Magnetic structure and magnetization process of NdCo$_{12-x}$V$_x$

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NdCo$_{12-x}$V$_x$ ($2.2 \leqslant x \leqslant 2.6$) crystallizes in the ThMn$_{12}$-type structure and exhibits an unusual jump in the magnetization at a critical field B_C that decreases with increasing V content. It was intriguing that the magnetization of the bulk samples below B_C was very close to that of YCo$_{12-x}$V$_x$ with the same V content. To investigate the nature of the magnetic order in these materials we have carried out powder neutron diffraction measurements as a function of temperature and magnetic field on the NdCo$_{9.5}$V$_{2.5}$ composition. In zero field we find that both the Nd and Co ions have substantial ordered moments ($\sim$2.9 and 0.4 μ_B, respectively) at low temperature (4 K), with the moments coupled ferromagnetically ($T_C = 180$ K) and aligned along the c axis. On a loose powder an applied field of 4 to 7 T rotates the particles so the c axis aligns with the field, indicating a strong uniaxial anisotropy that renders the system Ising-like. However, we find the same in-field magnetic structure and essentially the same values for the saturated magnetic moments as those in zero field. Magnetization data on magnetically prealigned samples reveal that for fields applied parallel to the (easy) c axis the magnetization saturates below 0.5 T at a magnitude that is in very good agreement with the moments determined from neutron diffraction. For fields applied perpendicular to the c axis, on the other hand, the magnetization data show a two-plateau behavior, explaining the original magnetization data on randomly oriented powders. The strong dependence of the magnetization on the direction of the applied magnetic fields indicates an occurrence of the first-order magnetization process due to the competing magnetocrystalline anisotropies of the Nd and the Co sublattices and of the higher-order terms of the anisotropy energy.

I. INTRODUCTION

Rare-earth (R)-transition-metal (T) intermetallic compounds with the ThMn$_{12}$-type structure (space group $I4/mmm$) belong to the family derived from the RT_5 compounds (CaCu$_5$-type structure, space group $P6/mmm$) by orderly substituting half of the R atoms in RT_5 with the dumbbells of T atoms. Binary RFe$_{12}$, which would be ideal for industrial applications, does not exist for any rare earth and a third element M is required to stabilize the Fe-based ternary intermetallics RFe$_{12-x}$M$_x$ (M=Ti, V, Cr, Mn, Mo, W, Re, Al, Si, etc.).[1–3] The RFe$_{12-x}$M$_x$ intermetallics have thus attracted considerable attention owing to their potential industrial applications as well as to their intriguing magnetic properties. In particular, SmFe$_{11}$Ti and SmFe$_{11}$V were reported to be promising candidates for permanent magnets applications.[4–6] A variety of spin reorientations was observed in RFe$_{12-x}$M$_x$ (Ref. 1) and a first-order magnetization process (FOMP), i.e., a discontinuous increase of magnetization at a critical applied magnetic field, was evidenced on the high-field magnetization curves of single crystals of DyFe$_{11}$Ti.[7] Theoretical calculations predicted that the substitutional disorder in YFe$_{12-x}$Mo$_x$ could lead to canted spin structures at low Mo content and to spin-glass-like behavior at higher Mo content.[8]

Compared to the RFe$_{12-x}$M$_x$ compounds, the Co-based RCo$_{12-x}$M$_x$ compounds have not been investigated in as much detail. As a general rule, the leading crystal field coefficient A_{20} for R has different signs in RCo$_{12-x}$M$_x$ and

RFe$_{12-x}$M$_x$,[9] and so does the second-order anisotropy constant K_1 for 3d atoms on each nonequivalent crystallographic site.[1,10] Since extensive studies of RFe$_{12-x}$M$_x$ demonstrate that the magnetic anisotropy of the Fe sublattice favors the c axis,[7,11] one would anticipate that the Co sublattice in RCo$_{12-x}$M$_x$ should exhibit a planar anisotropy. However, the easy magnetization direction (EMD) of YCo$_{10}$M$_2$ at room temperature is parallel to the tetragonal c axis for M=Mo or Ti, whereas the EMD is within the basal plane for M=Si or V.[12] It is argued that the preferential occupation of M on different 3d sites or the valence-electron concentration and the concomitant 3d-band filling is responsible for the different types of the magnetocrystalline anisotropy of the Co sublattice in RCo$_{12-x}$M$_x$.[13] It is also speculated that the occurrence of opposite contributions for Fe and Co could still be valid for the individual sites whereas the overall balance could lead to the different anisotropies.[14] This speculation implies that the anisotropy constant K_1 has different signs for the Co atoms on different sites, but unlike the Fe atoms in RFe$_{12-x}$M$_x$, for which the relationship $K_1(8i) \gg -K_1(8f) > K_1(8j)$ usually holds,[15] the K_1's of Co atoms on different sites are comparable in magnitude and therefore sensitive to the preferential occupation of M and the changes in electron-concentration and 3d-band filling. The subtle balance and competition of the contributions of Co atoms on different sites to the magnetocrystalline anisotropy was argued to be responsible for the spin reorientation observed in YCo$_{11}$Ti.[14] Considering these characters of the magnetocrystalline anisotropy for the Co sublattice, the mag-

