Neutron diffraction study on composite compound Nd_2Co_7*

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The crystallographic and the magnetic structures of the composite compound Nd_2Co_7 at 300 K are investigated by a combined refinement of X-ray diffraction data and high-resolution neutron diffraction data. The compound crystallizes into a hexagonal Ce_2Ni_7-type structure and consists of alternately stacking $MgZn_2$-type $NdCo_2$ and $CaCu_5$-type $NdCo_5$ structural blocks along the c axis. A magnetic structure model with the moments of all atoms aligning along the c axis provides a satisfactory fitting to the neutron diffraction data and coincides with the easy magnetization direction revealed by the X-ray diffraction experiments on magnetically pre-aligned fine particles. The refinement results show that the derived atomic moments of the Co atoms vary in a range of 0.7 μ_B–1.1 μ_B and the atomic moment of Nd in the $NdCo_5$ slab is close to the theoretical moment of a free trivalent Nd^{3+} ion, whereas the atomic moment of Nd in the $NdCo_2$ slab is much smaller than the theoretical value for a free Nd^{3+} ion. The remarkable difference in the atomic moment of Nd atoms between different structural slabs at room temperature is explained in terms of the magnetic characteristics of the $NdCo_2$ and $NdCo_5$ compounds and the local chemical environments of the Nd atoms in different structural slabs of the Nd_2Co_7 compound.

Keywords: Nd_2Co_7, neutron powder diffraction, magnetic structure, crystal structure

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1. Introduction

A composite compound consisting of two or more different structural blocks may exhibit unique properties or multi-functionality. Composite materials with special structures can be fabricated by many technologies such as molecular beam epitaxy, mechanical alloying and high pressure synthesizing, yet there are a number of natural compounds possessing composite structures such as the rare earth cobalt compound Nd_2Co_7. With the hexagonal Ce_2Ni_7-type structure, Nd_2Co_7 belongs to the structural series of $R_{m+n}T_{5m+2n}$ (R=rare earth atoms, T=transition metal atoms), which is composed of m layers of the C14 Laves-phase RT_2 slabs and n layers of the $CaCu_5$-type RT_5 slabs alternately stacked along the c direction.[1]

Extensive investigations have been performed on the C15 Laves phase intermetallic RCo_2 as a magneticaloric material below room temperature[2–5] and on the $CaCu_5$-type R–T compound as a hydrogen storage material in nickel–metal hydride battery or as a hard magnetic material with high Curie temperature and high saturation magnetization. Both the binary compounds $NdCo_2$ ($MgCu_2$-type) and $NdCo_5$ ($CaCu_5$-type) are stable in the Nd–Co system. The $NdCo_2$ compound exhibits a transition from second-order paramagnetism (PM) to ferromagnetism (FM) at a Curie temperature of $T_C = 100$ K and a coupled first-order magnetic-structural transition at about 42 K accompanied by an abrupt change of the Nd moment and a change of the easy magnetization direction.[6] The $NdCo_5$ compound experienced a PM–FM transition at $T_C \approx 910$ K and two spin-reorientation transitions (SRTs) below T_C.[7,8] As the temperature increased, a transition from an easy-plane to an easy-cone magnetocrystalline anisotropy occurred at $T_{SR1} = 250$ K and a transition from the easy-cone to

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the easy-c axis anisotropy took place at $T_{SR2} = 290$ K. The crystal structure of Nd_2Co_7 can be viewed as a composite structure consisting of alternately stacking $NdCo_2$ slabs with the $MgZn_2$-type structure and $NdCo_5$ slabs with the $CaCu_5$-type structure in 2:2 ratio along the c axis by sharing the Kagomé lattice composed of Co atoms. The Kagomé lattice is formed by the atoms on the 6h sites in the $MgZn_2$-type structure and by the atoms on the 3g sites in the $CaCu_5$-type structure. The magnetization behaviour of Nd_2Co_7 is similar to that of $NdCo_5$. Nd_2Co_7 showed a PM–FM transition with the T_C around 600 K, and it also experienced two SRTs at $T_{SR1} = 218$ K and $T_{SR2} = 261$ K, respectively.[9,10] Above $T_{SR2} = 261$ K, Nd_2Co_7 exhibited the easy-c axis magnetocrystalline anisotropy. It seems that the intervening $NdCo_2$ slab between the $NdCo_5$ slabs destabilizes the easy-plane anisotropy and enhances the easy c-axis anisotropy. It is of interest to look into the interplay of the $NdCo_2$ slabs and $NdCo_5$ slabs and the Nd–Co and Co–Co interactions in the composite compound Nd_2Co_7.

