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Journal of Alloys and Compounds 317–318 (2001) 546–549

Journal of ALLOYS AND COMPOUNDS

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Magnetic structure of $Nd_7Co_6Al_7$

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Abstract

Time-of-flight neutron powder diffraction has been used to determine the magnetic structure of the intermetallic compound $Nd_7Co_6Al_7$. The thermodynamic, magnetic and electrical properties of this compound indicate that it undergoes a paramagnetic–ferromagnetic transition at 15.5 K, and possesses a magnetic refrigerant capacity of approximately 40 J/kg. The average value of the high field saturation magnetic moment per Nd atom at low temperatures is almost 50% below that of the free ion value. Neutron powder diffraction measurements have been performed at 300 K, in order to confirm the details of the crystal structure, and below the magnetic ordering temperature, at 6 K, in order to establish the nature of the magnetic structure. The high temperature data clearly confirm that $Nd_7Co_6Al_7$ crystallizes in the $Pr_7Co_6Al_7$ structure (space group *P*4/*mbm*). The low temperature data show the presence of reflections at (100), (110), (200) and (210), reflections which are non-existent above the ordering temperature. The presence of the (100) reflection indicates the presence of antiferromagnetic configurations in this system. Models of the magnetic structure for $Nd_7Co_6Al_7$ will be presented and discussed.

Keywords: Magnetic structure; $Nd_7Co_6Al_7$; Intermetallic compound

1. Introduction

The magnetocalorific effect and ferromagnetic interactions in the ternary rare-earth intermetallic $Nd_7Co_6Al_7$ have been recently investigated in order to determine its suitability as a magnetic refrigerant [1]. This material crystallizes in the tetragonal structure $Pr_7Co_6Al_7$ [2] (*P*4/*mbm*), with three Nd atoms at 2(*a*), 8(*i*) and 4(*h*) sites, Co atoms at 4(*h*) and 8(*i*) sites whilst Al atoms are located at 8(*j*), 4(*h*) and 2(*d*) sites ($Z=2$), represented by a packing of trigonal prisms. Bulk magnetization and electrical resistivity data indicate that a magnetic transition occurs at 15.5 K, with a reported magnetic refrigerant capacity of 40 J/kg. The measured saturation magnetization at 5 K is 10.5 μ_B per formula unit. Since, in equiatomic binary and ternary rare-earth intermetallics, Co atoms are usually non-magnetic, the above value gives a magnetic moment of 1.5 μ_B per Nd atom, far below the free ion value of 3.27 μ_B. This can be attributed either to a large reduction of the free ion value caused by crystal field effects or, more likely, the presence of antiferromagnetic interactions which are not observable by bulk measurements.

Neutron diffraction is the ideal technique for determination of the orientation and magnitude of Nd moments present at the three Nd sites. In this paper, time-of-flight powder diffraction data as well as a preliminary analysis of the crystal and magnetic structure of $Nd_7Co_6Al_7$ is presented. Measurements have been performed at ambient temperature, far above the ordering temperature, in order to establish if there is any mixing of Co and Al atoms on the five available sites, and at 6 K in the magnetically ordered regime, in order to determine the details of the magnetic structure.

2. Experimental details

The compound $Nd_7Co_6Al_7$ was prepared by arc melting from starting materials with at least 3N purity, followed by annealing under high vacuum for 14 days at 973 K. The occurrence of a single phase was confirmed by micrographic analysis. X-ray powder diffraction patterns, obtained using a Guinier camera, were indexed on the basis of the tetragonal $Pr_7Co_6Al_7$ structure type with room temperature lattice constants $a=13.736(1)$ Å and $c=$

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0925-8388/01/$ – see front matter
PII: S0925-8388(00)01385-2

4.211(1) Å. Time-of-flight neutron powder diffraction measurements, with approximately 4 g of material, were performed on the ROTAX powder diffractometer installed at the ISIS spallation neutron source [3]. Data at 6 and 293 K were collected simultaneously in three separate detector banks, located at scattering angles of $2\theta=28.9°$, $2\theta=72.7°$ and $2\theta=122.4°$.

