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Structural and magnetic properties of $Nd_2Co_{17-x}V_x$ compounds

B.D. Liu[a,b], Y.X. Li[b], W.X. Li[a], H.Y. Liu[b], G.H. Wu[a], F.M. Yang[a,*], F.R. de Boer[c]

[a] *State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, 100080 Beijing, China*
[b] *School of Material Sciences and Engineering, Hebei University of Technology, Tianjin 300130, China*
[c] *Van der Waals-Zeeman Instituut, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands*

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Abstract

The effect of substitution of V for Co on the structure and magnetic properties of $Nd_2Co_{17-x}V_x$ compounds ($x = 0$, 0.5, 1, 1.5, 2) has been investigated by means of XRD and magnetic measurements. It is found that all compounds with x from 0 to 2 are almost single phase with the Th_2Zn_{17}-type of structure. The lattice constants a, c and the unit-cell volume V show a tendency to increase with increasing V content. The Curie temperature decreases linearly with increasing V content at a rate of 240 K per V atom substituted in Nd_2Co_{17}. A spin reorientation is observed in all compounds investigated and the spin-reorientation temperature T_{sr} changes from 147 K for $x = 0$ to 474 K for $x = 1.0$ and is almost independent of the V content above $x = 1.0$. The saturation magnetization M_s of $Nd_2Co_{17-x}V_x$ compounds and the Co moment μ_{Co} in these compounds decreases monotonically with increasing V content.

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Keywords: $Nd_2Co_{17-x}V_x$ compounds; Crystal structure; Spin reorientation

1. Introduction

Recently, much attention has been devoted to the research on the rare-earth–cobalt compounds of the R_2Co_{17} type (R stands for rare earth or Y) due to their high Curie temperature and high saturation magnetization as well as their potential application as high-temperature permanent magnets [1–3]. It is well known that all Co-based R_2Co_{17} compounds show planar anisotropy at room temperature, except for the compounds with R = Ce, Sm, Er and Tm [1]. However, Some Co-based R_2Co_{17} compounds with planar anisotropy, like Gd_2Co_{17}, show a transition from planar anisotropy at room temperature to easy-axis anisotropy by substitution of Ga [4], Al [5], or Si [6] for Co. In the past years, Nd_2Co_{17} [1] and the $Nd_2Co_{17-x}M_x$ compounds with M = Ga [7], Al [8] and Si [9] have been widely investigated. In order to investigate further the contribution of the

*Corresponding author. Tel.: +86-010-8264-9250; fax: +86-010-6256-2605.

E-mail address: fmyang@aphy.iphy.ac.cn (F.M. Yang).

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transition-metal atoms at the different crystallographic sites to the magnetic properties, like Curie temperature, saturation magnetization, and especially to the magnetocrystalline anisotropy, we have investigated the effect of substitution of a non-magnetic transition element on structure and magnetic properties. In this paper, the effect of substitution of V for Co on the structure and magnetic properties of $Nd_2Co_{17-x}V_x$ compounds is presented.

2. Experimental

Alloys with composition $Nd_2Co_{17-x}V_x$ ($x = 0$, 0.5, 1.0, 1.5, 2.0) were prepared by arc-melting the constituent elements with a purity of at least 99.9% in an argon atmosphere. All ingots were remelted at least four times to ensure homogenization. In order to compensate for the loss of Nd during the melting and annealing, 2% excess of Nd with respect to the ideal composition $Nd_2Co_{17-x}V_x$ was added. The as-cast ingots were wrapped in molybdenum foil and sealed in a quartz tube followed by annealing at1353 K for 72 h under protection of argon atmosphere, and then followed by quenching in water. X-ray diffraction (XRD) and thermomagnetic analysis were employed to check the phase homogeneity. Thermomagnetic curves were measured in a vibrating-sample magnetometer (VSM) from room temperature to above the Curie temperature in a low magnetic field of 0.05 T. The Curie temperature was derived from the M^2-T curves by extrapolating M^2 to zero. Magnetization curves were recorded in a SQUID magnetometer at 5 K in magnetic fields B up to 5 T. The saturation magnetization M_s was derived from M vs. $1/B$ curves by extrapolating $1/B$ to zero.