In the present work, multi-pattern refinement with neutron diffraction (NPD) data and X-ray diffraction (XRD) data was used to investigate the crystallographic and the magnetic structures of Nd_2Co_7. The preparation of the sample and powder diffraction experiments are described briefly in Section 2. The results and the discussion on magnetic structure and atomic moments are presented in Section 3, and a summary of the work is given in Section 4.

2. Experimental details

Polycrystalline Nd_2Co_7 alloy was prepared by arc-melting Nd (+99.9% purity) and Co (+99.98% purity) metals, followed by annealing at 1353 K in high-purity argon atmosphere for one week. The loss of weight of the alloy during melting and annealing was less than 0.3 wt%.

The sample was examined by X-ray powder diffraction and thermo-magnetic analysis. XRD data were collected on a Rigaku D/max-2500 diffractometer with Cu K_α radiation and a graphite monochromator. The XRD data were collected in a step-scan mode with a sampling time of 3 s and a sampling step of 0.02 ° in the 2θ range of 10°–145°.

Temperature dependence of magnetization was measured under a field of 0.1 T with a vibrating-sample magnetometer (VSM) from room temperature to above the Curie temperature. The ac magnetic susceptibility below 300 K was measured by a mutual inductance bridge at a fixed frequency of 320 Hz. Field dependence of magnetization at 300 K was measured on a SQUID magnetometer in magnetic fields up to 7 T and the saturation magnetization was derived according to the law of approach to saturation.

The easy-magnetization direction of the sample at room temperature was identified on the basis of the XRD pattern of magnetically pre-aligned specimens, which were prepared by solidifying the mixture of fine alloy particles with epoxy resin at room temperature in a field of about 1 T perpendicular to the specimen surface. More details of the experiment were described previously.[11]

NPD experiment was performed at the NIST Center for Neutron Research (NCNR). The data for refinement of the crystallographic and the magnetic structures 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 1.5403 Å (1 Å=0.1 nm). Collimator with horizontal divergences of 15, 20, and 7 min of arc was used before and after the monochromator and after the sample, respectively. The NPD data were collected in a 2θ range of 3°–167.75° with a step of 0.05°. The program FULLPROF[12,13] was used for the Rietveld refinement of the crystallographic and the magnetic structures of the compound, and the following values of the scattering amplitude for the atoms were used: b(Nd)=0.7690, b(Co)=0.2490 ($\times 10^{-12}$ cm).

3. Results and discussion

Single-phase sample of Nd_2Co_7 was prepared. The Curie temperature of the compound was determined to be $T_C = 628$ K, and two SRTs were detected by thermo-magnetic analysis at $T_{SR1} = 219$ K and $T_{SR2} = 261$ K, respectively. The saturation magnetization at room temperature of the compound is 11.5 μ_B/f.u. (Fig. 1).

The compound Nd_2Co_7 crystallized into the Ce_2Ni_7-type structure with space group $P6_3/mmc$. The XRD experiment on the magnetically pre-aligned sample indicates that it exhibits the easy-c axis magnetocrystalline anisotropy at room temperature.[11] Therefore, a magnetic structure model with the magnetic moments of all the atoms aligning along the [001] direction is constructed. Using the proposed model for the crystallographic and the magnetic structures, a satisfactory fitting is achieved to both the XRD

and NPD data at room temperature as shown in Fig. 2. The derived structural parameters and atomic moments are listed in Table 1. From the refinement results the saturation magnetization of 11.1(5) μ_B/f.u. is derived for the compound at 300 K, which is in good agreement with the value determined experimentally.

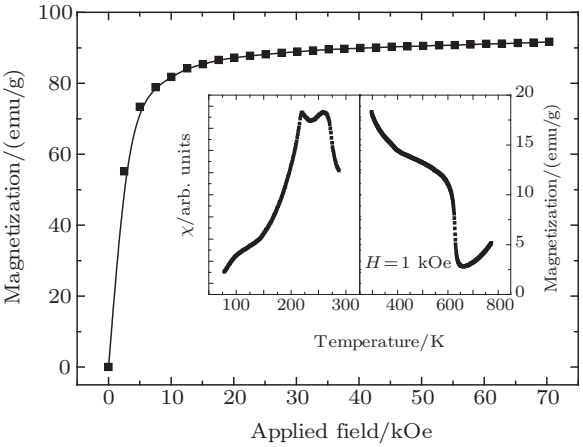


Fig. 1. Field dependence of magnetization of Nd_2Co_7 compound at 300 K. The insets show the temperature dependence of magnetization of Nd_2Co_7 (1 Oe=79.5775 A/m).

