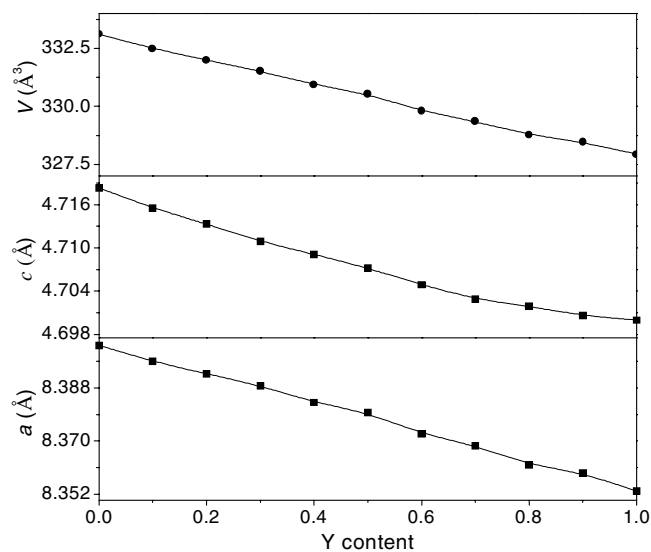

Figure 2. The Y content dependence of the lattice parameters a, c and the unit-cell volume V.

peak becomes broader and less obvious. According to the Landau theory, the critical peak χ_m can be discussed on the basis of the expression for the susceptibility $\chi(T, H) = 1/(C_1+C_3M^2)$, where C_1 and C_3 are the coefficients of the expression for the free energy [9]. For a second-order phase transition, this susceptibility shows a maximum at the Curie temperature, where $C_1(T'_C) = 0$. The Curie temperatures of Nd$_{1-x}$Y$_x$Co$_{9.5}$V$_{2.5}$ derived from the peak temperature are listed in table 1.

The temperature dependence of the magnetization was measured while warming under 500 Oe after cooling down from room temperature without an applied field and is shown in
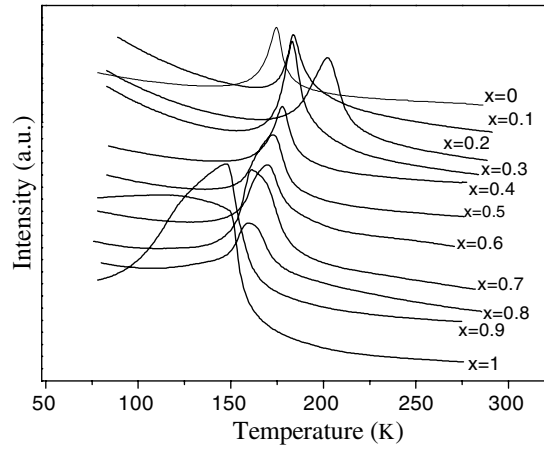
Figure 3. The temperature dependence of the ac susceptibility for $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$ compounds.

Table 1. Structural and magnetic properties of $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$ compounds; T'_C and T_C were derived from the ac susceptibility and the $M-T$ curve, respectively.

x	a (Å)	c (Å)	V (Å³)	T'_C (K)	T_C (K)	n_{RCo} (T fu/μ_B)	M_S (μ_B/fu)	H^H_{crit} (10^4 Oe)
0	8.4024	4.7183	333.113	177	180	23.55	7.8	6.25
0.1	8.397	4.7155	332.488	182	186	26.3	7.61	6.15
0.2	8.3928	4.7133	332.000	203	201	32.6	7.44	5.94
0.3	8.3888	4.7109	331.515	184	186	26.3	6.70	5.51
0.4	8.3831	4.7091	330.938	179	180	23.55	5.94	4.88
0.5	8.3796	4.7072	330.528	175	176	21.62	5.63	4.23
0.6	8.3724	4.7049	329.799	173	170	18.52	5.37	3.29
0.7	8.3685	4.7029	329.352	162	166	16.26	4.73	2.27
0.8	8.362	4.7019	328.771	160	160	12.37	4.52	1.57
0.9	8.3592	4.7006	328.460	153	156	9.10	3.73	0.59
1	8.353	4.7	327.931	152	151	—	3.12	0

figure 4. The Curie temperature T_C shown in figure 5 and listed in table 1 was taken as the temperature at which dM/dT exhibits a maximum on the high temperature part. The T_C derived from $M-T$ curves coincidences well with that corresponding to the temperature of the χ_{ac} peak and the value for $x = 1$ agrees well with that reported in [7]. As can be seen from figure 5, the Curie temperature increases first and then decreases with increasing Y content, showing a maximum at $x = 0.2$.

