Crystal and magnetic structures of Laves phase compound NdCo$_2$ in the temperature range between 9 and 300 K

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Abstract

The crystal and magnetic structures of the Laves phase compound NdCo$_2$ in the temperature range from 9 to 300 K are determined by Rietveld refinement technique, using high-resolution neutron powder diffraction data. The compound crystallizes in space group $Fd\bar{3}m$ above the magnetic ordering temperature T_C ($\approx$100 K), in space group $I4_1/amd$ below T_C and in space group $Imma$ below the tetragonal–orthorhombic structural/magnetic transitions at $T_M \approx 42$ K. The assignment of the space groups to the crystal structures of NdCo$_2$ in different temperature ranges complies with the reported Mössbauer studies. Detailed information of the crystal and magnetic structures of NdCo$_2$ at different temperatures are reported.
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Keywords: Crystal and magnetic structures; Neutron powder diffraction; Rietveld refinement; Laves phase NdCo$_2$

1. Introduction

For more than 20 years, rare earth (R) Laves phases RCo$_2$ have been an interesting subject in condensed matter physics and in the study of band metamagnetism, owing to their simple magnetic and crystallographic structures for testifying different physical models [1]. RCo$_2$ crystallizes in the MgCu$_2$-type structure (Laves C15 phase, space group $Fd\bar{3}m$), and the *3d*-subsystem exhibits a magnetic instability. Magnetic state of the *3d*-subsystem can be stabilized by applying a magnetic field higher than about 70 T or by the molecular field arising from the magnetic R-subsystem [1–5]. Accompanying the magnetic ordering of the *3d*-subsystem, large magnetovolume effect and anisotropic magnetostriction occur, giving rise to various lattice distortions of the cubic Laves phase structure. The character of the unit cell distortion is determined by the orientation of the easy magnetization direction (EMD) of the compounds for binary RCo$_2$ [6]. A close correlation between the EMD and the symmetry of the distorted Laves phase was observed, i.e. a

rhombohedral distortion corresponds to the EMD of [1 1 1] of the pseudo-cubic structure, a tetragonal distortion to the EMD of [1 0 0] and an orthorhombic distortion to the EMD of [1 1 0]. Among the RCo$_2$ compounds, NdCo$_2$ and HoCo$_2$ unusually exhibit another structural transition at low temperature, in addition to the one taking place at T_C [6,7].

Magnetization measurements, X-ray diffraction and neutron diffraction revealed that NdCo$_2$ undergoes a second-order transition from the cubic to a tetragonal structure at T_C ($\approx$100 K) and a first-order transition from the tetragonal to an orthorhombic structure at $T_M \approx 42$ K [6–9]. Refinements of magnetic structure showed that the Nd moment distinctly exhibits an abrupt increase at the first-order transition and the easy magnetization direction of the compound changes from [0 0 1] in the tetragonal lattice to [0 1 1] in the orthorhombic lattice (the directions are referred to the pseudo-cubic lattice), indicating a strong coupling between crystal structure and magnetic properties at zero field [9]. However, the space group $Fddd$ was assigned to the crystal structure of the orthorhombic NdCo$_2$ [9], which is inconsistent with the Mössbauer studies. Extensive Mössbauer studies on the rare earth-transition metal cubic Laves phase compounds indicated that there are two magnetically inequivalent transition metal sites with a relative population ratio of 3:1 for the

rhombohedrally distorted lattice, two sites with a ratio of 1:1 for the orthorhombically distorted lattice, and only one site for the tetragonally distorted lattice [10,11]. While the space groups $R\bar{3}m$ and $I4_1/amd$ describe well the symmetries of the rhombohedrally distorted lattice and the tetragonally distorted lattice, respectively, [9,12] and agree with the Mössbauer studies, the orthorhombically distorted $NdCo_2$ in term of the space group $Fddd$ has only one site for Co (16d) (Ref. [9]). Therefore, it is necessary to re-examine the space group of the orthorhombic $NdCo_2$ at low temperature.