netization process in $RCo_{12-x}M_x$ is expected to be more complicated than that in $RFe_{12-x}M_x$.

A first-order magnetization process (FOMP) has been observed in $NdCo_{10}Mo_2$.[16,17] In our recent investigation of the $NdCo_{12-x}V_x$ compounds, it was observed that the saturation magnetization derived from *M-H* curves (up to 5 T) was very close to that of $YCo_{12-x}V_x$ for $x=2.2-2.6$,[18] where the Y is a nonmagnetic element. Increasing the magnetic fields up to 14 T, however, a discontinuous increase of magnetization occurred at a critical field of about 6 T for $NdCo_{9.5}V_{2.5}$, with the derived saturation magnetization increasing by about 3.1 μ_B/f.u. from the magnetization at 5 T. The increment of magnetization is almost the same as the Nd free-ion moment ($g_J J \mu_B$) and it is intriguing that the Nd ions seem to make no contribution to the magnetization of the compound in the applied fields below 5 T. Further studies showed that substitution of yttrium for Nd reduces this critical field,[19] whereas substitution of Fe for Co initially increases the critical field and then decreases it at higher Fe content.[20]

In order to understand the magnetization process of $NdCo_{12-x}V_x$, we carried out systematic measurements of the magnetization up to 14 T for all the compounds with $2.2 \leq x \leq 2.6$. In addition, neutron powder diffraction experiments were performed on $NdCo_{9.5}V_{2.5}$ to determine its magnetic structure and to clarify the contribution of the Nd ions to the magnetization of the compounds in zero field and in the fields above the critical field. We found that the $NdCo_{12-x}V_x$ crystallizes in the $ThMn_{12}$-type structure and exhibits a first-order magnetization process (FOMP) at a critical field B_C that decreases with the increasing V content. Surprisingly, we find that $NdCo_{9.5}V_{2.5}$ possesses a collinear magnetic structure at 4 K in which both the Nd and the Co atoms have ordered moments that couple ferromagnetically along the *c* axis.

After a brief description of the experimental procedures for sample preparation and neutron diffraction in Sec. II, the results of magnetization measurements and refinements of magnetic structure are presented in Sec. III. Discussions about the observations will be given in Sec. IV, and the main results of this work are summarized in Sec. V.

II. EXPERIMENTAL PROCEDURES

Samples of polycrystalline $NdCo_{12-x}V_x$ ($x=2.2$, 2.3, 2.4, 2.5, and 2.6) were prepared by arc melting the appropriate amounts of the constituent elements (purity of 99.9%) under a high-purity argon atmosphere as described previously.[18] X-ray powder diffraction confirmed that the prepared compounds were single phase, crystallizing in the $ThMn_{12}$-type structure with space group $I4/mmm$ at room temperature. Composition analysis of the alloys by an inductively coupled plasma atomic emission spectroscopy confirms that the composition of the alloys is close to the nominal composition within an accuracy of 1 at. %. Magnetically aligned specimens were prepared by mixing fine powder particles with epoxy resin with a sample to resin weight ratio of 1:1 at room temperature, packing them in a cylinder container and then hardening the mixture in a field of about 1 T, which is parallel to the container axis. Magnetization measurements
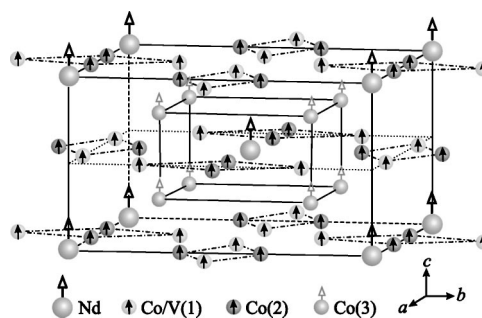

FIG. 1. Structure of $NdCo_{9.5}V_{2.5}$. Arrows indicate the magnetic moments, which couple ferromagnetically below T_C.

were made using a physical property measurement system (PPMS) with applied fields up to 14 T.