Within the molecular field approximation, the exchange interactions in the rare-earth intermetallics can be deduced from the expression for the magnetic ordering temperature [10]:

$$T_C = \tfrac{1}{2}\{T_{Co} + [(T_{Co} - T_R)^2 + 4T_{RCo}^2]^{1/2}\}$$

where T_{Co}, T_R and T_{RCo} represent the contributions due to the Co–Co, R–R and Co–R exchange interactions, respectively, and are given by

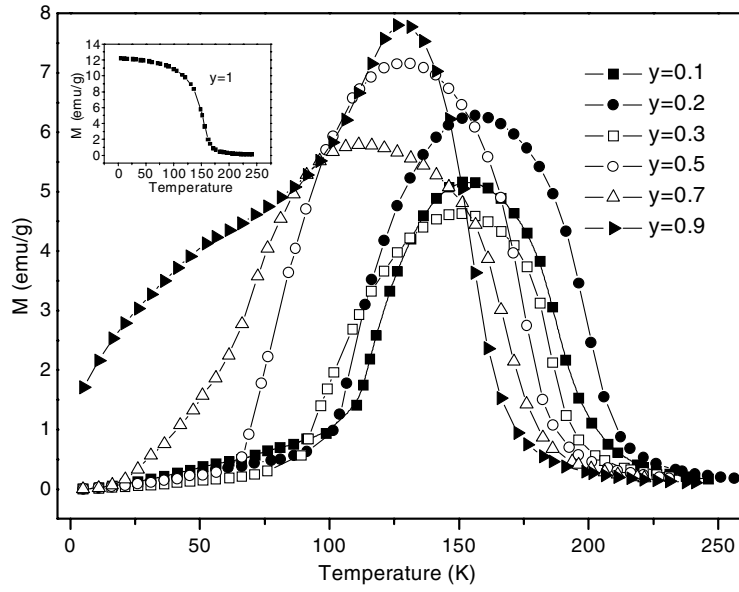$$T_{Co} = n_{CoCo}C_{Co},$$

$$T_R = 4[(g_J - 1)/g_J]^2 n_{RR}C_R$$

Figure 4. The temperature dependence of the magnetization for Nd$_{1-x}$Y$_x$Co$_{9.5}$V$_{2.5}$ compounds.
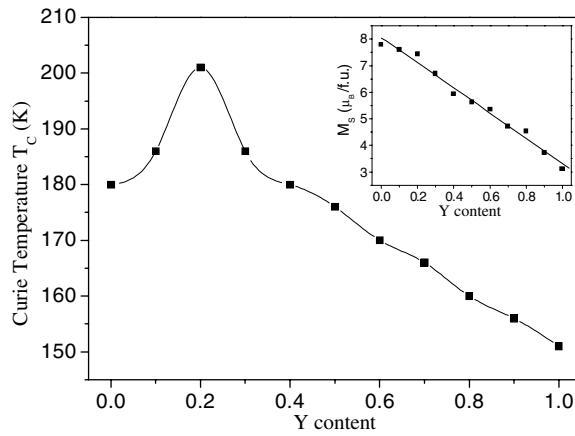

Figure 5. The concentration dependence of the Curie temperature T_C. The inset shows the concentration dependence of the saturation magnetization under 140 kOe.

and

$$T_{RCo} = [2(g_J - 1)/g_J]n_{RCo}\sqrt{C_R C_{Co}}$$

where

$$C_{Co} = 4N_{Co}S(S + 1)\mu_B^2/3k_B,$$

$$C_R = N_R g_J^2 J(J + 1)\mu_B^2/3k_B.$$

Here, N_R and N_{Co} are the numbers of R and Co atoms per unit volume, and n_{CoCo}, n_{RR} and n_{RCo} are exchange field coefficients for a given series of Co–R compounds. The $n_{CoCo}(T_{Co})$ and $n_{RR}(T_R)$ can be determined by means of isostructural nonmagnetic rare-earth compounds

(Y–M, La–M or Lu–M) and nonmagnetic or poorly magnetic transition-metal compounds (R–Cu, R–Mn, R–Ni and so on), respectively. Since the R–R interaction is very weak, n_{RR} may usually be neglected. The Co–Co exchange interaction of the $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$ systems can be deduced from the Curie temperature of the compounds with R = Y ($x = 1$). $2[S(S+1)]^{1/2}\mu_B$ is the effective atomic moment of Co in the paramagnetic state, taken as $3.1\,\mu_B$ from a comparison of the paramagnetic susceptibilities of the related compounds (RCo_2, RCo_3, R_2Co_7) [11–13]. n_{CoCo} for the system $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$ is estimated to be 7.4 T fu/μ_B.