3. Results and discussion

The neutron diffraction data reported here were analysed in standard fashion by the Rietveld profile refinement technique [4], using the GSAS suite of programs [5] for analysis of neutron time-of-flight diffraction data. The magnetic form factor for the Nd^{3+} ion, calculated in the dipole approximation, was employed [6]. The room temperature data were refined by placing Nd, Co and Al atoms on their respective sites, using the atomic positions determined by single crystal X-ray diffraction for $Pr_7Co_6Al_7$ [2]. Refinement parameters included an overall scale factor, lattice constants, Nd, Co and Al atomic co-ordinates and their associated isotropic temperature factors, initially set at the values obtained in the single crystal X-ray study of $Pr_7Co_6Al_7$. Neutron scattering lengths of $b_{Nd}=0.7690\times 10^{-12}$ cm, $b_{Co}=0.2490\times 10^{-12}$ cm and $b_{Al}=0.3449\times 10^{-12}$ cm were used in the profile refinement [7]. The room temperature refinement quickly converged to a R_{Bragg} refinement factor of 4.2%. No secondary phases were detected in the neutron diffraction patterns. In order to check for a possible preferential site occupation of Co and Al atoms, a further refinement of the Co site occupancy for each of the two Co and three Al sites was carried out. The structure was found to be perfectly ordered, with no site interchange of Co and Al atoms. Observed and calculated diffraction patterns for $Nd_7Co_6Al_7$ at room temperature are displayed in Fig. 1. Refined structural parameters at 293 K are displayed in Table 1.

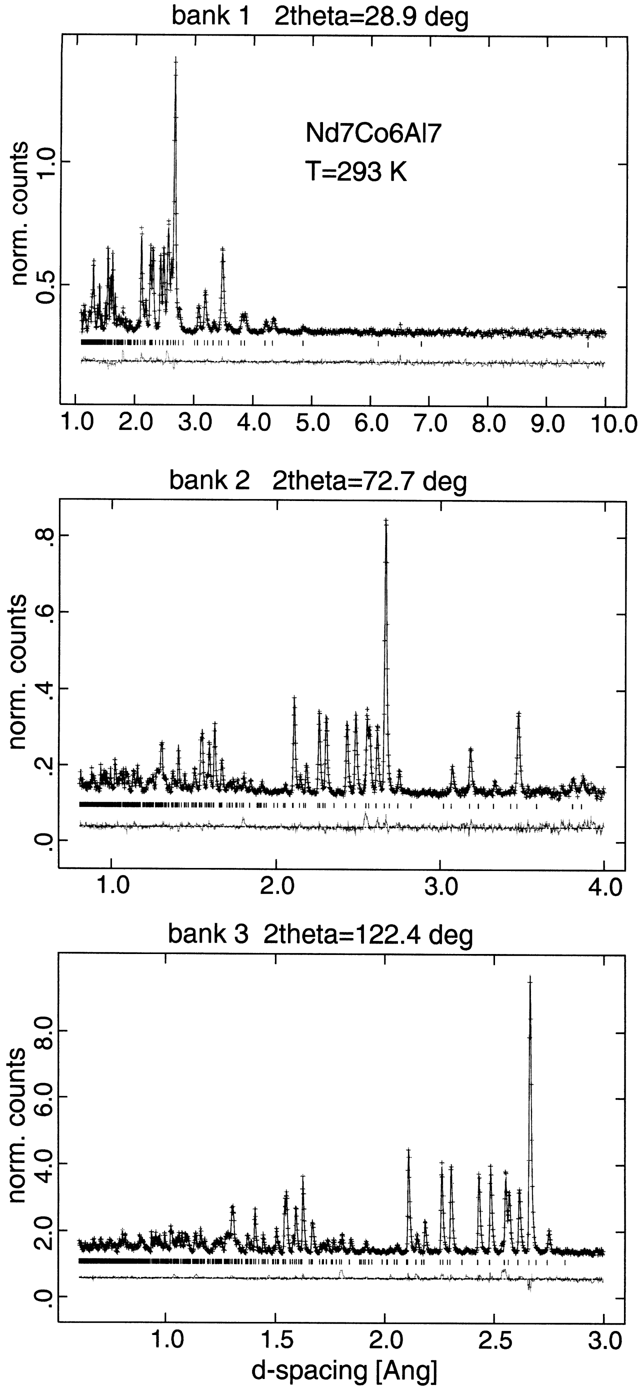

Fig. 1. Observed, calculated and difference neutron time-of-flight diffraction patterns for $Nd_7Co_6Al_7$ at 293 K. Tick marks indicate calculated nuclear peak positions.