Neutron powder diffraction (NPD) experiments for the $NdCo_{9.5}V_{2.5}$ were performed at the NIST Center for Neutron Research (NCNR). NPD data for the refinement of the nuclear structure and the magnetic structure were collected on the high-resolution, 32-counter BT-1 diffractometer. A Cu(311) monochromator was used to produce a monochromatic neutron beam of wavelength 1.5402(1) Å. Collimators with horizontal divergence of 15′, 20′, and 7′ full width at half maximum of arc were used before and after the monochromator and after the sample, respectively. Data were collected in the 2θ range of 3°–168° with a step of 0.05° at room temperature and 4 K with zero applied field, and at 4 K with an applied magnetic field of 4 and 7 T. The structure refinements were carried out using the program GSAS.[21] As the Curie temperature of $NdCo_{9.5}V_{2.5}$ is well below room temperature [$T_C=180$ K (Ref. 18)], the NPD data at room temperature were used to refine the nuclear structure of $NdCo_{9.5}V_{2.5}$ and confirms that it has the $ThMn_{12}$-type structure, as shown in Fig. 1.

The experimental and calculated NPD patterns at room temperature are shown in Fig. 2, and the results of the refinements are given in Table I. We found that the Nd 2*a*, Co 8*j*, and Co 8*f* sites are fully occupied. Recall that the coherent scattering amplitude for V is almost zero for practical purposes, the V atoms are invisible to neutrons and would appear as vacancies on the site. Hence we can conclude that the V atoms exclusively occupy the 8*i* positions in the structure, consistent with the atomic size and enthalpy considerations.[1,2,14] The Co occupancy of the 8*i* site gives a refined composition of $NdCo_{9.55}V_{2.56}$ assuming that the "unoccupied sites" are actually V atoms, which is in good agreement with both the nominal composition and the chemical composition analysis, indicating the actual number of vacancies in the structure is negligible. We also found no evidence of any chemical ordering of the Co and V on the 8*i* site.

III. MAGNETIC PROPERTIES AND MAGNETIC STRUCTURE

A. Magnetization

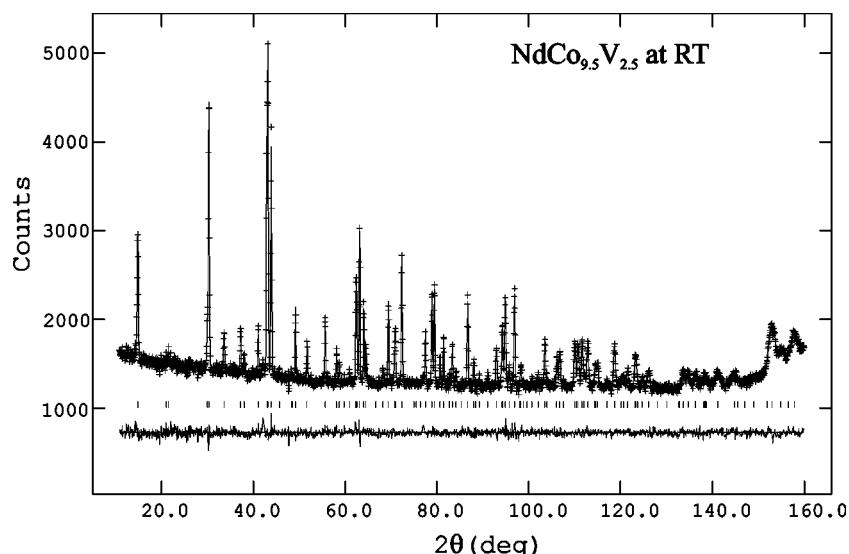The field dependence of magnetization of $NdCo_{12-x}V_x$ ($x=2.2-2.6$) at 5 K in fields up to 14 T is shown in Fig. 3.

FIG. 2. Observed (crosses) and calculated (solid line) NPD intensities of $NdCo_{9.5}V_{2.5}$ at room temperature. The vertical lines indicate the Bragg peak positions. The differences between the observed and calculated intensities are shown at the bottom of the figure.

