Structural disorder, magnetism, and electrical and thermoelectric properties of pyrochlore \( \text{Nd}_2\text{Ru}_2\text{O}_7 \)

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Abstract
Polycrystalline \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) samples have been prepared and examined using a combination of structural, magnetic, and electrical and thermal transport studies. Analysis of synchrotron x-ray and neutron diffraction patterns suggests some site disorder on the \( A \)-site in the pyrochlore sublattice: Ru substitutes on the Nd-site up to 7.0(3)\%, regardless of the different preparative conditions explored. Intrinsic magnetic and electrical transport properties have been measured. Ru 4d spins order antiferromagnetically at 143 K, as seen both in the susceptibility and in the specific heat, and there is a corresponding change in the electrical resistivity. The onset of a second antiferromagnetic ordering transition seen below 5 K is attributed to ordering of Nd 4f spins. \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) is an electrical insulator, and this behaviour is believed to be independent of the Ru-antisite disorder on the Nd-site. The electrical properties of \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) are presented in the light of data published on all \( A_2\text{Ru}_2\text{O}_7 \) pyrochlores, and we emphasize the special structural role that \( \text{Bi}^{3+} \) ions on the \( A \)-site play in driving metallic behaviour. High-temperature thermoelectric properties have also been measured. When considered in the context of known thermoelectric materials with useful figures-of-merit, it is clear that \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) has excessively high electrical resistivity which prevents it from being an effective thermoelectric. A method for screening candidate thermoelectrics is suggested.

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

1. Introduction

The \( A_2\text{B}_2\text{O}_6\text{O}' \) pyrochlore structure, shown in figure 1, comprises two interpenetrating \( \text{B}_2\text{O}_6 \) and \( A_2\text{O}' \) sublattices [1]. The electrical properties of pyrochlore ruthenium oxides (\( A_2\text{Ru}_2\text{O}_7, A = \text{Pr through Lu, Y, and Bi} \)) are of long-standing interest. In \( A_2\text{Ru}_2\text{O}_7 \) ruthenates, electrical conductivity is expected to take place through the network of corner-sharing \( \text{RuO}_6 \) octahedra (i.e., the \( \text{B}_2\text{O}_6 \) sublattice). While all the rare-earth members are insulating, \( \text{Bi}_2\text{Ru}_2\text{O}_7 \) is metallic.

Several investigators have sought to explain the difference in conductivity by examining changes in Ru–O–Ru bond angle—determined by the combination of Ru–O bond length and the size of \( A \)—and consequent changes in orbital overlap and bandwidth [2, 3]. Electron spectroscopic investigations of \( \text{Y}_2\text{Ru}_2\text{O}_7 \) compared with \( \text{Bi}_2\text{Ru}_2\text{O}_7 \) led Cox et al [4] to conclude that the principle difference seen is the participation in conduction of Bi 6s states in \( \text{Bi}_2\text{Ru}_2\text{O}_7 \). This participation broadens the Ru 4d band width sufficiently that a metallic ground state is preferred over one that is correlated and insulating. However, Shoemaker et al [5] contrasted the computed electronic structures of insulating \( \text{Bi}_2\text{Ti}_2\text{O}_7 \) with that of conducting \( \text{Bi}_2\text{Ru}_2\text{O}_7 \) and found no difference in the...
presence or absence of Bi 6s states near the Fermi energy in these two compounds.

Pyrochlore-type rare-earth ruthenium oxides are also of great interest for their magnetic properties. The sublattices of corner-connected \( A_2 \) and \( B_2 \) tetrahedra can result in magnetic frustration when either \( A \) or \( B \) is separately magnetic [6]. While magnetic properties of \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) have been reported previously [7], we show here that the presence of ferromagnetic impurity phases compromised the earlier analysis. There has also been some confusion in the literature about the nature of the ordering of the Ru 4d spins in \( \text{Nd}_2\text{Ru}_2\text{O}_7 \); several reports have suggested that the ordering is glassy [8–10]. We find compelling evidence that ordering of Ru 4d spins in \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) is not consistent with spin-glass behaviour, and propose a reason for the observed history-dependence of the ZFC–FC magnetic susceptibility and weak ferromagnetism below the ordering temperature. Heat capacity studies of the magnetic transition in \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) are also presented here.