The R–Co exchange interaction can be deduced from the molecular field approximation using the expression for the magnetic ordering temperature [10]; neglecting the R–R interactions, the exchange field coefficient is given by

$$n_{RCo} = \frac{[(T_C - T_{Co})T_C]^{1/2}}{2(C_{Co}C_R)^{1/2}(g_J - 1)/g_J}.$$

Taking the Co-sublattice ordering temperature $T_{Co} = 151$ K for $YCo_{9.5}V_{2.5}$, we obtained the values of n_{RCo} for the $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$ system listed in table 1. The n_{RCo} derived for $NdCo_{9.5}V_{2.5}$ is larger than that of the heavy rare-earth compounds [7]: 13.0 T fu/μ_B for $GdCo_{10}V_2$, 8.3 T fu/μ_B for $TbCo_{10}V_2$, 5.5 T fu/μ_B for $DyCo_{10}V_2$, 3.9 T fu/μ_B for $HoCo_{10}V_2$, 3.3 T fu/μ_B for $ErCo_{10}V_2$, following the usual trend of the rare-earth–3d transition-metal exchange interaction. Hu *et al* [14] reported that in R(Fe, M)$_{12}$ compounds the systematic decrease of n_{RFe} by a factor of 2 or more from the light rare-earth to the heavy rare-earth elements appears to be a general feature of rare-earth intermetallic compounds, which may be related to 4f–5d overlap. Liu *et al* [15] had also mentioned that an even stronger decrease of the radius of the 4f shell with increasing Z can lead to a smaller overlap of the 4f and 5d shells.

3.3. The domain wall pinning effect and high field saturation magnetization

At low temperature, a steep increase of the magnetization occurs as shown in the M–T curves (figure 4). This typical behaviour is characteristic of ferromagnetism when narrow domain walls are present, as found previously in other anisotropic rare-earth compounds. The inset of figure 6 shows the field dependence of the magnetization at 5 K from 0 to 10 000 Oe, which exhibits a field induced magnetic jump for all of the compounds. This behaviour can be due to the narrow domain wall pinning effect under the applied field. As shown in the inset of figure 7, the H_{crit}^L required to induce the magnetic jump, which was determined from the peak position in the differential of the magnetization with respect to the field ($dM/dH \sim H$), decreases with increasing Y content. It is well known that a competition between the magnetocrystalline anisotropy of the compound and the exchange energy can result in domain wall pinning. With substitution of Y for Nd, the rare-earth-sublattice magnetocrystalline anisotropy is weakened, which can lead to a decrease of the required H_{crit}^L.

As we argued previously, the Nd moment and Co moment in $NdCo_{9.5}V_{2.5}$ are nearly parallel exclusively at fields larger that 60 kOe. The field dependence of the magnetization of the samples with $x \leqslant 0.7$ was measured in a field up to 140 kOe and is shown in figure 6. According to the law of approach to saturation, the saturation moment M_S of $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$ is derived by extrapolating $1/H$ to zero from the linear part of the M versus $1/H$ curves; the results are listed in table 1 and shown in the inset of figure 5. The saturation magnetization M_S decreases with increasing Y content due to the substitution of the nonmagnetic atom Y for magnetic Nd atoms.
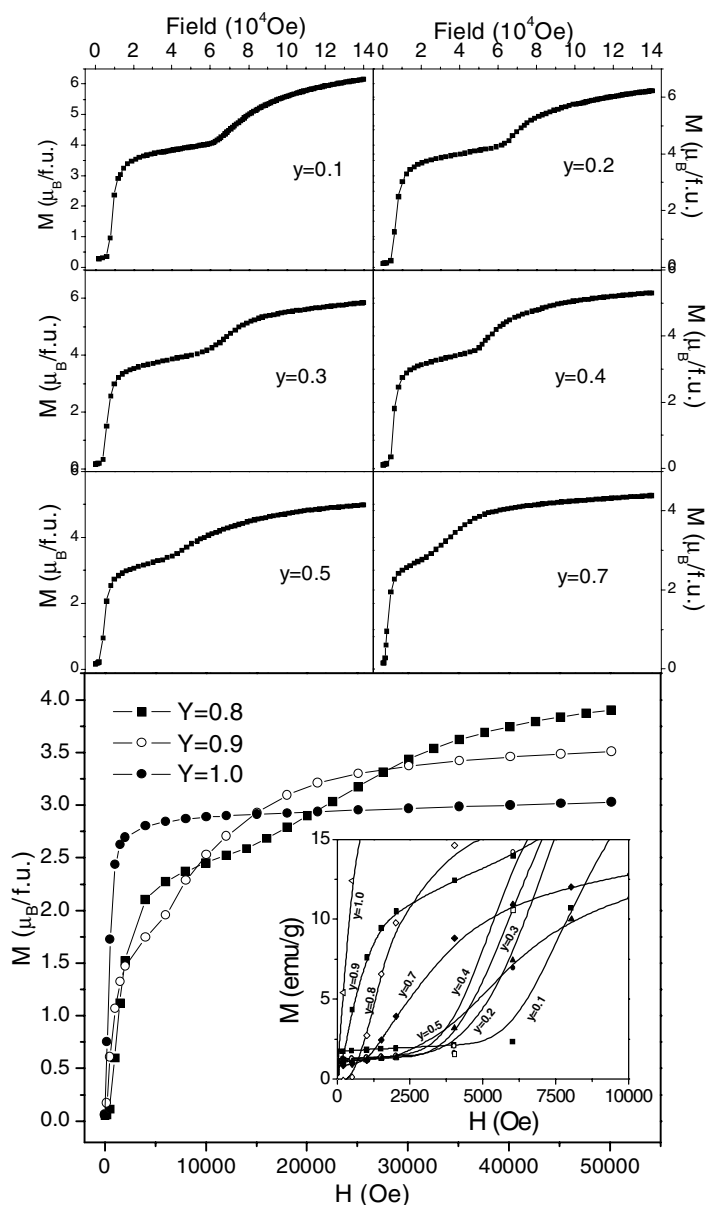
Figure 6. Magnetization curves of Nd$_{1-x}$Y$_x$Co$_{9.5}$V$_{2.5}$ compounds at 5 K. The inset shows the magnetization curves in the field range of 0–10 000 Oe.

