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Abstract

We present magnetic susceptibility, heat capacity, and neutron diffraction measurements of polycrystalline Nd$_2$Ru$_2$O$_7$ down to 0.4 K. Three anomalies in the magnetic susceptibility measurements at 146, 21 and 1.8 K are associated with an antiferromagnetic ordering of the Ru$^{4+}$ moments, a weak ferromagnetic signal attributed to a canting of the Ru$^{4+}$ and Nd$^{3+}$ moments, and a long-range-ordering of the Nd$^{3+}$ moments, respectively. The long-range order of the Nd$^{3+}$ moments was observed in all the measurements, indicating that the ground state of the compound is not a spin glass. The magnetic entropy of $R\ln 2$ accumulated up to 5 K, suggests the Nd$^{3+}$ has a doublet ground state. Lattice distortions accompany the transitions, as revealed by neutron diffraction measurements, and in agreement with earlier synchrotron x-ray studies. The magnetic moment of the Nd$^{3+}$ ion at 0.4 K is estimated to be 1.54(2)$\mu_B$ and the magnetic structure is all-in-all-out as determined by our neutron diffraction measurements.

Keywords: pyrochlores, neutron diffraction, magnetic properties, magnetic structure

(Some figures may appear in colour only in the online journal)

1. Introduction

Frustrated pyrochlore compounds with the general formula $A_2B_2O_7$ [1–7], where $A$ is a trivalent rare-earth ion and $B$ is a tetravalent transition-metal ion [1], with space group $Fd-3m$, are made up of interpenetrating $A_2O_7$′ and $B_2O_6$ sub-lattices composed of corner-sharing tetrahedra. Pyrochlore oxides have been extensively studied in the past few decades and various novel magnetic behaviours have been discovered including spin glass [2], spin ice [3, 4], and spin liquid [5]. These different magnetic states arise from the geometrical frustration of the pyrochlore lattice, which can lead to a macroscopically degenerate magnetic ground state rather than a conventional long-range ordered state. To date, many of the experimental results have been obtained on heavy rare-earth titanate pyrochlores possessing large 4f magnetic moments. These include Dy$_2$Ti$_2$O$_7$ [6] and Ho$_2$Ti$_2$O$_7$ [4] identified as spin ice, and Tb$_2$Ti$_2$O$_7$ [7] known as spin liquid. In spin ice materials, the ferromagnetic interactions between the magnetic moments sitting on the corners of the tetrahedra become frustrated because of the crystalline electric field (CEF). These crystal fields require the magnetic moments on the corners of the tetrahedra to align along the local cubic $\langle 111 \rangle$ directions, in such a way that the moments can point either in or out of the centre of the each tetrahedron. In spin-ice materials, this ‘two-in/two-out’ spin configuration is analogous to the proton arrangement in water ice [4]. Spin ice has been suggested to host unconventional low temperature magnetic and thermodynamic properties, including the Dirac strings observed in Dy$_2$Ti$_2$O$_7$ [8], while the quantum spin-ice candidate Yb$_2$Ti$_2$O$_7$...
is suggested to exhibit a Higgs transition [9]. In other pyrochlores, where the exchange interactions are antiferromagnetic and stronger than any dipolar interactions, long-range antiferromagnetic ordering is observed [10].

Recently, interest has moved to the pyrochlore compounds with smaller moments, in which different quantum effects such as novel low-energy spin dynamics and planar components to the spin symmetry have been observed [11]. Since the Nd$^{3+}$ ion possesses a relatively small magnetic moment, the strength of the dipole–dipole interaction is significantly reduced and the exchange interaction may dominate the system in a similar way to that seen in Yb$_2$Ti$_2$O$_7$ and hence, may result in long-range ordering [9]. Ruthenium pyrochlores have attracted a lot of attention over the last few years [12, 13]. For ruthenium pyrochlores, both the A ($16d$) and B ($16c$) sites are occupied by magnetic ions. The perturbation driven by the moment at the $16c$ site may cause a symmetry breaking and structural distortions [14]. Early studies on the ruthenium pyrochlores revealed that there is a $\lambda$-type jump in the specific heat in temperature range 75–160 K depending on the size of the rare-earth ion [15, 16]. The magnetic moment per Ru obtained from neutron diffraction [17] is reduced compared to the theoretical maximum expected for 4$d^9$ low-spin configuration, i.e. $2\mu_B$, indicating the observed Ru-moment is modified by the CEF. In case of Nd$_2$Ir$_2$O$_7$, a metal-insulator transition has been observed near 33 K and an all-in/all-out magnetic structure has been suggested by neutron diffraction and muon spin relaxation measurements [18, 19]. Long-range magnetic ordering below 0.55 K has been confirmed in Nd$_2$Hf$_2$O$_7$ by powder neutron diffraction measurements, with an all-in/all-out magnetic structure and an ordered magnetic moment of 0.62$\mu_B$ at 0.1 K [20]. Nd$_2$Zr$_2$O$_7$ has also been confirmed to show long-range magnetic ordering below 0.4 K with an all-in/all-out magnetic structure [21].

In published reports, the anomalies observed in the heat capacity and magnetic susceptibility measurements at 146 and 21 K in Nd$_2$Ru$_2$O$_7$ were associated with the Ru antiferromagnetic order temperature and a glassy-like transition, respectively [15, 16]. In the neodymium pyrochlore, the Nd$^{3+}$ ion site has trigonal symmetry and the CEF splits the ground state manifold into five Kramers doublets leading to a calculated magnetic moment of 3.62$\mu_B$ [20]. One of the interesting features of pyrochlores with a Kramers doublet, which have a well-separated ground state and first excited state, is that the ground state properties can be explained by the pseudo-spin $S = \frac{3}{2}$ [20]. In particular, the Kramers doublet systems with total angular momenta $J = \frac{3}{2}$ and $\frac{5}{2}$ (for Nd$^{3+}$) are very interesting as it has been observed that under certain conditions these doublets may behave like ‘dipolar–octupolar’ doublets [22], making Nd$_2$Ru$_2$O$_7$ an interesting compound for further studies.