In \( A_2\text{Ru}_2\text{O}_7 \) pyrochlores the structural modifications between metallic and semiconducting members are small, suggesting that the electrical transport properties are delicately positioned near the edge of localized and itinerant behaviour. This positioning, at the edge of metal–insulator divide, potentially serves as a prime locator for thermoelectric materials: a high Seebeck coefficient is generally found in insulators, with potentially acceptable electrical conductivity on the metallic side, striking the right balance in properties [11, 12]. For this reason, we investigate the high-temperature thermoelectric properties of \( \text{Nd}_2\text{Ru}_2\text{O}_7 \). When compared to well-known chalcopyrite thermoelectric materials (for example, \( \text{PbTe}, \text{Bi}_2\text{Se}_3 \), and \( \text{Bi}_2\text{Te}_3 \)), metal oxides are of interest due to the expectation of higher stability at elevated temperatures and the prospect of using less toxic and more abundant elements. The discovery of high thermoelectric performance in \( \text{Na}_2\text{CoO}_4 \) [13] has led to renewed interest in oxide thermoelectric materials, despite the figure of merit (\( zT \)) of this system and other bulk oxide materials being too small for widespread use [12, 14]. Towards the goal of a more directed and effective search for high-performance metal–oxide thermoelectric materials, we also introduce a new type of plot for data visualization that can be used to rapidly screen potential candidates for thermoelectric performance.

2. Experimental details

Polycrystalline samples were made by direct reaction of constituent oxide powders (\( \text{RuO}_2 \), 99.99%, Sigma-Aldrich; \( \text{Nd}_2\text{O}_3 \), 99.99%, Alfa Aesar). Owing to the volatility of Ru oxides in air at high temperatures (\( \geq 1040 \) °C), samples were prepared with a 1 mol% excess \( \text{RuO}_2 \). Pellets were cold-pressed and annealed at 1000 °C for 7 days with several intermediate grindings, after which starting materials were still found by lab XRD. Following this initial reaction, pellets were wrapped in Pt-foil and annealed in evacuated silica ampoules at 1100 °C for 7 days. The samples were cooled to 800 °C at 0.5 °C min\(^{-1}\), and further annealed at 800 °C for 7 days to promote healing of defects. Finally, samples were cooled slowly to room temperature at 0.5 °C min\(^{-1}\). If \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) is annealed in air at 1040 °C or 1060 °C for 12 days, Rietveld analysis of XRD patterns indicates the sample contains 78 mol% \( \text{Nd}_3\text{Ru}_7\text{O}_{27} \) and 22 mol% \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) when the annealing temperature is 1040 °C, and pure \( \text{Nd}_3\text{Ru}_7\text{O}_{27} \) when the annealing temperature is 1060 °C.