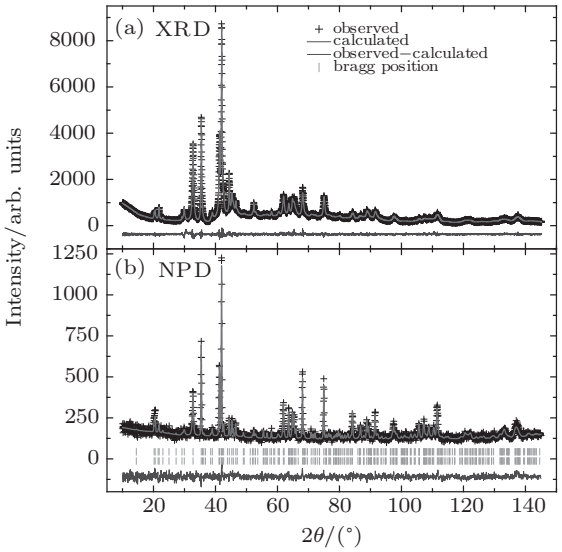


Fig. 2. Observed and calculated X-ray diffraction (a) and neutron powder diffraction (b) patterns of the compound Nd_2Co_7 at room temperature.

Table 1. Results of multi-pattern Rietveld refinement using neutron and X-ray diffraction data collected at 300 K. Space group $P6_3/mmc$, $a = 5.06281(4)$ Å, $c = 24.4469(2)$ Å.

Wyockoff site	Nd_1:4f (1/3, 2/3, z)	Nd_2:4f (1/3, 2/3 ,z)	Co_1:2a (0, 0, 0)	Co_2:4e (0, 0, z)	Co_3:4f (1/3, 2/3, z)	Co_4:6h (x, 2x, 1/4)	Co_5:12k (x, 2x, z)
x						0.8305(4)	0.8341(2)
z	0.02721(2)	0.17237(3)		0.17183(8)	0.83503(5)		0.08861(3)
Moment/μ_B	1.6(3)	3.0(2)	0.7(6)	1.1(4)	1.1(2)	0.9(2)	0.9(2)
B/Å^2	0.74(1)	0.81(1)	0.82(4)	0.47(2)	0.47(2)	0.78(3)	0.71(2)
R-factors		XRD	NPD				
	R_{wp}/%	6.34	7.9	total moment (μ_B/f.u.)		11.1(5)	
	R_p/%	4.67	6.3				
	χ^2	1.87	0.99				

The crystallographic structure of Nd_2Co_7 is shown in Fig. 3. Two $NdCo_5$ slabs ($CaCu_5$-type) with chemical formula $Z = 1$ intergrowth with an $NdCo_2$ slab ($Z = 2$, half the unit cell of the $MgZn_2$-type structure) by sharing a common Kagomé lattice composed of Co atoms (Co_5). The 4e and the 4f sites (i.e. the Co_2 and the Co_3 sites) in Nd_2Co_7 correspond to the 2c sites in the $NdCo_5$ structure and are located almost in the same plane as that the Nd atoms on the 4f sites (i.e. the Nd_2 sites) are located in. The 6h and the 12k sites (i.e. the Co_4 and Co_5 sites) correspond to the 3g site in the $NdCo_5$ structure and form the Kagomé lattices, respectively. In addition, the 12k sites in the Nd_2Co_7 structure also correspond to the 6h sites in the hypothetic $MgZn_2$-type $NdCo_2$ structure. Therefore, the Kagomé lattice composed of the 6h sites is within the $NdCo_5$ slabs, while that composed of the 12k sites is shared by the $NdCo_2$ slab and the $NdCo_5$ slab. The Nd_1 and the Nd_2 sites are located in the $NdCo_2$ slabs and the $NdCo_5$ slabs, respectively.