Here we have studied the behaviour of Nd$_2$Ru$_2$O$_7$ at low temperatures, in order to investigate the magnetic ground state. We report dc magnetic susceptibility $\chi_{dc}$, ac magnetic susceptibility $\chi_{ac}$, and heat capacity $C_p$ measurements on Nd$_2$Ru$_2$O$_7$ as a function of temperature and magnetic field. The cubic Fd-3m pyrochlore structure is confirmed by powder x-ray diffraction (XRD) measurements. The Ru$^{4+}$ moments order at 146 K, followed by an anomaly at 21 K due to a canting of the Ru$^{4+}$ moments and perhaps a polarization of the Nd$^{3+}$ spins. Magnetization and heat capacity measurements reveal the long-range order of the Nd$^{3+}$ spins at 1.8 K due to Ru$^{4+}$–Nd$^{3+}$ coupling. Powder neutron diffraction studies have confirmed antiferromagnetic ordering of the Nd moments below 1.8 K, and reveal an all-in-all-out magnetic structure in Nd$_2$Ru$_2$O$_7$ with an ordered magnetic moment of 1.54(2)$\mu_B$ at 0.4 K. To the best of our knowledge, this is the first report of long-range order of the Nd$^{3+}$ moments in Nd$_2$Ru$_2$O$_7$ below 1.8 K.

2. Experimental methods

Polycrystalline samples of Nd$_2$Ru$_2$O$_7$ were synthesized using stoichiometric quantities of high purity starting materials Nd$_2$O$_3$ (99.99%) and RuO$_2$ (99.99%) from Alfa Aesar. The powder materials were thoroughly mixed together by grinding with a mortar and pestle for more than an hour. The samples were then pre-sintered at 800 °C for 12 h. The finely ground powders were then pelletized using an isostatic cold press and sintered at 1150 °C for a period of 4 days with several intermediate grindings. We used alumina crucibles and the heat treatments were performed in air.

The crystal structure at the room temperature and phase purity of the samples were verified via powder XRD using Bruker AXS GmbH D2 Phaser desktop x-ray diffractometer. DC magnetization measurements were performed using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) above 1.8 K, while an iQuantum $^3$He insert was also used for the measurements below 1.8 K. Heat capacity measurements were carried out using a relaxation method in a Quantum Design Physical Property Measurement System (PPMS) equipped with a dilution refrigerator insert. Powder neutron diffraction measurements were performed using a $^3$He fridge on the WOMBAT high-intensity diffractometer at ANSTO, Australia using a neutron wavelength of 2.41 A. The sample was loaded in a Cu can. The $^3$He fridge was used to cool down the sample to 0.4 K and the diffraction patterns were taken at 0.4 and 8 K. The neutron diffraction measurements at high temperatures ($T > 8$ K) were performed with a CF-8 cryofurnace on the WOMBAT diffractometer.
magnetic, formed by two types of corner sharing tetrahedra where one type of tetrahedron has Nd atoms at its corners (shown by the large grey spheres) and the other tetrahedra have Ru atoms at the corners (shown by the small white spheres). The centre of each tetrahedron is occupied by an oxygen atom. The Nd\textsuperscript{3+} ions occupy 16d (½,½, 2) sites and Ru\textsuperscript{4+} ions occupy 16c (0, 0, 0) sites, while the O\textsuperscript{2−} ions occupy two types of anionic sites 8b (x, ½, ½) and 48f (x, ½, ½). In the pyrochlore structure, six O1 (denoted by 48f) anions are equivalent, while one O2 (denoted by 8b) occupies a distinct position in the structure. Therefore, the formula unit of the pyrochlore is represented as Nd\textsubscript{2}Ru\textsubscript{2}O\textsubscript{7}.

3.2. Magnetization measurements

We have studied the magnetic properties of polycrystalline samples of Nd\textsubscript{2}Ru\textsubscript{2}O\textsubscript{7} down to 0.4 K. Figure 2(a) shows the temperature dependence of the dc magnetic susceptibility, for both field-cooled (FC) and zero-field-cooled (ZFC) data, for Nd\textsubscript{2}Ru\textsubscript{2}O\textsubscript{7} in the temperature range 0.4 ≤ T ≤ 190 K. The susceptibility measurement down to 1.8 K were performed with an MPMS squid magnetometer and the measurements below 1.8 K were performed separately using an MPMS magnetometer with a \textsuperscript{3}He insert, as shown by the red zero-field-cooled warming (ZFCW) and blue field-cooled warming (FCW) curves (see inset of figure 2(a)). Various anomalies are observed in the dc susceptibility data.

The first anomaly observed around 146 K is due to the antiferromagnetic ordering of the Ru\textsuperscript{4+} spins, where we observe a small cusp-like feature in ZFCW magnetic susceptibility and splitting of ZFCW-FCW curves around 146 K (as shown in figure 2(b)). A corresponding peak is also observed in the specific heat data confirming the Ru\textsuperscript{4+} ordering.