At low fields ($B<1$ T) the magnetization increases abruptly, which is often observed in "hard" magnetic materials and can be well understood in terms of a pinning mechanism in a narrow domain-wall system.[22] Such a domain wall pinning effect is irreversible as the applied field decreases to zero.[18]

When the applied field is higher than 1.5 T, the magnetization exhibits a plateaulike feature up to 6 T. An abrupt increase of the magnetization is observed for each investigated composition around 6–7 T. The abrupt increase of magnetization exhibited little hysteresis when the applied field was

TABLE I. Crystallographic data and magnetic moments of $NdCo_{9.5}V_{2.5}$ at room temperature, at 4 K, and at 4 K with a field of 7 T, obtained from the refinements of the high-resolution neutron diffraction data. x, y, z are fractional coordinates of the atoms in a unit cell, U_{iso} is the isotropic temperature factor and μ_x, μ_y, μ_z are components of the magnetic moment along the a, b, c directions, respectively. R_p and R_{WP} are residuals of fitting to the pattern and weight pattern, respectively. χ^2 is a "goodness of fit" indicator (Ref. 21).

	Room temperature	4 K	4 K, 7 T
a (Å)	8.4063(2)	8.3850(2)	8.3876(4)
c (Å)	4.7195(1)	4.7104(1)	4.7105(5)
V (Å^3)	333.51(2)	331.18(2)	331.39(6)
Nd ($2a$) (0, 0, 0)			
100U$_{iso}$ (Å^2)	1.16(4)	0.35(4)	0.83(13)
$\mu_z=\mu$ (μ_B)		2.91(8)	2.9(1)
Co/V^a ($8i$) (x,0,0)			
x	0.3666(7)	0.3670(7)	0.368(2)
100U$_{iso}$ (Å^2)	1.35(22)	1.11(13)	2.00^b
$\mu_z=\mu$ (μ_B)		0.37(3)	0.37(4)
Co ($8j$) (x,1/2,0)			
x	0.2762(2)	0.2773(2)	0.2751(5)
100U$_{iso}$ (Å^2)	1.41(5)	1.18(6)	2.00^b
$\mu_z=\mu$ (μ_B)		0.34(4)	0.40(6)
Co ($8f$) (1/4,1/4,1/4)			
100U$_{iso}$ (Å^2)	1.36(4)	1.21(5)	2.00^b
$\mu_x=\mu_y$ (μ_B)		−0.01(2)	0.0
μ_z (μ_B)		0.44(3)	0.50(4)
μ (μ_B)		0.44(3)	0.50(4)
R_p(%)/R_{WP}(%)/χ^2	2.90/2.34/0.804	2.17/2.68/1.107	3.66/4.66/0.966

^{a}The ratio of Co/V on $8i$ site is 0.361(7)/0.639(7) derived from the refinement of room-temperature data and was fixed for the refinement of the 4 K data.
^{b}The temperature factor of the Co atoms was fixed at 0.02 Å^2 for the refinement of the NPD data at 4 K and a field of 7 T.
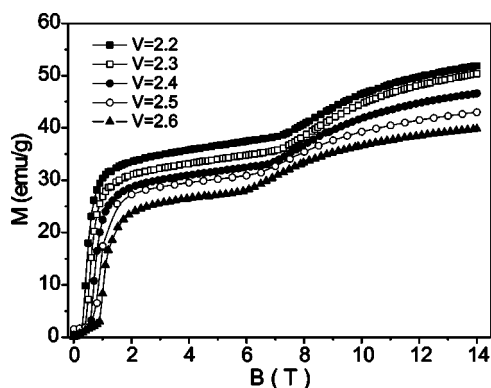
FIG. 3. Magnetization curves of $NdCo_{12-x}V_x$ compounds at 5 K measured on the PPMS.

TABLE II. Some magnetic data derived from the magnetization measurements at 5 K for $NdCo_{12-x}V_x$ on the PPMS magnetometer in the magnetic fields up to 14 T.

x	$M_S(\mu_B/\text{f.u.})$	$M_S'(\mu_B/\text{f.u.})$	$M(5\text{ T})$	$B_C(\text{T})$
2.2	9.3	6.0	5.5	7.18
2.3	9.1	5.7	5.1	7.15
2.4	8.4	5.3	4.8	6.85
2.5	7.6	5.1	4.5	6.46
2.6	7.0	4.5	4.0	5.92