To avoid the formation of \( \text{Nd}_3\text{Ru}_7\text{O}_{27} \) at the high temperatures and extended annealing times required for solid state reactions, polycrystalline samples of >99% purity were also made by ultrasonic spray pyrolysis (USP) of aqueous nitrate precursors (\( \text{Ru(NO)}_3\text{NO})_3 \), Sigma-Aldrich; and an aqueous solution of \( \text{Nd}^{3+} \), prepared by dissolving \( \text{Nd}_2\text{O}_3 \) in \( \approx 2 \text{M HNO}_3 \) [15, 16]. A modified ultrasonic humidifier was used to generate a mist, which was passed through a tube furnace (30.5 cm heating zone) at 700 °C with a positive pressure of air at a flow-rate of 5 scfm (\( \approx 140 \text{ l min}^{-1} \)). The product was collected in water, and the mixture was evaporated at 70 °C; the resulting black solid was cold-pressed into a pellet and annealed in air at 1100 °C for 8 h. Samples were then quenched in air (removed from the furnace at 1100 °C) or annealed in air for 7 days at 800 °C then cooled to room temperature at 1 °C min\(^{-1}\). Rietveld refinement of the structure with synchrotron XRD data revealed no significant differences in the bulk long-range structure between samples that were quenched rapidly and samples that were annealed at intermediate temperatures and cooled slowly, nor were there differences in structure between samples made by USP and samples made by solid state reaction. USP offers a rapid preparatory route to prepare \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) in \( \approx 24 \text{ h} \), rather than \( \approx 14 \text{ days} \).
Laboratory XRD was performed using a Philips X’Pert diffractometer with Cu Kα radiation and using mis-cut Si sample holders to reduce background signal. High-resolution synchrotron x-ray diffraction (XRD) data on finely ground powder was acquired at 100 K and 295 K at beamline 11-BM synchrotron x-ray diffraction (XRD) data on finely ground sample holders to reduce background signal. High-resolution a mixture of Si (SRM 640c) and Al₂O₃ (SRM 676) NIST standards run in a separate measurement. Samples were contained in 0.4 mm diameter Kapton capillaries and the packing density was low enough that absorption was not noticeable. Neutron powder diffraction was performed on the BT-1 diffractometer at the NIST Center for Neutron Research. A Cu(311) monochromator was used, with a constant wavelength of 0.15402(2) Å and a second-order contribution at 0.2. Data was collected at 300 K over the range of 3° to 168° 2θ with a step size of 0.05°. All diffraction data shown here are from a sample made by solid state reaction, though Rietveld analysis of data obtained by synchrotron XRD on other samples made by solid state reaction or USP led to identical results.

X-ray total scattering was performed at beamline 11-ID-B at the APS, using a wavelength of 0.137020 Å. The pair distribution function (PDF) was extracted with PDFgui [18] using Q = 28 Å⁻¹, and full-profile PDF structure refinement was completed using PDFgui [19]. Rρ and Δρ were refined on 1950 data points. Key instrumental parameters were Qbroad = 0.0551 Å⁻¹ and Qdamp = 0.00963 Å⁻¹, determined by using a CeO₂ standard in a separate measurement.

Magnetic properties of powders were measured using a Quantum Design MPMS XL-5 SQUID magnetometer. Zero-field cooled (ZFC) and field cooled (FC) measurements were performed between 2 K and 380 K with 100 Oe and 1000 Oe applied dc magnetic field. Data was collected in 0.5 K increments while heating or cooling at 1 K min⁻¹. In addition to dc measurements, frequency-dependent ac measurements were performed in a small temperature range between 130 K and 155 K. Low-temperature electrical transport properties and heat capacity were measured using a Quantum Design Physical Properties Measurement System. Samples for electrical transport measurements employed the 4-probe geometry on a pellet of sintered powder with dimensions of approximately 9 mm × 3 mm × 3 mm. Electrical contacts were made with copper wire and silver epoxy. Three samples were run to ensure reproducibility: two made using USP with apparent densities of 38% and 53%, and one made by ceramic preparation with an apparent density of 58%. Electrical resistivity at 300 K varied from 1.2 Ω cm to 2.4 Ω cm between the samples, and is consistent with previous reports of 1.8 Ω cm [20]. Despite slight differences in the magnitude of resistivity, all samples displayed consistent temperature-dependent behaviour. Heat capacity measurements were collected on a pellet of mass 13.90 mg made by pressing 50 wt% of sample and 50 wt% of silver powder (99.99%, Sigma-Aldrich) and analysed using the thermal relaxation dual-slope method. A thin layer of Apiezon N grease ensured thermal contact between the platform and the sample. The heat capacity of the Apiezon N grease and silver were collected separately and subtracted from the measured sample heat capacity.

High-temperature thermoelectric properties (electrical resistivity and Seebeck coefficient) were measured with an ULVAC Technologies ZEM-3. Sample pellets had approximate dimensions of 9 mm × 3 mm × 3 mm. Measurements were performed under a helium under-pressure, and data was collected through three heating and cooling cycles to ensure sample stability and reproducibility. No changes in physical properties were observed between cycles, and analysis of the lab XRD pattern of the materials after measurements showed no changes in structure nor new phases. Two different samples (USP and ceramic) were tested to verify consistency.