The derived magnetic moments at room temperature for Co atoms are in a range of 0.7 μ_B–1.1 μ_B, which are very close to the Co moments in Y_2Co_7 at 280 K.[14] The fact that the Curie temperature of Nd_2Co_7 (T_C = 628 K) is close to that of Y_2Co_7 (T_C = 639 K[15]) implies a weak Nd–Co interaction, thus the replacement of nonmagnetic Y by magnetic Nd does not affect much the magnetic moments of the Co atoms. However, the atomic moments of Nd_1 and Nd_2 are remarkably different. The atomic moment of

Nd_2 at room temperature is close to, while that of Nd_1 is much smaller than, the theoretical moment of a free trivalent Nd ion ($= gJ\mu_B = 3.27\ \mu_B$). This observation can readily be understood by considering the magnetic characters of the $NdCo_2$ and the $NdCo_5$ compounds and the local chemical environments of the Nd_1 and Nd_2 atoms in the Nd_2Co_7 compound.

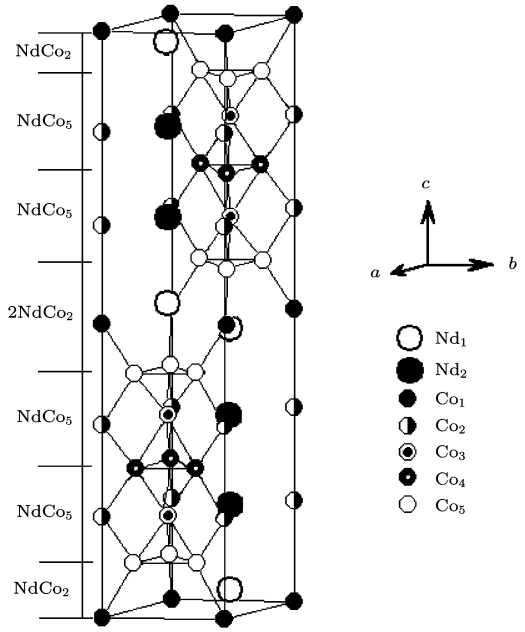


Fig. 3. Illustration of the crystallographic structure of Nd_2Co_7.

$NdCo_5$ is a strong ferromagnetic compound with a strong Co–Co interaction, which gives rise to the T_C as high as 910 K.[7,8] At high temperature, the ordering of Nd moments is stabilized by the Nd–Co exchange interaction, thus the observed Nd moment at relatively high temperature depends on the strength of the Nd–Co coupling and the number of the neighboring Co atoms. In contrast, the $MgCu_2$-type $NdCo_2$ exhibits an exchange enhanced paramagnetism or a metamagnetism of the Co sublattice, i.e., the ordering of the Co moments is induced by the molecular field exerted by the Nd sublattice. Therefore, the magnetic ordering in $NdCo_2$ is determined essentially by the Nd–Co and Nd–Nd exchange interactions, leading to the relatively low T_C of 100 K.[6]

The distances of each atom to its coordination atoms in the $MgCu_2$-type $NdCo_2$, the $CaCu_5$-type $NdCo_5$, and the Ce_2Ni_7-type Nd_2Co_7 compounds are listed in Table 2. The Nd_2 atoms are located in the $NdCo_5$ slab in Nd_2Co_7 and each Nd_2 atom has 6+12 Co atoms and 2 Nd atoms as the nearest neighbour atoms. The local chemical environment of the Nd_2 is similar to that in $NdCo_5$, which can lead to the high atomic moment of the Nd_2 via strong Nd–Co interaction. Similarly, the Nd_1 atoms are located in the $NdCo_2$ slab and have 12Co+4Nd atoms as the nearest neighbour atoms, among which three of the four coordinating Nd atoms are within the $NdCo_2$ slab. Therefore, the local chemical environment of the Nd_1 is also very similar to that in the $NdCo_2$ compound. The relatively weak Nd–Nd and Nd–Co interactions within the $NdCo_2$ slab, in comparison to the Nd–Co and Co–Co interactions in the $NdCo_5$ slabs, are susceptive to thermal fluctuation, which could be the reason for the seemingly lower atomic moment of Nd_1 at room temperature than that of Nd_2. Such a low atomic moment of Nd was also observed in the $NdCo_2$ compound in a temperature range of 80 K–90 K ($< T_C = 100$ K).[16] At low temperature, the thermal fluctuation is reduced and, in particular, the Nd–Nd exchange interaction is enhanced significantly, the average atomic moment of Nd will be increased. This is supported by the observation that the saturation magnetization of Nd_2Co_7 could reach as high as 13.6 μ_B/f.u. at 5 K.[11] Because of the instability of Co moment in R_2Co_7 with respect to both electron concentration in the 3d band and the Co–Co exchange interaction,[18] the average Co moment varies around 1.1 μ_B in R_2Co_7.[15,18–20] Then it can be deduced from the saturation magnetization at 5 K that the average atomic moments of both the Nd_1 and the Nd_2 in Nd_2Co_7 are close to the theoretical value of a free trivalent Nd ion.[11] Therefore, the ordering of the Nd moments in the $NdCo_2$ slabs is more susceptive to the thermal fluctuation than the ordering of the Nd moments in the $NdCo_5$ slabs. The different susceptibility to the thermal fluctuation of the magnetic ordering of the Nd atoms in different structural blocks implies a weak magnetic coupling between the $NdCo_2$ slabs and the $NdCo_5$ slabs in Nd_2Co_7.