decreased,[18] and disappeared at high temperature.[19] This phenomenon is usually recognized as the first-order magnetization process (FOMP) associated with an irreversible rotation of the magnetization vector between two inequivalent magnetization states with the same free energy.[23] The critical field B_C for the magnetization jump, which is defined as the applied field corresponding to the maximum of the dM/dB versus B curve, decreases with the V content x, ranging from 7.18 T for $x=2.2$ to 5.92 T for $x=2.6$. According to the law of approach to saturation, the saturation moment M_S of the compounds can be derived by extrapolating the high-field part of the M-$1/B$ curve to $1/B=0$. Since a plateau below 5 T is well defined, we can also estimate the "saturation" moment M_S' using the magnetization data below 5 T. The derived M_S' is a little different from the previously derived "saturation" magnetization based on the SQUID measurement up to 5 T. The difference may be attributed to the systematic errors of the different magnetometers (PPMS vs SQUID) as well as to the different orientation distribution of the polycrystalline samples as we will discuss later. The saturation moment M_S derived from the magnetization up to 14 T is 3.0–4.0 μ_B per formula unit ($\mu_B/\text{f.u.}$) larger than $M(5\text{ T})$, the magnetization measured by the PPMS at 5 T, and is 2.5–3.3 $\mu_B/\text{f.u.}$ larger than M_S'. Some specific data

B_C, M_S', $M(5\text{ T})$, and M_S, derived from present magnetization measurements, are given in Table II.

Since the differences between M_S and $M(5\text{ T})$ and between M_S and M_S' happen to be close to the free-ion moment for Nd, the magnetization measurements raise a question regarding the contribution of the Nd sublattice to the magnetization of $NdCo_{12-x}V_x$ compounds below 5 T. In Ref. 18 Liu *et al.* reported that the "saturation" moment of the $NdCo_{12-x}V_x$ derived from the magnetization curve measured by a SQUID magnetometer up to 5 T was very close to that of $YCo_{12-x}V_x$ with the same V content,[24,25] where Y is assumed nonmagnetic. Generally, within the two-sublattice model, the $3d$ and the $4f$ moments couple ferromagnetically in the light lanthanide compounds,[26] thus the saturation moment of $NdCo_{12-x}V_x$ would be expected to be larger than that of $YCo_{12-x}V_x$ by an amount of a Nd free-ion moment ($\sim3.27\ \mu_B$). Based on the available experimental information, Liu *et al.* invoked a local environment effect to explain the observations, i.e., the Nd moment shows an instability below 5 T and has to be induced by a high applied field. To verify this speculation, the magnetic structure of $NdCo_{9.5}V_{2.5}$ was determined by means of neutron powder diffraction.

B. Magnetic structure of $NdCo_{9.5}V_{2.5}$

The neutron diffraction pattern at 4 K exhibits no extra peaks due to a possible magnetic superlattice (Fig. 4). The
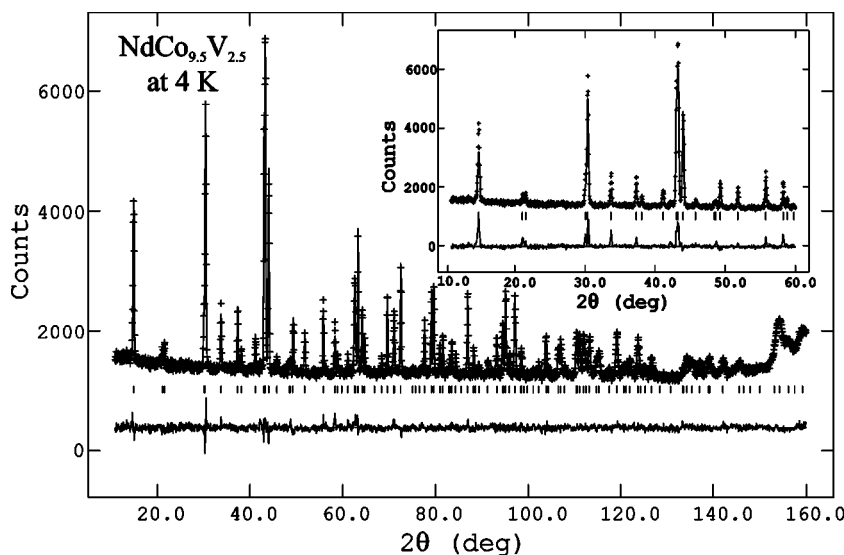