3. Results and discussion

3.1. Structure

The high symmetry ideal pyrochlore crystal structure is completely determined by the cubic cell parameter and a single positional structural parameter, given by the position x of O which is sited at (xO, 1/2, 1/2). However, there are many types of disorder that arise in this structure type, and a careful examination of the structure is necessary to understand properties. For example, Vanderah et al recently described the widespread presence of antisite disorder on the A-site; up to 25% of the large A-sites can be replaced with small B-site metal ions [21]. Placing large A-site ions on the smaller B-sites is less favourable, though previous studies have shown that antisite disorder on the B-site is also possible [22, 23]. Moreover, local off-centring of A-site cations is well-known in Ru pyrochlores such as Bi₂Ru₂O₇ [5, 24]. The presence of disordered oxygen vacancies has been observed in metallic members of A₂-,Bi₂Ru₂O₇ solid solutions [25]. Due to the relatively small x-ray scattering factor of O compared to the other elements present in A₂Ru₂O₇, use of only lab XRD has led to inaccurate determination of the O atomic position, as demonstrated by Kennedy and Vogt [25]. This inaccuracy has a large effect on the reported Ru–O–Ru bond angles, which are known to critically influence electrical properties. For example, in Bi₂Ru₂O₇, there is a 6° discrepancy, and for other A₂Ru₂O₇ members there is up to a 2° discrepancy in the reported Ru–O–Ru bond angles [3, 24, 26].

Combined Rietveld refinement was carried out using room-temperature data sets (figure 2), where the structure was refined on 51 295 data points. During the combined refinement, the synchrotron x-ray wavelength was fixed while the neutron wavelength was allowed to vary, though the refined wavelength was within two standard deviations of the starting value determined by previous instrumental calibration. Isotropic displacement parameters were used to describe the electron density of the atoms in the structure, as refinement of anisotropic displacement parameters did not improve the quality of the fit. Rietveld refinement...
Synchrotron x-ray diffraction studies offer the advantage that the Nd$^{3+}$ and Ru$^{4+}$ x-ray scattering factors are sufficiently distinct due to the large difference in atomic numbers. In contrast, neutron diffraction does not clearly distinguish between the similar coherent scattering lengths of Nd (7.03 fm) and Ru (7.69 fm) [30]. The synchrotron diffraction data allowed the recent findings of Vanderah et al regarding antisite disorder on the cation sites to be tested. The site occupancy and atomic displacement parameters are often correlated, so synchrotron x-ray data was collected at both 100 K and room temperature (295 K). However, these parameters were not strongly correlated in this investigation, and a combined Rietveld refinement using multiple temperatures did not change the outcome of the analysis. Accordingly, we continue our discussion using the combined Rietveld refinement of room-temperature x-ray and neutron diffraction datasets (figure 2). When Ru was allowed to substitute on the A-site, the refinement converged with 7.0(3) mol% Ru and a slight improvement in the fit. A similar trial refinement of Nd on the B-site did not improve the fit. The stability of all refined models (B-site disorder, A-site disorder, no antisite disorder) was verified by perturbing other parameters. Because allowing A-site disorder improves the fit only marginally, it is important to consider whether the improved fit is significant, or if the improvement is merely because more parameters are introduced. Use of a Hamilton test [31] shows the difference is statistically significant at <0.5% confidence interval. Indeed, with only one additional parameter between the two models, the large number of independent measurements makes virtually any improvement in $R_{wp}$ statistically significant. Visual inspection reveals only minor changes between the models, though in the limited areas where antisite disorder causes the largest changes, A-site disorder improves the fit to the experimental peak-shape (figure 3). The same results are obtained in samples made by USP and by solid state reaction. With these considerations in mind, the presence of A-site disorder is suggested.