As we decrease the temperature further, we observe a further splitting of ZFCW and FCW susceptibility curves around 21 K (shown in figure 2(c)). Contradictory conclusions are drawn by reports published in [16, 23] regarding the origin of the anomaly at 21 K and the divergence of the ZFCW-FCW curves below 21 K in Nd\textsubscript{2}Ru\textsubscript{2}O\textsubscript{7}, which we will discuss later.

As we further cool down the sample, we observe a peak in χ(T) near 1.8 K (as shown in the inset of figure 2(a)). A corresponding peak is also observed in the specific heat data.
This peak is associated with the long-range antiferromagnetic ordering of the Nd\(^{3+}\) spins, as confirmed by the powder neutron diffraction and specific heat measurements discussed later in this paper.

The inverse dc magnetic susceptibility data (shown in figure 2(d)) in the high temperature range 180 \(\leq T \leq 300\) K is fitted with the Curie–Weiss law, \(\chi(T) = C/(T - \theta_{CW})\) which gives a Curie constant, \(C = 2.62(1)\) emu-K/mol Nd. The effective moment was calculated using \(\mu_{\text{eff}}^2 = 3Ck_B/N_A\). The fit curve is shown by the solid line and gives \(\theta_{CW} = -178(2)\) K and a reduced effective paramagnetic moment, \(\mu_{\text{eff}} = 4.58(3)\) \(\mu_B\)/Nd. We cannot determine the exact contribution of Nd\(^{3+}\) and Ru\(^{4+}\) moments in the inverse susceptibility of Nd\(_2\)Ru\(_2\)O\(_7\). The fit curve deviates from the ideal Curie–Weiss law at lower temperatures, which is in good agreement with the earlier published reports [23], and indicates the presence of short-range ferromagnetic interactions at these temperatures.

As discussed in the heat capacity section below, we have estimated the first-excited crystal field level to be at about 188 K, therefore, because of the thermal population of higher CEF levels at \(T \geq 100\) K, the estimated values of \(\theta_{CW}\) and \(\mu_{\text{eff}}\) for the Ising ground state obtained by the analysis of \(\chi(T)\) above are not accurate. To try to address this problem we fit \(\chi(T)\) at temperatures below 20 K to a modified Curie–Weiss law i.e. \(\chi(T) = \chi_0 + C/(T - \theta_{CW})\).
The solid curves represent fits of the equation (1) as shown in figure 3, giving $g = 4.467(1)$ for $T = 2\text{ K}$, which is lower than the expected value for a pure $m_J = \pm \frac{3}{2}$ doublet, $g = 2g_J J = 6.54$ ($g_J = \frac{\sqrt{3}}{2}$, $J = \frac{9}{2}$), because of the mixing of the $m_J$ ground states by the crystal electric field. For Nd$_3$Hf$_2$O$_7$ g is found to be 5.01 [20] and for Nd$_3$Zr$_2$O$_7$ it is found to be 4.793 [27]. For an effective factor $g = 4.467(1)$ and $S = \frac{1}{2}$, the paramagnetic moment is expected to be $m = g\mu_B/\text{Nd} = 2.23\mu_B/\text{Nd}$. In case of a powder sample, the effective magnetic moment is related to the $g$-factor and is given as $\mu_{\text{eff}} = \frac{2}{\sqrt{3}} \mu_B/\text{Nd}$, where $\mu_B = (g_\perp^2 + 2g_\parallel^2)^{1/3}$. As $g_\perp = 0$ and $g_\parallel = 4.467(1)$, we obtain $\mu_{\text{eff}} = 2.23\mu_B/\text{Nd}$, which is close to the $\mu_{\text{eff}} = 2.37(4)\mu_B/\text{Nd}$ obtained above from the dc susceptibility analysis. Furthermore, it can be seen from the isothermal curve at $T = 2\text{ K}$ in figure 3 that fitting with equation (1) predicts a saturation of moment at the high fields, however, the measured moment shows a little increase at the high field $>40\text{ Koe}$. This behaviour of $M(H)$ suggests the presence of spin fluctuations or a non-Ising contribution. Similar behaviour for $M(H)$ was observed in the case of Pr$_2$Hf$_2$O$_7$ [29].

The nearest neighbour dipole–dipole interactions $D_{nn}$ can be estimated using our effective magnetic moment $\mu_{\text{eff}} = 2.37(4)\mu_B/\text{Nd}$ and lattice parameter $a = 10.3544(5)\text{ Å}$ using equation [20, 29]

$$D_{nn} = \frac{5}{3} \left( \frac{\mu_0}{4\pi} \right) g_{\text{eff}}^2 r_{nn}^2 \approx 0.16\text{ K},$$