In order to measure the 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 will correspond to the hard magnetization direction (HMD).

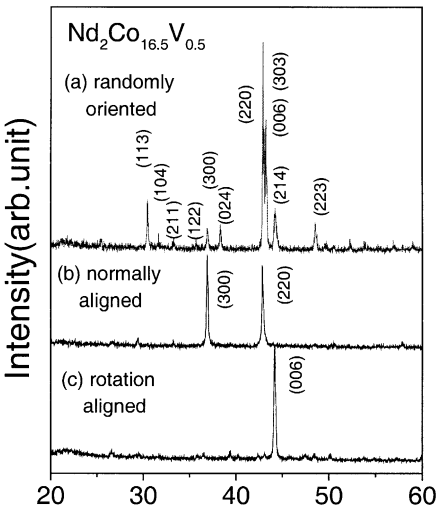

Fig. 1. XRD patterns of (a) randomly oriented, (b) normally aligned and (c) rotation-aligned powder samples of $Nd_2Co_{17-x}V_x$ compounds.

3. Results and discussion

Both the XRD patterns and the thermomagnetic analysis show that single-phase $Nd_2Co_{17-x}V_x$ compounds with the Th_2Zn_{17}-type of structure were obtained for $x = 0$–2. As an example, Fig. 1(a) shows the XRD pattern of randomly oriented $Nd_2Co_{16.5}V_{0.5}$ powder, which was quite well indexed by the Th_2Zn_{17}-type of structure. The lattice constants a, c and the unit-cell volume V derived from the XRD patterns are listed in Table 1. It can be seen that the lattice constants and the unit-cell volume show a tendency to increase with increasing V content, due to the larger radius of V compared with that of Co. The XRD pattern of a normally aligned powder sample of $Nd_2Co_{16.5}V_{0.5}$ is shown in Fig. 1(b). Compared with the XRD pattern of a randomly aligned powder sample of the same

Table 1
Lattice constants a and c, volume V of $Nd_2Co_{17-x}V_x$ compounds

x	a (nm)	c (nm)	V (nm^3)
0	0.8416	1.2221	0.7496
0.5	0.8430	1.2272	0.7552
1	0.8436	1.2280	0.7569
1.5	0.8438	1.2290	0.7585
2	0.8438	1.2289	0.7589

compound shown in Fig. 1(a), it is found that in the XRD patterns of the normally aligned powder sample the (3 0 0) reflection and the (2 2 0) reflection are strongly enhanced, whereas the other reflections have almost disappeared. This indicates that $Nd_2Co_{16.5}V_{0.5}$ has planar anisotropy at room temperature. The XRD pattern of a rotation-aligned-powder sample of $Nd_2Co_{16.5}V_{0.5}$ is shown in Fig. 1(c). It can be seen that in the XRD pattern of rotation-aligned-powder sample the (0 0 6) reflection is dominant and the other reflections have disappeared. This confirms further that the EMD in these compounds is in the plane perpendicular to the [0 0 6] direction and that the HMD in these compounds can be obtained by the rotation-alignment method.

Fig. 2 shows the thermomagnetic curves of $Nd_2Co_{17-x}V_x$ compounds with $x = 0-2.0$, measured at a low field of 0.05 T at temperatures ranging from 120 K to room temperature (Fig. 2(a)) and from room temperature to above the Curie temperature (Fig. 2(b)). The values of T_C are listed in Table 2 (the value for $x = 0$ has been taken from Ref. [10]) and are also shown in Fig. 3. It can be seen that the Curie temperature decreases monotonically with increasing V content. The rate of decrease of T_C is 240 K per V atom substituted in Nd_2Co_{17}. In rare-earth (R)–transition-metal (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 these three exchange interactions, the T–T exchange interaction is the strongest while the R–R interaction is