3.4. Metamagnetic transition

From figure 6, one can see that there exists a field induced magnetic transition for each sample when measuring at higher field, as observed in [3]. Using the same method as for deriving $H_{\text{crit}}^{\text{L}}$ in low field, $H_{\text{crit}}^{\text{H}}$ at higher field is shown in figure 7 and listed in table 1. $H_{\text{crit}}^{\text{H}}$ decreases with increasing Y content and disappears at Y = 1.0. One of the possible causes for the observed metamagnetic transition is the strong anisotropy field of Nd ions—the Nd
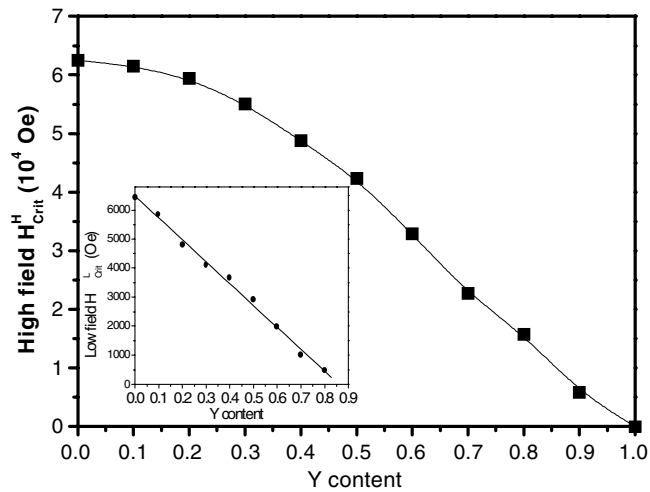
Figure 7. The Y content dependence of the critical field for the metamagnetic transition. The inset shows the concentration dependence of the critical field for domain wall pinning.
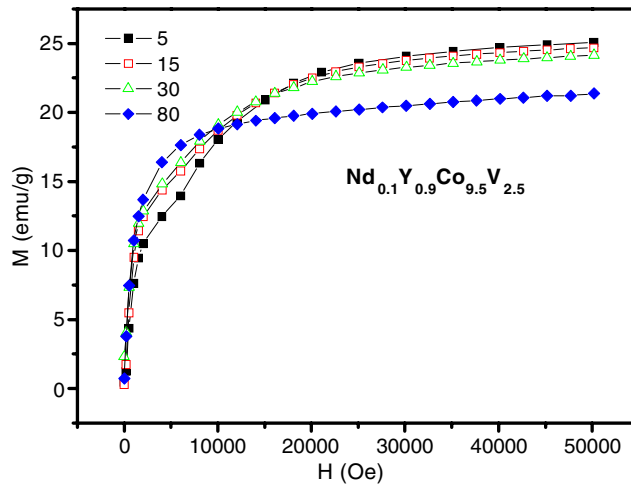