where $\mu_0$ is the magnetic permeability of the vacuum and $r_{nn} = \left( \frac{g}{2} \right) \sqrt{2}$ is the nearest neighbour distance. $D_{nn} = +0.12\text{ K}$ has been reported for Nd$_3$Hf$_2$O$_7$ [20]. Following the procedure discussed in [20, 30], we can roughly estimate the nearest neighbour exchange interaction between the $(111)$ Ising moments by fitting the dc susceptibility data with the expression $\chi(T) = \left( \frac{C}{T} \right) \left[ 1 + \frac{C}{T} \right]$, where $C_2$ can be decomposed as sum of dipolar and exchange interactions, $C_2 = \left( \frac{\alpha_S^2}{4} \right) \left[ 2.18D_{nn} + 2.67J_{nn} \right]$. By fitting the $\chi(T)$ data with this expression in the temperature range $5 \leq T \leq 18\text{ K}$, we get $C_2 = -0.57(2)\text{ K}$. Using the estimated values of $D_{nn} \approx 0.16\text{ K}$, we obtain $J_{nn} \approx -0.70\text{ K}$. $J_{nn} \approx -0.77\text{ K}$ was observed for Nd$_3$Hf$_2$O$_7$ [20]. The value of $J_{nn}$ indicates that antiferromagnetic interactions dominate over dipolar interactions in Nd$_3$Ru$_2$O$_7$. The presence of antiferromagnetic exchange interactions in Nd$_3$Ru$_2$O$_7$ ultimately leads to a long-range ordered ground state of the Nd$^{3+}$ spins around 1.8 K as evidenced by the specific heat and neutron diffraction measurements. Hertog et al [31] predicted by Monte Carlo simulations that long-range antiferromagnetic ordering with an all-in-all-out magnetic structure in pyrochlores is possible for $J_{nn}/D_{nn} < -0.91$. This theoretical condition is fulfilled for Nd$_3$Ru$_2$O$_7$ as $J_{nn}/D_{nn} \approx -4 < -0.91$ and experimentally we have observed antiferromagnetic ordering of Nd$^{3+}$ spins with an all-in-all-out magnetic structure at 0.4 K as discussed in the neutron diffraction section.
3.3. Heat capacity measurements

Figure 4(a) shows the temperature variation of specific heat for Nd3Ru2O7 in the temperature range 0.4–150 K in \( H = 0 \) Oe. The peak around 1.8 K represents the long-range ordering of Nd\(^{3+}\) spins and transition near 144 K is due to the antiferromagnetic ordering of Ru\(^{4+}\) ions, which is in agreement with the dc magnetic susceptibility measurements. An upturn has been observed in Cp below 5 K (shown in the lower inset in figure 4(a)) indicating short-range magnetic correlations, consistent with the inverse susceptibility analysis. Previous studies \[16\] on the specific heat of Nd3Ru2O7 have reported an anomaly at 21 K, which is not present in our samples. This is possibly because the anomaly at 21 K is due to a canting of an already ordered moment and not due to a magnetic phase transition from a disordered to an ordered state. The temperature dependence of the specific heat above 10 K is well described by the relation \( C_p = \beta T^3 + \delta T^2 \); the electronic heat capacity coefficient \( \gamma = 0 \), because of the insulating nature of Nd3Ru2O7 at low temperatures. A fit to \( C_p/T \) versus \( T^2 \) with \( C_p/T = \beta T^2 + \delta T^4 \), as shown by the solid line in the inset of figure 4(a), for \( 9 \leq T \leq 22 \) K yields \( \beta = 5.6(4) \times 10^{-4} \) J K\(^{-1}\) mol\(^{-1}\) and \( \delta = 3.7(5) \times 10^{-7} \) J K\(^{-6}\) mol\(^{-1}\). The Debye temperature \( \theta_D = 337(3) \) K is obtained from \( \beta = (12/5) n \pi^2 R \theta_D^3 \), where \( n = 11 \) is the number of atoms per formula unit, \( R = 8.314 \) J mol\(^{-1}\) K\(^{-1}\) is the gas constant. The \( \theta_D \) in pyrochlores has been found to be temperature dependent. In case of Nd3Hf2O7, the low temperature \( C_p(T) \) yields \( \theta_D = 436 \) K, while the high temperature \( \theta_D = 785 \) K \[20\]. For Nd3Zr2O7, the low temperature \( C_p(T) \) yields \( \theta_D = 514 \) K, while the high temperature \( C_p(T) \) gives \( \theta_D = 741 \) K \[21\].

To obtain a more reliable value for \( \theta_D \) we have analyzed the \( C_p(T) \) data between 2 and 140 K using a combination of the Debye \( (C_V \text{Debye}) \) and Einstein \( (C_V \text{Einstein}) \) models of the lattice heat capacity, which take into account acoustic and optic phonon modes, respectively. In addition, we have considered the magnetic contribution \( C_{\text{CEF}} \) to \( C_p(T) \) of the Nd\(^{3+}\) ions due to the crystal electric field of the Ru\(^{4+}\) ions. Thus the \( C_p(T) \) data are fit using the relation:

\[
C_p(T) = m C_V \text{Debye} (T) + (1 - m) C_V \text{Einstein} (T) + C_{\text{CEF}} (T).
\]

The lattice contributions \( C_V \text{Debye} \) and \( C_V \text{Einstein} \) are given by \[32\]:

\[
C_V \text{Debye} (T) = 9 R \left( \frac{T^3}{\theta_B^3} \right) \int_0^{\theta_B/T} x^4 e^{x} \left( e^{x} - 1 \right)^2 dx,
\]

\[
C_V \text{Einstein} (T) = 3 n R \left( \frac{\theta_E}{T^2} \right) \frac{e^{\theta_E/T}}{\left( e^{\theta_E/T} - 1 \right)},
\]

where \( \theta_E \) is the Einstein temperature. For a two level system the crystal field contribution, \( C_{\text{CEF}} \) is given by \[32\]:

\[
C_{\text{CEF}} (T) = R \left( \frac{\Delta^2}{T^2} \right) \frac{g_0 g_1 e^{-\Delta/T}}{(g_0 + g_1 e^{-\Delta/T})^2},
\]

where \( g_0 \) is the degeneracy of ground state, \( g_1 \) is the degeneracy of first excited state and \( \Delta \) is the energy gap between ground state and first excited state.