FIG. 4. Observed (crosses) and calculated (solid line) NPD intensities of $NdCo_{9.5}V_{2.5}$ at 4 K. The vertical lines indicate the Bragg peak positions. The difference curve is shown at the bottom of the figure. The inset shows the fit without consideration of the magnetic contribution, where the peaks found on the difference curve reveal that the magnetic intensities superpose on the nuclear peaks.
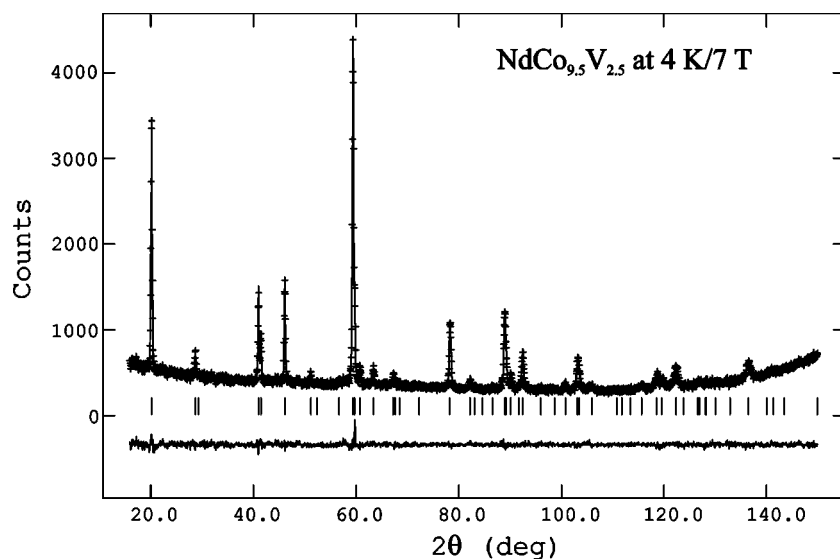
FIG. 5. Observed (crosses) and calculated (solid line) NPD intensities of $NdCo_{9.5}V_{2.5}$ at 4 K under an applied field of 7 T. The vertical lines indicate the Bragg peak positions. The difference curve is shown at the bottom of the figure. Data were collected using the Ge(311) monochromator with wavelength 2.0785 Å.

inset in the Fig. 4 shows the fit without consideration of the magnetic contribution, and the difference curve clearly indicates that the magnetic intensities superpose on the nuclear peaks, suggesting that the system orders ferromagnetically.

The Shubnikov space group $I4/mm'm'$ was used for the magnetic structure refinements. This symmetry allows the moments of Nd on the 2a sites, the Co/V moments on the 8i sites, and the Co moments on the 8j sites to align parallel to the c axis, while the moments on the Co 8f sites may have a c-component as well as components on the basal plane. The refinement results reveal that the components on the basal plane for the Co 8f sites are essentially zero, i.e., all the moments of the atoms in $NdCo_{9.5}V_{2.5}$ couple ferromagnetically along the c axis and the compound exhibits an easy c-axis magnetocrystalline anisotropy, as shown in Fig. 1. Such a magnetic structure model gives a satisfactory fitting to the NPD pattern (Fig. 4). The refined structural parameters and atomic moments of $NdCo_{9.5}V_{2.5}$ at 4 K are listed in Table I.

The calculated magnetic moment of $NdCo_{9.5}V_{2.5}$ is 7.51 μ_B/f.u., which is very close to the saturation moment derived from the magnetization measurement up to 14 T (M_S=7.58 μ_B/f.u.). In particular, the refinement of the zero-field magnetic structure reveals that the Nd moments in the compound do order and couple ferromagnetically with the Co moments, in contrast to the speculation of Liu *et al.*[18] The refined moment of the Nd atom is 2.91 μ_B, which is close to its free-ion value ($\sim$3.27 μ_B). Assuming that the V atoms have no moment, the moment of Co on the 8i sites is 1.03 μ_B, and the site dependence of the Co moments on the 8i, 8j, and 8f sites would then follow the general trend observed for $RCo_{12-x}M_x$ compounds.[1,14]

Neutron diffraction was also performed on the free powder sample of $NdCo_{9.5}V_{2.5}$ at 4 K under magnetic fields of 4 and 7 T, applied perpendicular to the scattering plane. The neutron wavelength employed for these measurements was 2.0785 Å. The NPD patterns collected at 4 and 7 T showed no significant difference, and therefore the data at 7 T, which were collected with better statistics, were used for the refinement. Compared to the NPD pattern of zero field, there were

no new peaks appearing under the applied field. However, we found a strong preference for the particles to align with their c axis parallel to the field direction, indicative of a large Ising-like magnetic anisotropy. Taking into account the large preferred orientation induced by the field, we found that the same zero-field collinear magnetic structure model, with the moments of all atoms coupled ferromagnetically along the c axis, fits the data well. In this refinement we fixed the (isotropic) temperature factors for the Co atoms at a reasonable value (U_{iso}=0.02 Å^2) in the final refinement due to the strong correlation found in this case between the magnetic moments and temperature factors of the Co atoms. Under this constrain for the isotropic temperature factor, the refined moments for the Nd and the Co atoms are essentially the same as in the zero-field structure. The resulting saturation moment was determined to be 7.98 μ_B/f.u. The refinement results are shown in Fig. 5 and listed in Table I.