Table 2 shows that the local chemical environment of Co_1 in Nd_2Co_7 is the same as that of Co in the $NdCo_2$ compound with six equidistant Co atoms and six equidistant Nd atoms as the nearest neighbour atoms. In particular, all the coordinating atoms of the Co_1 in Nd_2Co_7 are located within the $NdCo_2$ blocks. Considering exclusively the nearest neighbour interactions within the first order approximation, it is anticipated that the magnetism of the Co atoms on

the Co_1 sites in Nd_2Co_7 will exhibit the characteristic of the Co atoms in the $NdCo_2$ compound. Since the Co sublattice in the $NdCo_2$ compound is of metamagnetic feature and the Nd_1 moment in Nd_2Co_7 at room temperature is much lower than the theoretical value of a free trivalent Nd ion, the molecular field experienced by the Co atoms on the Co_1 sites may not be strong enough to trigger the metamagnetic transition. In this case, the atomic moment on the Co_1 site will be too small to be detected accurately by the NPD experiment at room temperature, leading to the large estimated standard deviation for the derived atomic moment of the Co atoms on the Co_1 site as shown in Table 1.

Table 2. Atomic coordinations and bond distances in $NdCo_2$, $NdCo_5$, and Nd_2Co_7 compounds. The crystallographic data are taken from Refs. [16] and [17] and present work.

Centre atom & site	Coord. atom & count	Bond distance/Å	Centre atom & site	Coord. atom & count	Bond distance/Å
$NdCo_2$	space group: $Fd\bar{3}m$		$NdCo_5$	space group: $P6/mmm$	
Nd 8a	$-$Co$\times$12	3.0285	Nd 1a	$-$Co$\times$6	2.9018
	$-$Nd$\times$4	3.1631		$-$Co$\times$12	3.2024
				$-$Nd$\times$2	3.9700
Co 16d	$-$Co$\times$6	2.5827	Co 2c	$-$Co$\times$6	2.4587
	$-$Nd$\times$6	3.0285		$-$Nd$\times$3	2.9018
				$-$Co$\times$3	2.9018
			Co 3g	$-$Co$\times$4	2.4587
				$-$Co$\times$4	2.5130
				$-$Nd$\times$4	3.2024
Nd_2Co_7	pace group: $P6_3/mmc$				
Nd_1 4f	$-Co_5\times6$	2.943(1)	Nd_2 4f	$-Co_2\times3$	2.9230(2)
	$-Co_1\times3$	2.9977(2)		$-Co_3\times3$	2.9286(2)
	$-Co_5\times3$	3.190(1)		$-Co_4\times6$	3.164(3)
	$-Nd_1\times3$	3.2115(3)		$-Co_5\times6$	3.257(1)
	$-Nd_2\times1$	3.5487(9)		$-Nd_1\times1$	3.556(2)
				$-Nd_2\times1$	3.796(1)
Co_1 2a	$-Co_5\times6$	2.609(1)	Co_2 4e	$-Co_4\times3$	2.441(2)
	$-Nd_1\times6$	2.9977(2)		$-Co_5\times3$	2.501(2)
				$-Nd_2\times3$	2.9230(2)
				$-Co_3\times3$	2.9278(3)
Co_5 12k	$-Co_3\times1$	2.375(2)	Co_3 4f	$-Co_5\times3$	2.375(2)
	$-Co_2\times1$	2.501(2)		$-Co_4\times3$	2.527(2)
	$-Co_5\times2$	2.520(2)		$-Co_2\times3$	2.9278(3)
	$-Co_5\times2$	2.543(3)		$-Nd_2\times3$	2.9286(2)
	$-Co_1\times1$	2.609(1)	Co_4 6h	$-Co_2\times2$	2.421(3)
	$-Nd_1\times2$	2.943(1)		$-Co_4\times2$	2.488(3)
	$-Nd_1\times1$	3.190(1)		$-Co_3\times2$	2.527(2)
	$-Nd_2\times2$	3.256(1)		$-Co_4\times2$	2.574(6)
				$-Nd_2\times4$	3.164(2)