Inelastic neutron scattering (INS) measurements revealed \[21\] that the CEF splits the \((2J + 1)\)-fold degenerate ground state of Nd\(^{3+}\) \((J = \frac{7}{2})\) into five doublets, therefore \( g_0 = g_1 = 2 \). The specific heat is fit with equation (3) as shown by the solid line in figure 4(a) and we obtain \( \Delta = 188(3) \) K. The lattice heat capacity is obtained from the difference \( C_p(T) - C_{\text{CEF}}(T) \) and by fitting this difference using the Debye plus Einstein models in the temperature range \( 2 \leq T \leq 140 \) K, we obtain \( \theta_D = 790(6) \) K, \( \theta_E = 102(5) \) K, with \( m = 0.94 \), indicating a 94\% weight to the Debye term and a 6\% weight to the Einstein term. The value of \( \theta_D \) is comparable to other Nd-pyrochlores, where \( \theta_D \) is \( 785 \) K for Nd3Hf2O7 \[20\] and \( \theta_D = 741 \) K for Nd3Zr2O7 \[21\]. The value of \( \Delta \) obtained from fitting is not accurate and can only be accurately obtained from INS measurements. In the case of Nd3Zr2O7, \( \Delta = 23.4 \) meV \( \approx 270 \) K was obtained for Nd\(^{3+}\) moments by INS measurements \[21\]. This indicates that there will be a thermal population of the higher CEF levels at \( T > 100 \) K for the Nd\(^{3+}\) moments.

Figure 4(b) shows the specific heat for Nd3Ru2O7 on the (left-hand axis) in the low-temperature range \( (T < 5 \) K). The magnetic contribution \( (C_m) \) to the heat capacity has been obtained by subtracting the lattice contribution \( (C_p) \) of non-magnetic Y2Ru2O7 from the total heat capacity of Nd3Ru2O7. The magnetic entropy is calculated by integrating \( C_m(T)/T \) with respect to temperature using the formula:

\[
\Delta S_m = \int_{T^*}^{T^*} C_m(T)/T \ dT,
\]

where \( T^* \) and \( T^{*}\) are the initial and final temperatures taken for the integration interval. As we can observe from the temperature dependence of entropy (shown on the right-hand axis in figure 4(b)), a zero-point or residual entropy of \( \frac{2}{3} \ln 2 \) seen in spin ice does not appear in Nd3Ru2O7 and \( \Delta S_m \) saturates near 5 K attaining a value of 5.92 J mol\(^{-1}\) K\(^{-1}\), which is close to the spin freezing condition \( R \ln 2 = 5.76 \) J mol\(^{-1}\) K\(^{-1}\), and indicates Nd\(^{3+}\) has a doublet ground state.

3.4. Neutron diffraction studies

We have studied the magnetic structure of Nd3Ru2O7 at temperatures down to 0.4 K using powder neutron diffraction experiments. Neutron diffraction patterns recorded at 0.4 and 8 K are shown in figure 5(a) for 20 range 19° to 133°. The data contain three peaks (denoted by "i") from scattering due to Al and a peak at 83° (denoted by +) due to scattering from the Cu sample holder. The neutron diffraction data were refined using the FULLPROF suite \[33\]. Figure 5(b) shows the results of the Rietveld refinement of the magnetic structure of Nd3Ru2O7 at 0.4 K (after subtracting the 8 K nuclear pattern), where the red line is the experimentally observed data, the black line is the theoretically calculated intensity, and the line in blue represents the difference between the two patterns. We can observe the enhancement in intensity of the (220) and (113) magnetic peaks at 38° and 45° respectively (shown in the inset of Figure 5(a)), which correspond to the most prominent peaks in the ordered state. A similar enhancement in the intensity of
magnetic peaks is also observed for Nd$_2$Hf$_2$O$_7$ [20]. An additional magnetic peak at $(4 2 0)$ has been observed near $63^\circ$, which confirms the antiferromagnetic ordering of the Nd$^{3+}$ spins. The magnetic peak $(4 2 0)$ is not reproduced completely in the refinement, possibly because of its vicinity to an Al-peak.

Figure 4. (a) Temperature dependence of the specific heat of Nd$_2$Ru$_2$O$_7$ in the temperature range 0.4–150 K at $H = 0$ Oe. The solid line represents a fit to the Debye + Einstein + CEF model given by equation (3) for $2 \leq T \leq 140$ K. The upper inset shows $C_p/T$ versus $T$ for $10 \leq T \leq 22$ K. The solid line is a fit to $C_p = \beta T^3 + \delta T^4$ for $10 \leq T \leq 22$ K. The lower inset shows the upturn in $C_p$ observed before the Nd$^{3+}$ ordering. (b) Left axis: Temperature dependence of the specific heat of Nd$_2$Ru$_2$O$_7$ for $T < 5$ K. The peak at 1.8 K represents the long-range ordering of the Nd$^{3+}$ moments. Right axis: temperature variation of the magnetic entropy of Nd$_2$Ru$_2$O$_7$. The increase in entropy saturates near 5 K and reaches the maximum value $R \ln 2$, which indicates the doublet ground state of the Nd$^{3+}$ ions. The raw $C_p$ data have been divided by 2 to obtain the specific heat per mole of Nd.