Figure 8. Magnetization curves of the powder sample of $Nd_{0.1}Y_{0.9}Co_{9.5}V_{2.5}$ at different temperatures.

moment could not respond to the applied magnetic field when the field is not strong enough. Such a phenomenon is associated with the first-order magnetization process (FOMP) [16]. The substitution of Y for Nd decreases the anisotropy field of the R sublattice and therefore reduces the critical field $H_{\text{crit}}^{\text{H}}$ for the FOMP. In order to investigate the temperature dependence of the metamagnetic transition behaviour, we measured the magnetization curves at various temperatures for $Nd_{0.1}Y_{0.9}Co_{9.5}V_{2.5}$ (see figure 8) and $Nd_{0.2}Y_{0.8}Co_{9.5}V_{2.5}$ (see figure 9). It is apparent that the metamagnetic transition depends on the temperature. It can be seen from figures 8 and 9 that the transition, which is sharp at low temperatures, becomes broadened with increasing temperature and disappears at higher temperature. The same phenomenon was also observed in [17–19] and can be explained by the temperature variations of the magnetic anisotropy of the R sublattice.
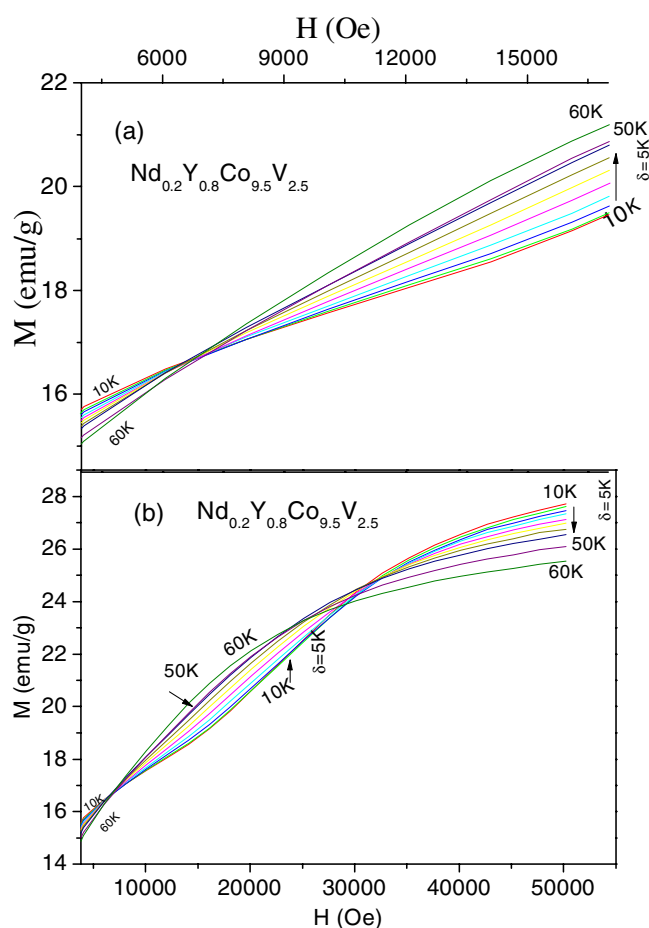
Figure 9. (a) Magnetization curves of the powder sample of Nd$_{0.2}$Y$_{0.8}$Co$_{9.5}$V$_{2.5}$ at different temperatures in the field range of 4000–17 000 Oe and (b) magnetization curves of the powder sample of Nd$_{0.1}$Y$_{0.9}$Co$_{9.5}$V$_{2.5}$ at different temperatures in the field range of 3800–50 000 Oe.

4. Conclusion

The Nd$_{1-x}$Y$_x$Co$_{9.5}$V$_{2.5}$ compounds with $x = 0$–1 crystallize in the tetragonal ThMn$_{12}$ structure. The lattice parameters a, c and the cell volume V decrease with increasing Y content. The Curie temperature first increases for $x \leqslant 0.2$, then decreases with increase of the Y content. The exchange field coefficient n_{RCo} derived from Curie temperature follows the general trend of rare-earth–3d intermetallic interaction exchange. The high field saturation magnetization decreases due to the substitution of nonmagnetic Y atoms for the magnetic Nd atoms. A domain wall pinning phenomenon was observed in all of the compounds and the substitution of Y for Nd makes this phenomenon less obvious due to the weakened R-sublattice anisotropy. High field measurements of the magnetization show a field induced metamagnetic transition in each compound and the critical field H_{crit}^{H} decreases with increasing Y content.

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