In this work, we performed Rietveld refinements of the crystal and magnetic structures of $NdCo_2$ from 9 to 300 K. The space group $Imma$, which is a sub-group of $I4_1/amd$ and provides two inequivalent crystallographic sites for Co with a relative population ratio of 1:1, is adopted for the orthorhombic $NdCo_2$ below $T_M = 42$ K. Isotropic temperature factor of Nd is derived from the refinements for the whole temperature range investigated under the assumption that the temperature factor of Co below T_C is fixed to the value extrapolated from those above T_C. Detailed information of crystal and magnetic structures of $NdCo_2$ from 9 to 300 K are presented, which are the basic data for understanding the physics of the Laves phase RCo_2 compounds and for further theoretical studies.

2. Experimental

A polycrystalline sample of $NdCo_2$ was prepared by arc melting the constituent elements with a purity of 99.9% in an atmosphere of high-purity argon as described in Ref. [9]. All the neutron powder diffraction (NPD) experiments were performed at the NIST Center for Neutron Research (NCNR). NPD data for refinement of the crystal and the magnetic structures were collected on the high-resolution, 32-counter BT-1 diffractometer. A Cu (3 1 1) monochromator was used to produce a monochromatic neutron beam of wavelength 1.5402(1) Å. Collimators with horizontal divergence of 15, 20, and 7 min of arc were used before and after the monochromator and after the sample, respectively. Data were collected in the 2θ range of 10–160° with a step of 0.05°. The program Fullprof [13] was used for the Rietveld refinement of the crystal and the magnetic structures of the compound, using the following values of the scattering amplitudes: $b(Nd) = 0.769$ and $b(Co) = 0.249$ ($\times 10^{-12}$ cm).

3. Results

The NPD experiments [9] show that $NdCo_2$ crystallizes in the cubic Laves phase C15 structure at room temperature, undergoes a tetragonal distortion around $T_C \approx 100$ K and an orthorhombic distortion at $T_M \approx 42$ K, in consistent with the X-ray powder diffraction results [6]. Representative NPD patterns of $NdCo_2$ in different temperature ranges are shown in Fig. 1. All patterns exhibit a few weak peaks arising from impurity, and the strongest impurity peaks occur at $2\theta \approx 30.7°$ and $37.4°$. The impurity phase is most probably the Nd_4Co_3 reported by Singh and Raman [14]. Isostructural phase Pr_4Co_3 was also reported by Wu et al. [15] and Du et al. [16]. Since the amount of impurity phase is small and the crystallographic data of Nd_4Co_3 is incomplete, the impurity phase is not included in the following refinements.

For the cubic Laves phase structure at $T > T_C$, the space group is $Fd\bar{3}m$. The Nd atoms occupy the 8a sites (1/8, 1/8, 1/8) and the Co atoms occupy the 16d sites (1/2, 1/2, 1/2). The
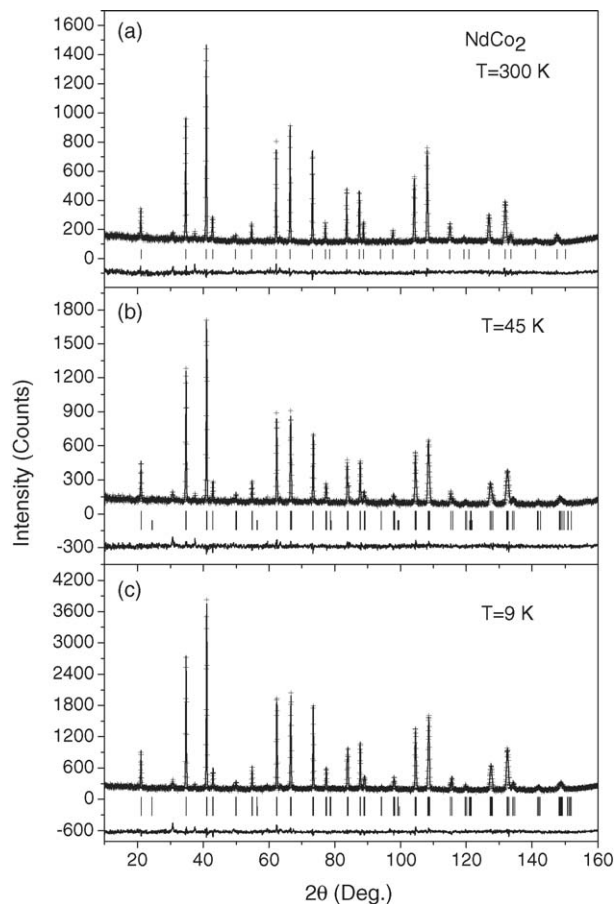