C. Magnetization of the magnetically prealigned sample

Figure 6 shows the magnetization curves of the magnetically prealigned powder sample and the bulk sample of $NdCo_{9.8}V_{2.2}$ at 5 K. The preferred orientation of the aligned sample was confirmed by XRD as illustrated in the inset. The magnetization ($M\parallel$) with the applied field parallel to the easy magnetization direction (EMD) saturates very quickly without any anomaly up to 14 T. The saturation magnetization is in very good agreement with the moments determined from neutrons diffraction. This feature coincides with the neutron diffraction in 7 T of the free powder sample of $NdCo_{9.5}V_{2.5}$, the EMD of which is forced along the field direction. In contrast, the magnetization ($M\perp$) with the applied field perpendicular to the EMD is less than half of the $M\parallel$ below $\sim$6 T, and shows a larger increase of magnetization in comparison to the bulk sample. It is therefore clear that the jump in the magnetization is associated with a change in spin reorientation when the field is applied on the a-b plane. For bulk sample only those crystallites with their c axis deviating from the direction of the applied field contribute to the magnetization jump. The crossover from $M\perp < M_B$ to
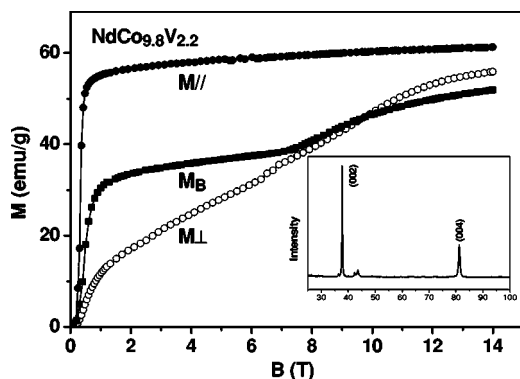
FIG. 6. Magnetization curves at 5 K for the randomly oriented (bulk) sample (M_B), and for the magnetically prealigned $NdCo_{9.8}V_{2.2}$ sample with the field aligned along the c axis [the easy magnetization direction (EMD)] and perpendicular to the c axis. The inset shows the XRD pattern of the prealigned sample, indicating the EMD along the c axis at room temperature.

$M\perp > M_B$ manifests a larger change in magnetization of the prealigned sample than that of the bulk sample, which is indicative of a relatively larger population of the crystallites aligned along the c axis in the former. The wide transition range in the applied field for $M\perp$ can be attributed to an incomplete alignment due to the close proximity of the Curie temperature of $NdCo_{9.8}V_{2.2}$ [$T_C = 309$ K (Ref. 18)] to room temperature. Thus the M_S of $NdCo_{12-x}V_x$ derived from the magnetization of the bulk sample up to 5 T is close to that of $YCo_{12-x}V_x$ exclusively by accident. Note that for the case of $M\|$ the field direction is unique in the crystal, while in the case of $M\perp$ the field makes all angles with respective to a or b axis, so it is difficult to speculate the detailed changes that are occurring in the magnetic structure.

IV. DISCUSSIONS

A first-order magnetization process (FOMP) is an interesting phenomenon exhibited by many magnetic materials. The nature of the phenomenon is similar to that of the spin-reorientation with changing temperature. One origin of the FOMP is that two relative minima appear in the total energy as a function of the angle between a particular crystallographic direction and the magnetization vector. As the applied field increases, the two energy minima compete with each other and a sudden rotation of the magnetization vector occurs when the two energies cross. A FOMP is distinguished from other temperature- or field-driven magnetic phase transitions in character:[23,27] (1) the critical field B_C and the magnitude of the magnetization jump strongly depend on the direction of the applied field as shown in Fig. 6. The magnetization jump is most distinct when the magnetic field is perpendicular to the EMD and quickly smears when the applied field deviates slightly from direction perpendicular to the EMD. But the critical field B_C increases with the slight deviation of the direction of the applied field,[27] whereas no anomaly on magnetization curve occurs when the magnetic fields are applied along the EMD. (2) A hysteresis in FOMP is hard to be observed except perhaps at very low tempera-