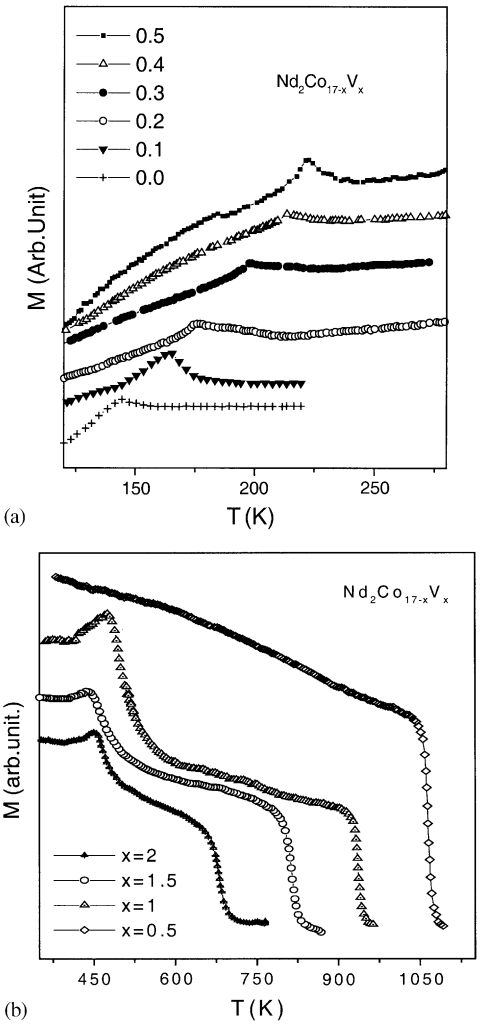

Fig. 2. Thermomagnetic curves for $Nd_2Co_{17-x}V_x$ compounds measured in a low field of 0.05 T in the temperature range (a) from 120 K to room temperature and (b) from room temperature to above the Curie temperature.

Table 2
Curie temperature T_C, spin-reorientation temperature T_{sr}, saturation magnetization M_s and Co moment μ_{Co} of the $Nd_2Co_{17-x}V_x$ compounds

x	T_C (K)	T_{sr} (K)	M_s (μ_B/f.u.) (5 K)	μ_{Co} (μ_B/f.u.)
0	1180 [9]	147	31.5	1.44
0.5	1070	223	28.53	1.31
1	942	474	24.06	1.07
1.5	825	448	21.89	0.96
2	700	454	19.77	0.85

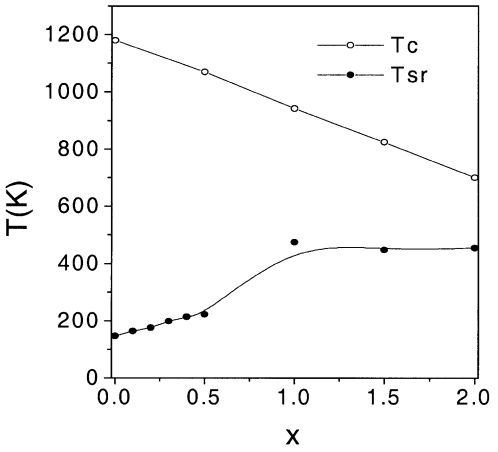

Fig. 3. Dependence of the Curie temperature T_C and the spin-reorientation temperature T_{sr} of $Nd_2Co_{17-x}V_x$ compounds on the V composition.