Fig. 1. Calculated and experimental NPD patterns at (a) 300 K, (b) 45 K and (c) 9 K. The crosses are experimental data, and the solid lines are the calculated patterns. At the bottom is shown the difference between the experimental and calculated intensities. The vertical bars indicate the expected Bragg reflection positions for nuclear structure (upper row) and magnetic structure (lower row).

Rietveld refinements converge satisfactorily with well-defined temperature factors for Nd and Co atoms. The refinements results are listed in Table 1. The comparison between the calculated and experimental NPD patterns at 300 K is shown in Fig. 1(a).

For the tetragonal $NdCo_2$ in the temperature range 42 K $< T < T_C$, the space group is $I4_1/amd$ as reported in Ref. [9]. The Nd atoms locate on the 4b sites (0, 1/4, 3/8), and Co atoms on the 8c sites (0, 0, 0). Since the temperature factor B and magnetic moment are strongly correlated and the Co moment is smaller than that of Nd, the B_{Co} below T_C is fixed to the value extrapolated from those in cubic structure in the temperature range 100 K $\leq T \leq 300$ K. Then the B_{Nd} can be derived from the refinements and shows an almost linear variation with temperature in the whole temperature range investigated as illustrated in Fig. 2. The same approach of manipulating the temperature factors was used for $TbCo_2$ [12]. Based on the extensive studies on RCo_2 compounds, a collinear magnetic structure with the moments of all atoms aligning along the c direction, which corresponds to the [0 0 1] direction of the cubic lattice, is assumed for the tetragonal $NdCo_2$. The refinement results of the crystal and magnetic structures are listed in Table 2. The comparison

Table 1
Rietveld refinement results of the crystal structure of cubic NdCo$_2$

T (K)	100	105	110	120	150	200	300
a (Å)	7.2827(2)	7.2831(2)	7.2832(2)	7.2837(2)	7.2863(2)	7.2915(2)	7.3049(1)
V (Å^3)	386.27(2)	386.31(2)	386.33(1)	386.41(2)	386.83(2)	387.65(2)	389.80(1)
Nd at 8a (1/8, 1/8, 1/8)							
$\quad B$ (Å^2)	0.28(3)	0.27(3)	0.30(3)	0.30(3)	0.41(3)	0.55(3)	0.66(2)
Co at 16d (1/2, 1/2, 1/2)							
$\quad B$ (Å^2)	0.35(5)	0.43(5)	0.36(8)	0.41(5)	0.37(5)	0.48(5)	0.65(3)
R_p (%)	6.91	7.09	5.88	7.02	6.80	6.82	4.37
R_{wp} (%)	8.93	9.19	7.61	9.15	8.65	8.76	5.34
χ^2	1.01	0.993	1.07	0.967	0.972	1.01	1.20

Space group: $Fd\bar{3}m$, $Z = 8$.