tures, which is probably due to the very low coercivity inherent in this type of magnetization process because the transition actually occurs through domain wall nucleation and displacement. The FOMP phenomenon has been observed in many rare earth transition metal compounds, e.g., $Nd_2Fe_{14}B$, $Nd_2Co_{14}B$, R_2Fe_{17}, $RFe_{11}Ti$, RMn_6Sn_6, and $Sm_{1-x}Nd_xCo_5$.[7,23,27] However, the observed FOMP usually takes place gradually, even in single crystals.[7] For transition-metal-rich compounds, the wide plateau on the magnetization curve below the critical field B_C of the FOMP, as observed in $NdCo_{10}Mo_2$ (Refs. 16 and 17) and $NdCo_{12-x}V_x$, is uncommon, which sometimes can mislead one to conclude that the magnetization is approaching saturation. Measurements of magnetization on a magnetically aligned powder sample are helpful to unravel this ambiguity.

Asti and Bolzoni developed a phenomenological theory to deal with the FOMP by considering the competition of magnetic anisotropy constants K_n up to sixth order,[23] which can give rise to two minima of the anisotropy energy as a function of θ, the angle between the magnetization vector and a specific crystallographic symmetry axis (the c axis for the tetragonal lattice).[27] When an external field is applied perpendicular to the EMD, the two minima of the total energy compete with each other according to the temperature and the strength of the applied field and a FOMP takes place when the two minima of the total energy have the same value at a critical field.

Studies on $Nd_{1-x}Y_xCo_{9.5}V_{2.5}$ compounds showed that the critical field B_C decreases rapidly with the Y content,[19] and no FOMP was observed in $YCo_{12-x}V_x$ compounds.[19,25] Therefore, the occurrence of the FOMP in $NdCo_{12-x}V_x$ should be attributed to the presence of Nd atoms. $NdCo_{12-x}V_x$ exhibits an easy c axis magnetocrystalline anisotropy[18] while the $YCo_{12-x}V_x$ is of easy-plane anisotropy.[24] Within the two-sublattice model, the Nd sublattice favors an easy-axis anisotropy and the Co sublattice favors an easy-plane anisotropy, thus the anisotropy of the Nd-sublattice dominates in the $NdCo_{12-x}V_x$ compounds. Neutron diffraction reveals that in zero field the moment of the Nd sublattice couples ferromagnetically with that of the Co sublattice along the c axis. Intuitively, when an external field is applied perpendicular to the c axis, the anisotropy of the Nd sublattice resists the alignment of the moments along the direction of the applied field, whereas the anisotropy of the Co sublattice favors such an alignment of the moment. Therefore, at low fields applied perpendicular to the c axis, the Nd moments prefer to stay along the c axis while the Co moments will tend to realign in the a-b plane, leading to a tilting off the c axis of the magnetization vector corresponding to one of the two minima of the total energy. As the applied field increases, the energy gain from the Zeeman interaction will overcome the easy-c anisotropy of the Nd sublattice and the Nd moments will be pulled into the a-b plane, leading to the occurrence of the FOMP from the low magnetization state to the high magnetization state and producing a two-step behavior on the magnetization curve.

V. SUMMARY

$NdCo_{12-x}V_x$ compounds crystallize in the $TnMn_{12}$-type structure for $2.2 \leq x \leq 2.6$. Magnetization at 5 K measured in

magnetic fields up to 14 T reveals a FOMP phenomenon for all the investigated compounds at a critical field B_C of 6–7 T. The critical field for the FOMP decreases with the V content. Neutron powder diffraction and magnetic structure refinements indicate that $NdCo_{9.5}V_{2.5}$ possesses a collinear magnetic structure at 4 K and zero field, in which the moments of the Nd atoms and the Co atoms couple ferromagnetically along the c axis. When neutron diffraction on free powdered $NdCo_{9.5}V_{2.5}$ was performed under a magnetic field of 4 or 7 T at 4 K, a strong preferential orientation of the particles along the c axis was observed. The same ferromagnetic structure model as that at zero field fits the NPD data at 7 T satisfactorily. The magnetization calculated from the magnetic structure refinement results agrees well with that derived from magnetization up to 14 T. The peculiar magnetization process of $NdCo_{12-x}V_x$ is argued to be associated with the competing magnetocrystalline anisotropies of the Nd sublattice and the Co sublattice and with the contribution of the higher-order terms of the anisotropy energy. The present investigation indicates that the M_S of $NdCo_{12-x}V_x$ derived from the magnetization of the bulk sample up 5 T is close to that of $YCo_{12-x}V_x$ exclusively by a coincidence and the Nd moments do order and couple with the Co moments ferromagnetically below T_C in zero field, ruling out the local environment effect proposed in Ref. 18.

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