4. Summary

The crystallographic and the magnetic structures at room temperature of the composite compound Nd_2Co_7 are determined by a multi-pattern refinement with NPD and XRD data. The compound crystallizes into the Ce_2Ni_7-type structure. The magnetic structure model with the moments of all atoms aligning along the c axis at 300 K fits the experimental NPD data satisfactorily and coincides with the easy magnetization direction revealed by the XRD experiments on magnetically pre-aligned fine particles. At room temperature, the derived atomic moments of the Co atoms vary in a range between 0.7 μ_B and 1.1 μ_B, the atomic moment of Nd in the $NdCo_5$ slab is very close to the theoretical moment of a free trivalent Nd

ion, whereas the atomic moment of Nd in the $NdCo_2$ slab is much smaller than the theoretical value for a free trivalent Nd ion. The remarkable difference in the atomic moment of the Nd atoms between different structural slabs at room temperature is interpreted in terms of the magnetic characteristics of the $NdCo_2$ and $NdCo_5$ compounds and the local chemical environments of the Nd atoms in different structural slabs of the Nd_2Co_7 compound. The seemingly low atomic moment of the Nd atom in the $NdCo_2$ slab at room temperature is attributed to the thermal fluctuation of the ordering of the Nd moments in the $NdCo_2$ slabs.

References

[1] Parthé E and Chabot B 1984 *Handbook on the Physics and Chemistry of Rare Earths* ed. Gschneidner Jr K A and Eyring L Vol. 7 (Amsterdam: North-Holland) p. 186

[2] Pecharsky V K and Gschneidner Jr K A 1999 *J. Magn. Magn. Mater.* **200** 44

[3] von Ranke P J, Pecharsky V K and Gschneidner Jr K A 1998 *Phys. Rev.* B **58** 12110

[4] von Ranke P J, de Oliveira N A, de Sousa V S R, Garcia D C, de Oliveira I G, Magnus A, Carvalho G and Gama S 2007 *J. Magn. Magn. Mater.* **313** 176

[5] Campoy J C P, Plaza E J R, Coelho A A and Gama S 2006 *Phys. Rev.* B **74** 134410

[6] Ouyang Z W, Wang F W, Huang Q, Liu W F, Xiao Y G, Lynn J W, Liang J K and Rao G H 2005 *Phys. Rev.* B **71** 064405

[7] Bartholin H, van Laar B, Lemaire R and Schweizer J 1966 *J. Phys. Chem. Solids* **27** 1287

[8] Nikitin S A, Skokov K P, Koshkid'ko Yu S, Pastushenkov Yu G and Ivanova T I 2010 *Phys. Rev. Lett.* **105** 137205

[9] Andreev A V, Bartashevich M I, Deryagin A V, Zadvorkin S M and Tarasov Ye N 1988 *Phys. Met. Metallogr.* **65** 61

[10] Bartashevish M I, Goto T and Yamaguchi M 1992 *J. Magn. Magn. Mater.* **111** 83

[11] Yang Y Q, Rao G H, Wang T, Li J B, Luo J, Liu G Y, Chen X J and Zhao J L 2010 *J. Alloys Compd.* **506** 766

[12] Rietveld H M 1967 *Acta Crystallogr.* **229** 151

[13] Rodríguez-Carvajal J L 1993 *Physica* B **192** 55

[14] Kirchamyr H R and Burzo E 1990 *The Landolt–Börnstein Database New Series* Vol. 19d2 (Berlin: Springer-Verlag) p. 217

[15] Koen E, Schweizer J and Tasset F 1969 *Phys. Rev.* **186** 479

[16] Xiao Y G, Huang Q, Ouyang Z W, Lynn J W, Liang J K and Rao G H 2006 *J. Alloys Compd.* **420** 29

[17] Alamede J H, Givord D, Jeandey C, Li H S, Lu Q and Oddou J L 1987 *J. Less-Common Metals* **133** 215

[18] Bartashevich M I, Mushnikov N V, Andreev A V and Goto T 2009 *J. Alloys Compd.* **478** 34

[19] Velge W A J J and Buschow K H J 1969 *J. Appl. Phys.* **39** 1717

[20] Buschow K H J 1973 *J. Less-Common Metals* **33** 311