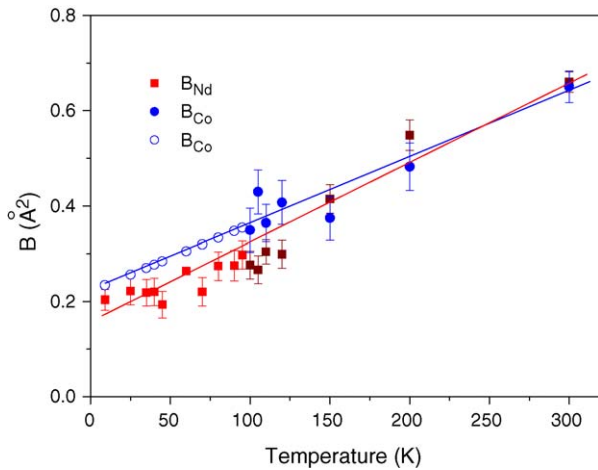Fig. 2. Temperature dependence of temperature factors of Nd and Co. B_{Co} for $T < 100$ K is fixed to the value extrapolated from those for $T > 100$ K (see text).

between the calculated and experimental NPD patterns at 45 K is shown in Fig. 1(b).

Taking into consideration of the Mössbauer studies, the space group *Imma* is assigned to the orthorhombic NdCo$_2$ in the temperature range $T < T_M$ (≈ 42 K), which is different from the previous report [9]. The space group *Imma* is one of the sub-groups of $I4_1/amd$. The 8c sites in $I4_1/amd$ are split into two inequivalent

sites 4a and 4d, in consistent with the Mössbauer studies. The Nd atoms occupy the 4e sites (0, 1/4, z), the Co atoms occupy the 4a sites (0, 0, 0) and the 4d sites (1/4, 1/4, 3/4). The B_{Co} is fixed to the value extrapolated from those in cubic structure and the B_{Nd} is then derived from the Rietveld refinements. A collinear magnetic structure is assumed and the models with the moments of Nd and Co along the *a*- or *b*-direction of the orthorhombic lattice are tested. Only the model with the moments along the *b*-direction ($M_a = M_c = 0$) reaches stable results for all NPD data at $T < T_M$. Therefore, the final magnetic structure model corresponds to the EMD along the [1 1 0] direction of the cubic lattice as expected. The refinement results of the crystal and magnetic structures are listed in Table 3. The comparison between the calculated and experimental NPD patterns at 9 K is shown in Fig. 1(c).

The refinement results listed in Table 3 indicate that the Nd at 4e position in *Imma* shifts little from its ideal position in $I4_1/amd$ ($z = 0.375$), while the atomic coordinates of Co are the same as in $I4_1/amd$. For the *Fddd* assignment, the atomic coordinates of both Nd and Co are in fact the same as in $I4_1/amd$ [9]. Therefore, it is difficult to distinguish the space groups *Imma* and *Fddd* for the orthorhombic NdCo$_2$ by diffraction technique. Thanks to the high-energy resolution of Mössbauer spectroscopy, the two inequivalent Co positions in orthorhombic RCo$_2$ are well resolved in extensive Mössbauer studies [10,11].

Table 2
Rietveld refinement results of the crystal and magnetic structures of tetragonal NdCo$_2$

T (K)	45	60	70	80	90	95
a (Å)	5.1578(2)	5.1564(2)	5.1557(2)	5.1545(2)	5.1534(3)	5.1507(2)
c (Å)	7.2683(3)	7.2705(3)	7.2742(4)	7.2763(5)	7.2778(7)	7.2822(6)
V (Å^3)	193.36(1)	193.32(1)	193.36(1)	193.32(2)	193.27(2)	193.19(2)
Nd at 4b (0, 1/4, 3/8)						
$\quad B$ (Å^2)	0.19(3)	0.264(6)	0.22(3)	0.27(3)	0.28(3)	0.30(3)
$\quad M_a = M_b$ (μ_B)	0	0	0	0	0	0
$\quad M_c$ (μ_B)	2.40(9)	2.20(8)	2.13(9)	1.95(10)	1.54(13)	1.33(13)
Co at 8c (0, 0, 0)						
$\quad B$ (Å^2)	0.284	0.305	0.319	0.333	0.347	0.354
$\quad M_a = M_b$ (μ_B)	0	0	0	0	0	0
$\quad M_c$ (μ_B)	0.57(6)	0.56(5)	0.61(7)	0.51(7)	0.33(9)	0.35(9)
R_p (%)	6.79	6.89	7.04	6.88	7.46	6.29
R_{wp} (%)	8.87	8.96	9.21	9.08	9.75	8.10
χ^2	0.956	0.954	0.991	0.952	1.06	0.905

Space group: $I4_1/amd$, $Z = 4$. The B_{Co} is fixed to the value extrapolated from those of the cubic structure.