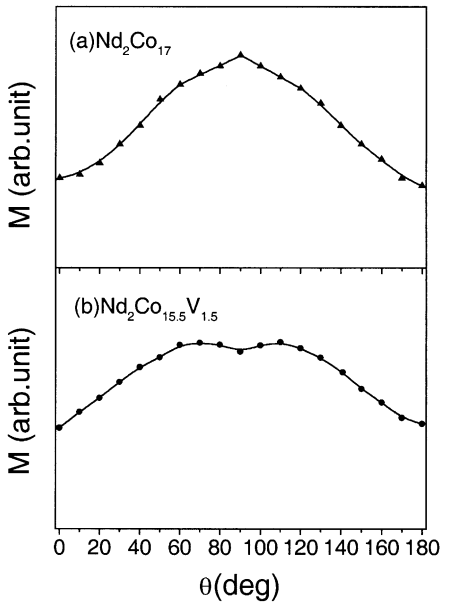

Fig. 4. Magnetization at room temperature as a function of the angle θ between the alignment direction and the external field in a field of 0.5 T for (a) Nd_2Co_{17} and (b) $Nd_2Co_{17-x}V_x$.

the weakest, and usually is neglected. In general, the T–T interaction is much larger than R–T interaction. Therefore, the Curie temperature is mainly determined by the T–T interaction. When the V content x increases, the number of Co atoms decreases, so that the Co–Co exchange interaction is weakened, which leads to a decrease of the Curie temperature. Moreover, substitution of V for Co leads to a decrease of the Co moment (see Fig. 6(b)), which is also an important factor resulting in a decrease of the Curie temperature.

It is clear from Fig. 2 that for all compounds investigated with $x = 0$–2.0, there exists a sharp peak at a certain temperature in thermomagnetic curves that corresponds to a spin reorientation, as has been reported for the Nd_2Co_{17} compound [1]. The spin-reorientation phenomenon also has been observed in some Nd-based 2:17, 1:12 and 3:29 compounds [10–12]. The temperatures T_{sr} at which the spin reorientation occurs were derived from the positions of the peaks in the thermomagnetic curves and are plotted as a function of the V content in Fig. 3. The values of T_{sr} are listed in Table 2 where it can be seen that T_{sr} increases rapidly from 147 K for $x = 0$ to 474 K for $x = 1.0$. From $x = 1.0$–2.0, T_{sr} is almost independent of the V content.

In order to investigate what happens at T_{sr}, we measured the dependence of magnetization of several magnetically aligned-powder samples on the angle θ between the alignment direction and the external field at room temperature. Generally, if the anisotropy is of easy-axis or easy-plane type, there exists one maximum between 0° and 180° in the $M-\theta$ curve while two maxima appear at θ_{max1} and θ_{max2} in the case of easy-cone type of anisotropy. The cone angle θ_c can be derived by $\theta_c = (\theta_{max2} - \theta_{max1})/2$. As an example, Fig. 4 shows the dependence of the magnetization at room temperature of magnetically aligned powder samples of Nd_2Co_{17} (Fig. 4(a)) and $Nd_2Co_{15.5}V_{1.5}$ (Fig. 4(b)) on the angle θ between the alignment direction and the external field. It can be seen that there is only one maximum for Nd_2Co_{17}, but there are two for $Nd_2Co_{15.5}V_{1.5}$. This suggests that at room temperature the anisotropy of Nd_2Co_{17} is of easy-plane type and that the anisotropy of $Nd_2Co_{15.5}V_{1.5}$ is of easy-cone type. The cone angle at room temperature is 20°. Therefore, in fact, Fig. 3 represents a spin phase diagram of $Nd_2Co_{17-x}V_x$ compounds. In the higher-temperature region near the Curie temperature, all

compounds show easy-plane type of anisotropy. With decreasing temperature, a spin reorientation occurs at T_{sr} from easy-plane to easy-cone type of anisotropy.