A comparison between the room temperature and low temperature neutron diffraction patterns is displayed in Fig. 2. The low temperature pattern shows the presence of magnetic reflections in addition to nuclear reflections which were observed at room temperature. These magnetic peaks can be simply indexed on the basis of the chemical unit cell. The indices for the first eight peaks are displayed in the bottom half of Fig. 2. The (100) and (300) reflections have zero nuclear structure factors (these are forbidden by the space group), so that their origin must be magnetic. Similarly, even though reflections (110), (200) and (210) have very small nuclear structure factors, the large increase in the intensity of these reflections below the ordering temperature must also be due to magnetic ordering. The simplest model of the magnetic structure possible in this scenario is to consider that Nd moments on one or two of the three sublattices are aligned anti-ferromagnetically whilst Nd moments on the remaining sublattice are aligned ferromagnetically. A simple calculation shows that, for example, if Nd atoms at the 2*a* site, $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ are aligned anti-parallel to each other along the tetragonal *c*-axis, intensity at (100) and (300) positions will be observed. A reduction of the crystal symmetry by removing the 2_1 screw axis operation will allow intensity at (100) and (300) positions. Applying this reduction to the

Table 1
Results of Rietveld profile refinements of neutron diffraction data for $Nd_7Co_6Al_7$ at 293 K[a]

Atom	x/a	y/a	z/c	Occupancy	B ($Å^2$)
Nd_1 (2*a*)	0	0	0	1.00	0.60(2)
Nd_2 (4*h*)	0.3681(1)	0.8681(1)	$\frac{1}{2}$	1.00	0.60(2)
Nd_3 (8*i*)	0.2612(1)	0.0471(1)	0	1.00	0.60(2)
Co_1 (4*h*)	0.0741(2)	0.5741(2)	$\frac{1}{2}$	1.00	1.03(6)
Co_2 (8*i*)	0.2908(2)	0.3354(2)	0	1.00	1.03(6)
Al_1 (2*d*)	0	$\frac{1}{2}$	0	1.00	1.03(5)
Al_2 (4*h*)	0.2138(2)	0.7138(2)	$\frac{1}{2}$	1.00	1.03(5)
Al_3 (8*i*)	0.0957(2)	0.1358(2)	0	1.00	1.03(5)

[a] Quality of fit values are listed at the bottom of the table. Errors refer to estimated standard deviations calculated by the Rietveld refinement. a (Å) = 13.7362(1), c (Å) = 4.2124(1) at 293 K. $R_{\mathrm{Bragg,\ nucl}}$ (%) = 4.2, χ^2 = 2.8%.

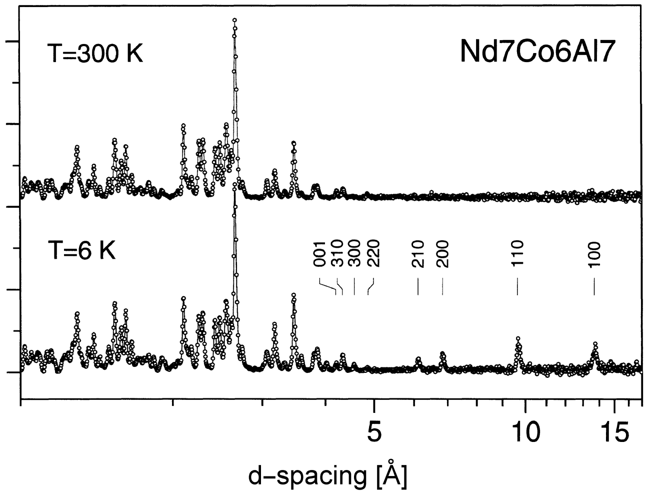

Fig. 2. Observed neutron time-of-flight diffraction patterns of $Nd_7Co_6Al_7$ at 6 K for the forward scattering bank ($2\theta = 28.9°$) in comparison to the room temperature diffraction pattern. Indices of the first eight reflections are indicated.