Table 3
Rietveld refinement results of the crystal and magnetic structures of orthorhombic $NdCo_2$

T (K)	9	25	35	40
a (Å)	5.1512(2)	5.1506(5)	5.1500(6)	5.1507(5)
b (Å)	5.1431(2)	5.1446(6)	5.1449(7)	5.1450(6)
c (Å)	7.2973(2)	7.2970(4)	7.2965(4)	7.2960(4)
V (Å^3)	193.33(1)	193.35(3)	193.33(3)	193.35(3)
Nd at 4e (0, 1/4, z), $M_a = M_c = 0$				
z	0.3744(3)	0.3740(5)	0.3742(6)	0.3747(6)
B (Å^2)	0.20(2)	0.22(3)	0.22(3)	0.22(3)
M_b (μ_B)	2.38(7)	2.45(9)	2.62(8)	2.45(9)
Co1 at 4a (0, 0, 0), $M_a = M_c = 0$				
B (Å^2)	0.234	0.256	0.270	0.277
M_b (μ_B)	0.65(6)	0.72(8)	0.86(8)	0.76(8)
Co2 at 4d (1/4, 1/4, 3/4), $M_a = M_c = 0$				
B (Å^2)	0.234	0.256	0.270	0.277
M_b (μ_B)	0.63(10)	0.69(13)	0.82(12)	0.68(13)
R_p (%)	5.25	7.04	6.65	6.77
R_{wp} (%)	7.07	9.27	8.79	8.91
χ^2	1.22	0.994	0.931	0.985

Space group: *Imma*, $Z = 4$. The B_{Co} is fixed to the value extrapolated from those of the cubic structure.

4. Discussion

Fig. 3 shows the temperature dependence of lattice parameters of $NdCo_2$, which is in good agreement with those, including the setting of the orthorhombic unit cell, derived from XRD reported by Gratz et al. [6]. Substantial lattice distortion is exhibited below T_C and discontinuous changes of lattice parameters occur around $T_M \approx 42$ K, indicative of the first-order magnetic/structural transitions. At T_C, the compound shows a large magnetovolume effect, but the change in unit cell volume is very small at T_M as shown in the inset of Fig. 3.

For the magnetic structures below T_C, the refinement results show that the moments of Nd couple ferromagnetically with the moments of Co, following the general rule of the magnetic coupling between light rare earth sublattice and transition metal sublattice [17]. Below 0.8 T_C (≈ 80 K), the derived Nd moment falls in the range of 1.95–2.62μ_B. The theoretical value of a free
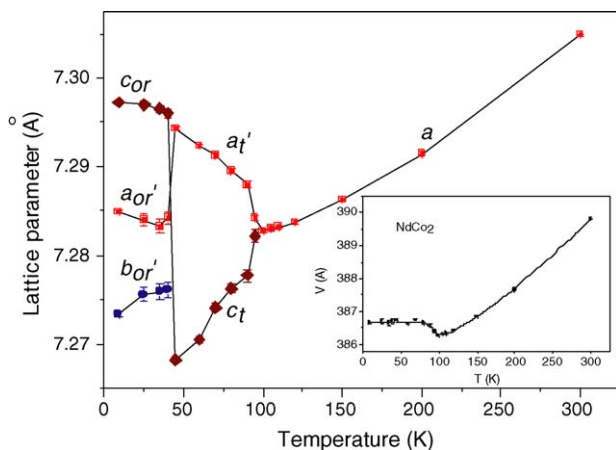