In general, a spin-reorientation results from the competition of two magnetic-sublattice anisotropies, which have different types of anisotropy and show different temperature dependencies. It has been found that there exists a spin reorientation from easy-axis to easy-plane type of anisotropy at 1038 K in Y_2Co_{17} [1]. It is well known that, in R_2Co_{17} compounds, the R atoms occupy 6c sites, and the Co atoms occupy four different crystallographic sites: the 9d, 18f, 18h and 6c sites. A NMR study on Y_2Co_{17} [13] has pointed out that in Y_2Co_{17} the Co atoms at 18f sites contribute positively to the anisotropy while the Co atoms at 6c, 9d, and 18h sites have a negative contribution to the anisotropy. Therefore, the spin reorientation occurring in Y_2Co_{17} may result from the competition of the two Co-sublattice anisotropies resulting from the 18f sites and from the 6c, 9d and 18h sites.

In order to examine the mechanism of the spin reorientation occurring in $Nd_2Co_{17-x}V_x$ compounds, it is necessary to examine the contribution of the Nd sublattice to the anisotropy. In lowest-order approximation, the anisotropy of the Nd sublattice in $Nd_2Co_{17-x}V_x$ compounds can be written as

$$K_1(\mathrm{Nd}) = -\tfrac{3}{2}\alpha_J \langle r^2 \rangle \langle O_{20} \rangle A_{20}, \quad (1)$$

where α_J is the Stevens factor of the Nd ion, $\langle r^2 \rangle$ is the mean value of the square of the 4f radius. $\langle O_{20} \rangle$ is the thermal average of the quantum-mechanical expectation value corresponding to the second-order Stevens operator. A_{20} is the second-order crystal-field parameter that depends on the crystal structure and on the composition of a given compound. Because α_J is negative for Nd and A_{20} is negative for the presently investigated 2:17-type of compounds [14], K_1(Nd) is negative, meaning that the Nd sublattice contributes easy-plane type of anisotropy if we only consider the contribution resulting from the lowest-order anisotropy constant K_1(Nd). The occurrence of the spin-reorientation transition in Nd_2Co_{17} at 147 K may be due to the contribution of the higher-order crystal–field interaction. The fast rate at which T_{sr} increases with increasing V content from $x = 0$–1.0 may be associated with the preferential occupation of V atoms of 6c, 9d and 18h sites, where the Co ions contribute easy-plane type of anisotropy. Substitution of V for Co leads to a decrease of the easy-plane type of anisotropy of the Co sublattice, with as a result that T_{sr} increases with V content x. For V content x larger than 1.0, T_{sr} becomes almost independent of V content. It may be that, for x larger than 1.0, the V atoms occupy the various Co sites randomly, making the net contribution resulting from the various Co sites almost independent of the V content.

Fig. 5 shows the magnetization curves of $Nd_2Co_{17-x}V_x$ compounds, measured at 5 K in a SQUID magnetometer in applied magnetic fields up to 5 T. It can be seen that all magnetization curves reach saturation at about 1 T. The values of the saturation magnetization M_s are listed in Table 2 and are also shown in Fig. 6(a). It can be seen that M_s decreases monotonically with increasing V content x.

In R–T intermetallic compounds, the light-rare-earth moments couple ferromagnetically with the transition-metal moments. If we assume that the

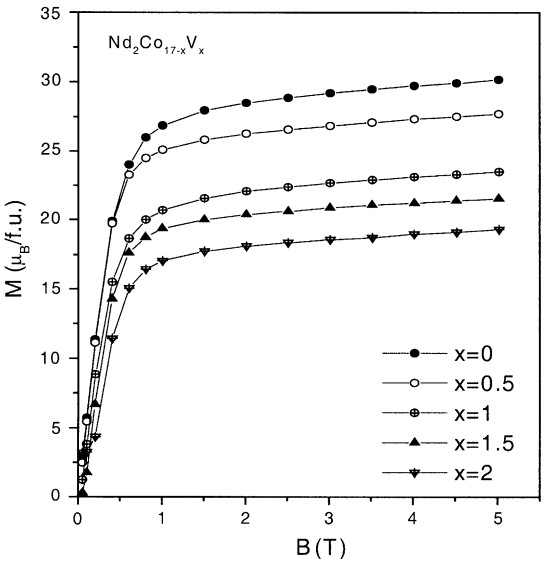

Fig. 5. Magnetization curves at 5 K of $Nd_2Co_{17-x}V_x$ compounds.