Figure 5. (a) Neutron diffraction pattern of Nd$_2$Ru$_2$O$_7$ recorded at 0.4 and 8 K. (b) Rietveld refinement of the magnetic structure of Nd$_2$Ru$_2$O$_7$ at 0.4 K (after subtracting the 8 K nuclear pattern), where the observed data is shown in red, the black line is the theoretically calculated intensity, and the blue line shows the difference between the two. The green vertical lines indicate the positions of the Bragg peaks in the diffraction pattern. The neutron data are best modelled by the irreducible representation $1$ with an all-in-all-out spin configuration of the Nd$^{3+}$ ions. The peaks at 61°, 74°, and 115° (denoted by “*) are due to scattering from Al in the sample environment, the peak at 83° (denoted by “+) is due to the Cu sample holder. The peaks have been shifted upwards by 20 000 for clarity. (c) The all-in-all-out configuration of the magnetic moments. (d) Magnetic structure refinement profile of Nd$_2$Ru$_2$O$_7$ at 0.4 K (after subtracting the 8 K nuclear pattern), where the regions with background peaks have been excluded. The neutron wavelength used was 2.41 Å.
Table 2. Irreducible representations (IRs) and associated basis vectors ψ for the Nd (16d) sites in space group Fd-3m with propagation vector k = (0, 0, 0) for Nd₃Ru₂O₇ obtained from SARAh software [30]. The atoms of the non-primitive basis are defined according to Nd1: (0.5, 0.5, 0.5), Nd2: (0.5, 0.25, 0.25), Nd3: (0.25, 0.5, 0.25) and Nd4: (0.25, 0.25, 0.5).

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<td>(1 − 10)</td>
<td>(110)</td>
<td>(−10)</td>
<td>(−110)</td>
</tr>
<tr>
<td>Γ₇</td>
<td>Ψ₄</td>
<td>(0 − 22)</td>
<td>(02 − 2)</td>
<td>(022)</td>
<td>(0 − 2)</td>
</tr>
<tr>
<td>Γ₇</td>
<td>Ψ₅</td>
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<td>(−20 − 2)</td>
<td>(−202)</td>
<td>(202)</td>
</tr>
<tr>
<td>Γ₇</td>
<td>Ψ₆</td>
<td>(−220)</td>
<td>(220)</td>
<td>(−220)</td>
<td>(2 − 20)</td>
</tr>
<tr>
<td>Γ₉</td>
<td>Ψ₇</td>
<td>(200)</td>
<td>(200)</td>
<td>(200)</td>
<td>(200)</td>
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<tr>
<td>Ψ₈</td>
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<td>(0 − 1 − 1)</td>
<td>(0 − 11)</td>
<td>(01 − 1)</td>
<td></td>
</tr>
<tr>
<td>Ψ₉</td>
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<td>(020)</td>
<td>(020)</td>
<td>(020)</td>
<td></td>
</tr>
<tr>
<td>Ψ₁₀</td>
<td>(101)</td>
<td>(−101)</td>
<td>(−10 − 1)</td>
<td>(10 − 1)</td>
<td></td>
</tr>
<tr>
<td>Ψ₁₁</td>
<td>(002)</td>
<td>(002)</td>
<td>(002)</td>
<td>(002)</td>
<td></td>
</tr>
<tr>
<td>Ψ₁₂</td>
<td>(110)</td>
<td>(−110)</td>
<td>(−110)</td>
<td>(1 − 10)</td>
<td></td>
</tr>
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Table 3. Magnetic peaks corresponding to each basis vector ψ.

<table>
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<th>ψ</th>
<th>Magnetic peaks</th>
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<td>Ψ₁</td>
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</tr>
<tr>
<td>Ψ₂</td>
<td>(111), (220), (113)</td>
</tr>
<tr>
<td>Ψ₃</td>
<td>(111), (220), (113)</td>
</tr>
<tr>
<td>Ψ₆</td>
<td>(111), (002), (220), (113)</td>
</tr>
<tr>
<td>Ψ₇</td>
<td>(111), (220), (113), (222)</td>
</tr>
<tr>
<td>Ψ₁₂</td>
<td>(111), (220), (113)</td>
</tr>
</tbody>
</table>

synchrotron studies on Nd₃Ru₂O₇ down to 10 K, we observed a change in the lattice parameter, and a variation in the Ru–O, Nd–O and Ru–O–Ru bond lengths, which have been discussed in detail in our previous work on Nd₃Ru₂O₇ [14].

To further study the compatibility of the magnetic structure with the space group symmetry, we carried out a representative analysis using the SARAh software [34]. The symmetry analysis for the propagation vector k = (0, 0, 0) and space group Fd-3m resulted in four nonzero irreducible representations (IRs) for the Nd(16d) site: Γ₃, Γ₅, Γ₇ and Γ₉ [35]. Table 2 shows basis vectors (ψ) corresponding to each IR. By combining the basis vectors of the IRs we can obtain different possible models of the magnetic structure. Out of four IRs, the magnetic structure of Nd₃Ru₂O₇ is best modelled by the IR Γ₃ (with a magnetic R-factor of 32.4%), with all-in-all-out spin configuration of the Nd³⁺ ions as represented in figure 5(c).

The ordered moment obtained from the refinement is 1.54(2)µB/Nd. Figure 5(d) shows the Rietveld refinement profile of the difference intensity 0.4–8 K (similar to figure 5(b), where the regions with background peaks have been excluded. The magnetic R-factor is reduced to 10.7% and all the peaks due to magnetic structure have been reproduced e.g. (220), (1 1 3) etc. The ordered magnetic moment obtained from the refinement is reduced to 1.47(4)µB/Nd.

In order to determine the magnetic structure from the presence or absence of the magnetic peaks at 2θ < 50°, we make the list of the non-zero magnetic peaks for each basis vector ψ, as shown in table 3. We find that the magnetic structure corresponds to basis vector ψ₁. We can exclude the possibility of basis vectors ψ₂, ψ₃, ψ₆, ψ₇, ψ₁₂ and their allowable linear combinations, because corresponding magnetic structures lead to the sizable (111) magnetic peak, which is not observed in the experimental data.