Fig. 3. Temperature dependence of lattice parameters of $NdCo_2$. $a_t' = \sqrt{2}a_t$, $a_{or}' = \sqrt{2}a_{or}$, and $b_{or}' = \sqrt{2}b_{or}$. The inset shows the variation of unit cell volume (the volume is doubled for tetragonal and orthorhombic structures).
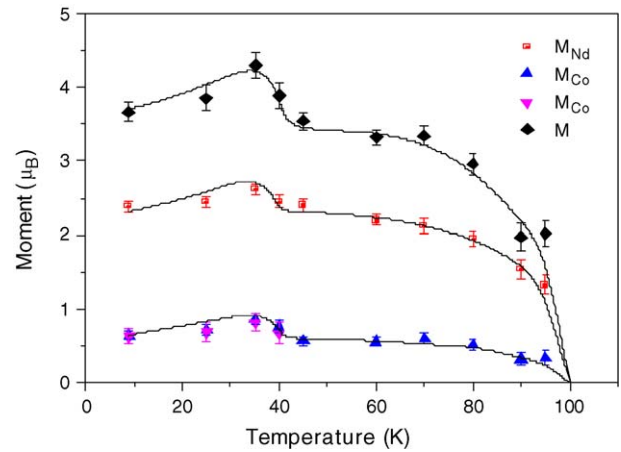

Fig. 4. Temperature dependence of atomic moments (M_{Nd} and M_{Co}) and the total moment (M in μ_B/f.u.). The solid lines are guides to the eye.

trivalent Nd ion is 3.27μ_B (=$g_J J \mu_B$), but it is well known the crystalline-electric-field (CEF) effects can reduce the moment of rare earth metal in intermetallic compounds. For $NdCo_2$, the CEF effects can produce a quenched Nd^{3+} moment as low as 1.8μ_B [11]. The moment of Co derived from Rietveld refinements is in the range of 0.51–0.86μ_B, in consistent with the typical value of the Co moment in Laves phase RCo_2. Extensive studies on RCo_2 compounds show that the average Co moment in the metamagnetic Co-sublattice falls in the range of 0.45–1.1μ_B/Co [6].

Fig. 4 shows the temperature dependence of Nd moment (M_{Nd}), Co moment (M_{Co}) and the total moment of the $NdCo_2$ ($M = M_{Nd} + 2M_{Co}$ in μ_B/f.u.). All the three quantities (M_{Nd}, M_{Co} and M) exhibit distinct jumps around T_M, which is in consistent with the magnetization measurement [8] and with the variation of the NPD counts of the (1 1 1) peak [9] and suggests a magnetic transition involving the changes in both magnitude and direction of the moments. In addition, the EMD is always along the shortest axis, i.e. the c-direction in the tetragonal structure and the b-direction in the orthorhombic structure. In the orthorhombic structure, the Co moments in two crystallographically inequivalent sites are almost the same, in analogy to the case of the rhombohedral $TbCo_2$ [12]. The slight decrease of the moments below T_M shown in Fig. 4 might be an artefact due to possible correlation between the refined moment and the isotropic temperature factor.

5. Summary

The Laves phase compound $NdCo_2$ exhibits two magnetic/structural transitions: one occurs at $T_C \approx 100$ K and is accompanied by a tetragonal lattice distortion, the other happens at $T_M \approx 42$ K and is accompanied by an orthorhombic lattice distortion. The space groups $Fd\bar{3}m$, $I4_1/amd$ and *Imma* are assigned to the crystal structures of cubic, tetragonal and orthorhombic $NdCo_2$, respectively, to comply with the reported Mössbauer studies. The crystal and magnetic structures of the $NdCo_2$ are refined based on high-resolution neutron powder diffraction data in the temperature range between 9 and 300 K. The Nd moments

and Co moments couple ferromagnetically and form a collinear magnetic structure with the easy magnetization direction along the [0 0 1] direction of the cubic lattice in the temperature range of $T_M < T < T_C$ and along the [1 1 0] direction for $T < T_M$. The derived atomic moments and the total moment of the compound exhibit a distinct jump around T_M. Detailed information of crystal and magnetic structures, including space group, lattice parameters, atomic parameters, isotropic temperature factors and atomic moments, of $NdCo_2$ at different temperatures are presented.

Acknowledgements

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