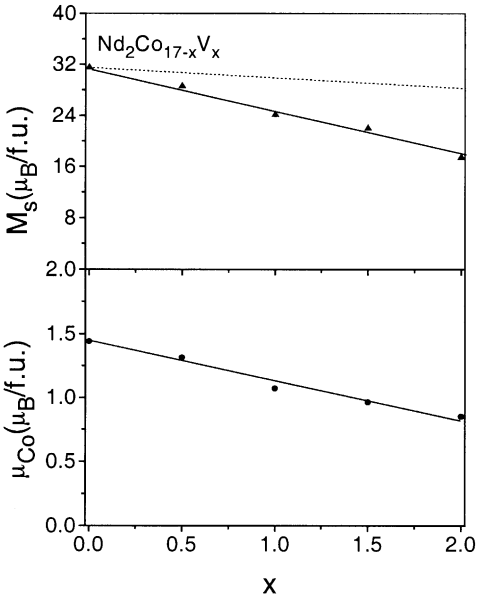

Fig. 6. Composition dependence of (a) the experimental and the calculated saturation magnetization M_s for $Nd_2Co_{17-x}V_x$ compounds and (b) the Co moment μ_{Co} in $Nd_2Co_{17-x}V_x$ compounds.

Nd moments are perfectly parallel to those of Co at low temperature and that the values of Nd and Co moments are independent of the V content, a simple dilution model describes the saturation magnetization M_s of $Nd_2Co_{17-x}V_x$ compounds as

$$M_s = M_0 - x\mu_{Co}, \quad (2)$$

where M_0 and μ_{Co} are the saturation moment of Nd_2Co_{17} and the Co moment, respectively. Taking the value of the Co moment equal to $1.58\mu_B$ [15] we can calculate M_s using Eq. (2). The calculated results are listed in Table 2 and are also represented in Fig. 6(a) by the dashed line. It can be seen that the decrease of the experimental M_s with increasing V content is much faster than that calculated in a simple dilution model. If we assume that at 5 K the Nd moment μ_{Nd} possesses its free-ion value of $3.27\mu_B$, the Co atomic moment μ_{Co} can be calculated by $\mu_{Co} = (M_s - 2\mu_{Nd})/(17 - x)$. The results are listed in Table 2 and also shown in Fig. 6(b). It is found that the Co moment decreases with increasing V content with a large average decrease rate of $0.3\mu_B$ per substituted V atom. It can be concluded that substitution of V for Co not only leads to dilution of the Co atoms, but also results in a decrease of the Co magnetic moment, which provides an important contribution to the decrease of the Curie temperature with increasing V content.

4. Conclusions

In summary, the formation and the magnetic properties of $Nd_2Co_{17-x}V_x$ compounds have been investigated. It is found that single-phase $Nd_2Co_{17-x}V_x$ compounds with Th_2Zn_{17}-type of structure are obtained for $x = 0$–2. The lattice constant a, c and the unit-cell volume V show a tendency to increase with increasing V content. The Curie temperature decreases monotonously with increasing x with a large rate of 240 K per substituted V atom. All compounds investigated possess easy-plane type of anisotropy at high temperature near the Curie temperature. As the temperature decreases, a spin-reorientation transition from easy-plane type to easy-cone type of anisotropy occurs in all $Nd_2Co_{17-x}V_x$ compounds investigated. The spin-reorientation temperatures increases monotonically with increasing V content in the range from $x = 0$–1 and then becomes nearly independent of the V content. The saturation magnetization of $Nd_2Co_{17-x}V_x$ compounds decreases with increasing V content. Substitution of V for Co leads to a decrease of the Co moment in $Nd_2Co_{17-x}V_x$ compounds, which may give an important contribution to the decrease of Curie temperature with increasing V content.

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