For an effective factor g = 4.467(1) and S = ½, the ordered moment is expected to be m = gBSµB = 2.23µB/Nd. However, the effective magnetic moment of Nd³⁺ at 0.4 K is estimated to be 1.54(2)µB/Nd, which is smaller than the expected ordered moment. The reduced magnetic moment at the low temperatures indicates the presence of the quantum fluctuations which persist in the ordered state down to 0.4 K. A similar reduction in the magnetic moment of Nd³⁺ is also observed in Nd₂Hf₂O₇ [20] and Nd₂Zr₂O₇ [21].

3.5. Magnetic ordering in Nd₃Ru₂O₇

We have primarily focused on the low-temperature magnetic properties of Nd₃Ru₂O₇. In addition, we have tried to clarify the nature of the transitions at 21 and 146 K. Long-range magnetic order was observed at 18 K in all our measurements, indicating an antiferromagnetic ordering of the Nd³⁺ moments below 1.8 K. Previously published reports have indicated that the transition at 146 K is due to an antiferromagnetic ordering of Ru⁴⁺ 4d spins, as a similar transition has been observed in Y₃Ru₂O₇, where there is no 4f spin on the A-site [10, 15, 23]. The negative Curie–Weiss temperature, obtained from the fitting of inverse susceptibility curve also shows that the dominant magnetic interactions in Nd₃Ru₂O₇ are antiferromagnetic. However, contradictory reports are available in the literature regarding the ordering of Ru⁴⁺ spins in Nd₃Ru₂O₇ and other analogous Ru-pyrochlores. Some studies have reported a glassy nature to the freezing of the Ru⁴⁺ moments, which is evident from the reported bulk magnetic susceptibility measurements [15–17, 36, 37]. On the other hand, neutron diffraction experiments have shown long-range ordering of the Ru⁴⁺ moments below the magnetic transition temperature of 146 K, with a long correlation length [15, 17].

Experimental evidence for spin-glass behaviour can be provided by ac susceptibility measurements, where the magnetic freezing temperature should vary with the frequency of the applied magnetic field [38]. In case of Nd₃Ru₂O₇ it has been reported that the real, in phase component of the ac susceptibility measurements [10–16, 36, 37, 39]. On the other hand, neutron diffraction experiments have shown long-range ordering of the Ru⁴⁺ moments below the magnetic transition temperature of 146 K, with a long correlation length [15, 17].

Contradictory conclusions are also drawn from the reports published in [16, 23] regarding the origin of the cusp-like anomaly at 21 K and the divergence of the ZFCW-FCW curves below 21 K in Nd₃Ru₂O₇. Taira et al [16] reported that the feature near 21 K might be due to a spin-glass transition, while Gaultois et al [23] did not observe any transition around 21 K in their samples and concluded that the feature reported near 21 K in [16] resulted from the presence of a secondary phase in the
samples. In case of our samples, the presence of a secondary phase is excluded by an analysis of synchrotron x-ray data [14]. We have also performed ac susceptibility measurements in the temperature range 14–28 K as shown in the figure 6(a). The temperature dependence of the in-phase component of the ac susceptibility, \( \chi_{\text{ac}}^\prime (T) \) shows that transition temperature is independent of the frequency of the ac field. We have also performed powder neutron diffraction measurements (shown in figure 6(b)) below (18 K) and above (25 K) the transition at 21 K. We have normalized the intensity at 25 K with respect to the intensity at 18 K, and then calculated the subtracted intensity \( I(I(18\,K) - I_{\text{normalized}}(25\,K)) \). We do not observe any noteworthy features in the subtracted intensity data. This indicates that there is no dramatic change in the magnetic structure of the Ru\(^{4+}\) spins around 21 K. Furthermore, we have observed that the Nd\(^{3+}\) spins remain paramagnetic down to 1.8 K, where magnetic susceptibility increases with decrease in the temperature. We therefore rule out the explanations proposed in [16, 23] regarding the origin of the transition at 21 K. There is no possibility of any structural (or dramatic magnetic) transition at 21 K, as there is no clear feature in the heat capacity data around this temperature. Moreover, no additional diffraction peaks or phase transformation is observed in our XRD experiments down to 10 K [14].

Previous studies on ruthenium pyrochlores have shown that the weak exchange coupling between the rare earth (\( A^{3+}\)) and Ru\(^{4+}\) ions polarizes the \( A^{3+}\) moment and consequently, the behaviour of \( A^{3+}\) moments is not purely paramagnetic below the ordering of Ru\(^{4+}\) spins [10, 28, 31]. Evidence for weak exchange coupling has been observed in our samples as discussed above in the dc susceptibility data analysis. We suspect a canting of Ru\(^{4+}\) moments occurs because of the exchange coupling between the Nd\(^{3+}\) and Ru\(^{4+}\), which is evidenced by the positive \( \theta_{\text{CW}} \) obtained in the dc susceptibility analysis at low temperatures. The presence of a weak ferromagnetic component associated with antiferromagnetic ordering of Ru\(^{4+}\) spins is also evident from the sharply reduced Ru–O–Ru bond length at low temperatures in Nd\(_2\)Ru\(_2\)O\(_7\), as explained in detail in our synchrotron studies [14]. Gauloitis et al [23], also reported the presence of weak ferromagnetic interactions associated with the antiferromagnetic ordering of Ru\(^{4+}\) spins below 146 K in Nd\(_2\)Ru\(_2\)O\(_7\). In addition, Taira et al [16], have reported hysteresis curve at 5 K in Nd\(_3\)Ru\(_2\)O\(_7\) samples, indicating the ferromagnetic component in the magnetic behaviour. The competition between the weak ferromagnetic and dominant antiferromagnetic interactions at the low temperatures might lead to a spin canting. This canting would then produce a splitting of the ZFCW and FCW curves at 21 K in the dc susceptibility. Thus, we suggest that the anomaly at 21 K is due to a weak ferromagnetic component produced by a polarization of the Nd\(^{3+}\) moments and/or a canting of the ordered Ru\(^{4+}\) moments. In principle, if some canting is present, the powder neutron diffraction patterns should not be the same at 18 and 25 K. However, the change in Ru–O–Ru bond angle is very small (\( \approx 1^\circ \)) as observed in our synchrotron studies [14]. Therefore, the ferromagnetic component is very weak which will produce weak magnetic signal that might not be detected in the powder neutron diffraction experiments. That is why there is no noticeable difference between the neutron diffraction patterns collected at 18 and 25 K.