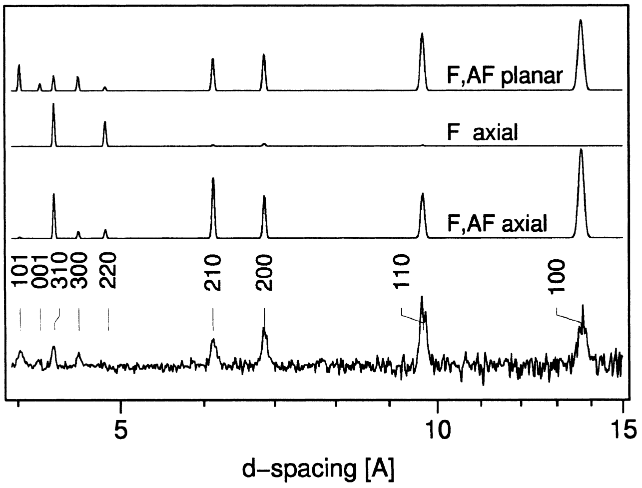

Fig. 3. Calculated forward scattering patterns in comparison to the 6–293 K difference diffraction pattern which contains only magnetic reflections (bottom curve). Model curves refer to the axial and planar models proposed in the text.

other two Nd sites 4*h* (at general positions: $(x, x+\frac{1}{2}, \frac{1}{2})$, $(-x, -x+\frac{1}{2}, \frac{1}{2})$, $(x+\frac{1}{2}, -x, \frac{1}{2})$, $(-x+\frac{1}{2}, x, \frac{1}{2})$) and 8*i* (at general positions $(x, y, 0)$, $(-x, -y, 0)$, $(-y, x, 0)$, $(y, -x, 0)$, $(-x+\frac{1}{2}, y+\frac{1}{2}, 0)$, $(x+\frac{1}{2}, -y+\frac{1}{2}, 0)$, $(y+\frac{1}{2}, x+\frac{1}{2}, 0)$, $(-y+\frac{1}{2}, -x+\frac{1}{2}, 0)$), it can be seen that intensity at (100) and (300) will also result if moments on each sublattice are aligned antiparallel.

Bulk magnetization measurements indicate a saturation moment of at least 10.5 μ_B per formula unit suggesting that at least one of the Nd sites is ferromagnetically ordered whereas inspection of the diffraction data shows the presence of an antiferromagnetic sublattice. Magnetic structure modes were derived from the eight magnetic space groups of *P*4/*mbm* [8]. This limits the number of variable magnetic moment components, which are collected in Table 2 for each of the three Nd sites, 2*a*, 4*h* and 8*i*. Fig. 3 shows the temperature difference pattern 6–293 K of $Nd_7Co_6Al_7$ in comparison with pattern simulations. A strong prerequisite for an appropriate model to be chosen from four possible axial (moments parallel *c*-axis) and four planar (moments perpendicular to *c*-axis) magnetic groups is that the (220) magnetic reflection observed at a d-spacing of 4.8 Å has zero observed intensity. This finding rules out a ferromagnetic 8*i* site. A pure ferromagnetic model (F, axial) can be rejected (Fig. 3) as explained above. Planar modes (e.g. ferro F(4*h*), antiferro AF(8*i*))

Table 2
Magnetic space groups, allowed magnetic moment components and ordering directions for 2*a*, 4*h* and 8*i* sites in the space group *P*4/*mbm*[a]

Magnetic group	Allowed components			Ordering direction
	2*a*	4*h*	8*i*	
*P*4/*mbm*	m_z	0	m_z	Axial
*P*4′/*mb*′*m*	0	0	m_z	Axial
*P*4′/*mbm*′	0	m_z	m_z	Axial
*P*4/*mb*′*m*′	m_z	m_z	m_z	Axial
*P*4′/*m*′*bm*	0	m_x, $-m_y$	m_x, m_y	Planar
*P*4′/*m*′*b*′*m*	0	m_x, $-m_y$	m_x, m_y	Planar
*P*4′/*m*′*bm*′	0	m_x, m_y	m_x, m_y	Planar
*P*4/*m*′*b*′*m*′	0	m_x, m_y	m_x, m_y	Planar

[a] By symmetry, $m_x = m_y$, and $m_x = -m_y$.

Table 3
Results of Rietveld profile refinements of neutron diffraction data for $Nd_7Co_6Al_7$ at 6 K[a]

Atom	x/a	y/a	z/b	Occupancy	m_x (μ_B)	B (Å^2)
Nd_1 (2*a*)	0	0	0	1.00	0	0.15(2)
Nd_2 (4*h*)	0.3688(1)	0.8688(1)	$\frac{1}{2}$	1.00	1.5 (F)	0.15(2)
Nd_3 (8*i*)	0.2612(1)	0.0470(1)	0	1.00	2.2 (AF)	0.15(2)
Co_1 (4*h*)	0.0745(4)	0.5745(4)	$\frac{1}{2}$	1.00		0.55(6)
Co_2 (8*i*)	0.2891(3)	0.3346(3)	0	1.00		0.55(6)
Al_1 (2*d*)	0	$\frac{1}{2}$	0	1.00		0.69(4)
Al_2 (4*h*)	0.2141(2)	0.7142(2)	$\frac{1}{2}$	1.00		0.69(4)
Al_3 (8*i*)	0.0945(2)	0.1369(2)	0	1.00		0.69(4)

[a] Quality of fit values are listed at the bottom of the table. Errors refer to estimated standard deviations calculated by the Rietveld refinement code (a typical detection limit of neutron magnetic powder diffraction is ±0.2 μ_B). The magnetic parameters refer to a planar model (see text). a (Å) = 13.6953(1), c (Å) = 4.2039(1). $R_{\text{Bragg, nucl}}$ (%) = 3.5, $R_{\text{Bragg, mag}}$ (%) = 13%, $\chi^2 = 6.0\%$.

rather than axial modes (e.g. F(4*h*), AF(8*i*)) are favoured by the diffraction data (Fig. 3). Planar magnetic groups of $P4/mbm$, however, require a non-magnetic 2*a* site, leaving the following magnetic moment components to be refined: m_x of F(4*h*) and m_x, m_y of AF(8*i*). A reasonable fit to the data ($R_{\text{Bragg-mag}} = 13\%$) was achieved with $m_y(8i) = 0$ and an AF(8*i*) spin sequence $(++----++-)$ referring to the sequence of 8*i* symmetry operators given above. Refined moment parameters $m_x(4h)$ and $m_x(8i)$ are given in Table 3 together with refined crystal structure parameters at 6 K.

The four proposed different planar models cannot be distinguished on the basis of the present powder diffraction data alone [9], but the qualitative picture, as presented here, is consistent with magnetization results in that there is a net ferromagnetic moment per unit cell. The contrast in the magnitudes of the moment values derived from macroscopic measurements and the present neutron diffraction investigation is particularly striking. The model of the magnetic structure presented here gives a calculated net zero magnetic field magnetization of 6 μ_B, in contrast with the bulk saturation magnetization result of 10.5 μ_B. This could be indicative of a magnetic field induced metamagnetic transition. Magnetization measurements on a single crystal sample are clearly highly desirable, since this would allow for a more meaningful confrontation with the neutron data. A more detailed analysis of the neutron diffraction data for this system as well as neutron diffraction data also already collected by the authors for the isomorphous compound $Pr_7Co_6Al_7$ is in preparation [10].

Acknowledgements

Financial support by the Italian MURST National Research Program ‘Alloys and Intermetallic Compounds: Thermodynamics, Physical Properties, Reactivity’ and the German BMBF, under contract no. KI5BO3, is gratefully acknowledged.

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