The weak exchange coupling between the rare earth \( A^{3+}\) and the Ru\(^{4+}\) ions below the ordering temperature of the Ru\(^{4+}\) moments [39], eventually leads to the antiferromagnetic ordering of Nd\(^{3+}\) spins below 1.8 K. This exchange dominates any dipole–dipole interactions between the Nd\(^{3+}\) ions as discussed in the dc susceptibility analysis above. This result is supported by neutron diffraction experiments on the related systems Er\(_2\)Ru\(_2\)O\(_7\) [39, 40] and Tb\(_2\)Ru\(_2\)O\(_7\) [41], which confirm the long-range ordering of \( A^{3+}\) 4f spins. Ordering of Tb\(^{3+}\) lattice is observed in the ruthenate pyrochlore Tb\(_2\)Ru\(_2\)O\(_7\) at 3.5 K, however, no such ordering of the Tb\(^{3+}\) sublattice is observed in the corresponding titanate pyrochlore Tb\(_2\)Ti\(_2\)O\(_7\) down to 17 mK. Therefore, it is assumed that ordering of Tb\(^{3+}\) moments in Tb\(_2\)Ru\(_2\)O\(_7\) happens because of the internal field of Ru\(^{4+}\) ions, which is supposed to relieve the frustration. A similar conclusion was arrived at for Ho\(_2\)Ru\(_2\)O\(_7\) [42].
4. Summary

Polycrystalline pyrochlore Nd$_2$Ru$_2$O$_7$ has been prepared and examined using a combination of x-ray and neutron diffraction, magnetic, and heat capacity studies. A combination of ac and dc magnetic susceptibility measurements reveal three magnetic transitions in Nd$_2$Ru$_2$O$_7$ at 146, 21 and 1.8 K that are associated with an antiferromagnetic ordering of the Ru$^{4+}$ moments, a weak ferromagnetic signal attributed to a canting of the Ru$^{4+}$ ions and perhaps a polarization of the Nd$^{3+}$ moments, and a long-range ordering of the Nd$^{3+}$ moments, respectively. $M(H)$ data indicate the Nd moments exhibit a local (1 1 1) Ising anisotropic behaviour with an effective $g = 4.467(1)$ at $T = 2$ K, and an effective magnetic moment $\mu = 2.33 \mu_B$/Nd. The low-temperature dc susceptibility yields an effective moment $\mu_{\text{eff}} = 2.37(4) \mu_B$/Nd for the Ising ground state and the positive value of $\theta_{\text{CW}}$ indicates the presence of weak ferromagnetic interactions between the Nd moments, although these moments eventually order antiferromagnetically below 1.8 K. The fitting of the $C_p(T)$ data using a Debye + Einstein + CEF model predicts the separation between ground state doublet and first excited state to be around 188(3) K. The magnetic entropy released up to 5 K is $R n_2$, suggesting the Nd$^{3+}$ has a doublet ground state.

Above 9 K, the specific heat data are well described by the relation $C_p = \beta T^3 + \delta T^3$, and a fit between 22 and 22 K yields $\beta = 5.6(4) \times 10^{-4}$ J K$^{-4}$ mol$^{-1}$ giving a Debye temperature $\theta_D = 337(3)$ K. A more accurate value for $\theta_D = 790(6)$ K is obtained by analysing the $C_p(T)$ data using a combination of a Debye and an Einstein model of the lattice heat capacity, and an additional magnetic contribution from the Nd$^{3+}$ ions due to the crystal electric field of Ru$^{4+}$ ions. This is comparable to the $\theta_D$ values for similar pyrochlores.

Powder neutron diffraction and our previous synchrotron XRD measurements reveal the nature of the magnetic ordering transitions and the presence of lattice distortions accompanying the magnetic transitions. The peaks at 47° and 101° (denoted by \#) in the powder neutron pattern might be present due to the distortion of the crystal structure at low temperatures. An additional magnetic peak at 420° has been observed at 63°, which confirms the antiferromagnetic ordering of Nd$^{3+}$ spins. The neutron diffraction data of Nd$_2$Ru$_2$O$_7$ is best modelled by the IR $\Gamma'$. The magnetic moment of Nd$^{3+}$ ion at 0.4 K is estimated as 1.54(2)$\mu_B$ and the magnetic structure is all-in-all-out as determined by neutron experiments. The reduced magnetic moment indicates the strong quantum fluctuations, which persist down to 0.4 K. The reduction in the magnetic moment and the presence of quantum fluctuations might be because of the dipolar–octupolar nature of Kramers doublet ground state of Nd$^{3+}$ [22]. Due to the presence of the octupolar term, the Nd$_2$Ru$_2$O$_7$ may not behave strictly like a dipolar system and this non-Ising contribution can cause quantum fluctuations. Further theoretical and experimental work needs to be done to confirm this.

Acknowledgments

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