The x-ray pair distribution function (PDF) obtained by total scattering agrees well with the model generated by the average, long-range structure (figure 4). Refinement of partial Ru substitution on the A-site was attempted, but the refined occupancy converged to unphysical values, potentially due to strong correlation with the scale factor. Ideal cation site ordering Nd$_2$Ru$_2$O$_7$ yielded a refinement $R = 10.05\%$ and allowing 7.0% Ru to occupy the Nd-site, as suggested from Rietveld refinement, yielded $R = 10.02\%$. The numerical improvement of the fit is marginal, and visual inspection reveals the difference between the models is much less than the level of noise present in the fit to the data. Rietveld refinement of Bragg scattering suggests partial antisite disorder, whereas PDF analysis of the total scattering shows no strong preference between full ordering or partial antisite disorder. This likely occurs because the PDF refinement is strongly weighted by near-neighbour correlations, which has been previously noted in the system La$_2$LiAuOs [32].

3.2. Magnetic and electrical transport behaviour

Zero-field cooled (ZFC) and field cooled (FC) measurements of the magnetic susceptibility show magnetic ordering of
Refinement with A-site disorder converges to 7.0(3)% Ru on the A-site and slightly improves the fit to the data, as demonstrated above by the better description of the peak-shape. Changes in the calculated diffraction pattern due to site disorder are small, with the most significant and diagnostic change occurring at the 311 reflection. For comparison, the most intense peak in this pattern has 85 000 counts.

Analysis of the synchrotron x-ray PDF reveals Nd$_2$Ru$_2$O$_7$ is well-described by an average long-range structural model.

Nd$_2$Ru$_2$O$_7$ at $T_N = 143$ K (figure 5), with a small cusp in the ZFC susceptibility. The higher-temperature region (340–380 K) of the susceptibility data was fitted to the Curie–Weiss equation, $\chi = C/(T - \Theta_{CW})$. The effective moment was extracted using the relationship $\mu_{eff}^2 = 3CK_B/N$, while the estimated spin-only and unquenched moments of Nd$_2$Ru$_2$O$_7$ were calculated using $\mu_{eff}^2 = 2\mu_{Ru}^2 + 2\mu_{Nd}^2$. The determined effective paramagnetic moment was $\mu_{eff} = 6.4 \mu_B$ per Nd$_2$Ru$_2$O$_7$ formula unit and the Weiss temperature was $\Theta_{CW} = -168$ K. The $\mu_{eff}$ is close to the calculated spin-only value of $\mu_S = 6.5 \mu_B$, and significantly less than the calculated unquenched $\mu_{L+S} = 11.9 \mu_B$. Curie–Weiss analysis reveals a negative $\Theta_{CW}$, indicating that the dominant magnetic interactions are antiferromagnetic. However, it is apparent from the first derivative (not shown) that the inverse susceptibility remains mildly non-linear as a function of temperature, indicating that Nd$_2$Ru$_2$O$_7$ does not display pure Curie–Weiss paramagnetism at these higher temperatures. Consequently, the determined Weiss temperature and $\mu_{eff}$ should be treated only qualitatively.

Rearranging the Curie–Weiss equation allows the scaled inverse susceptibility $C/(\chi T_{CW}) - 1$ to be displayed as a function of $T/|\Theta_{CW}|$ and provides a convenient way to visualize deviations from ideal Curie–Weiss paramagnetism (figure 5(b)) [33]. These deviations from Curie–Weiss behaviour are due to short-range interactions, and the negative deviation seen in Nd$_2$Ru$_2$O$_7$ arises from uncompensated moments. Additionally, the plot provides a convenient method to visualize magnetic frustration (the frustration index $f = \Theta_{CW}/T_N$) [34]. Moderately frustrated systems tend to have $f \geq 3$ [34], whereas for Nd$_2$Ru$_2$O$_7$ $f = 1.2$, indicating the antiferromagnetic ordering is not strongly frustrated.

Previous studies have shown that the transition at 143 K is the result of antiferromagnetic ordering of Ru$^{4+}$ 4d spins, as an analogous transition is observed in Y$_2$Ru$_2$O$_7$, where...
Figure 6. (a) The Ru antiferromagnetic ordering seen in the dc magnetic susceptibility at 143 K leads to decreasing $\chi T$ with decreasing temperature, and corresponds closely with (b) the single anomaly in the heat capacity with a maximum at 142 K. At low temperatures ($T < 5$ K), shown in the left panels, a downturn in $\chi T$ and an increase in heat capacity are observed, consistent with the onset of Nd antiferromagnetic order.

there are no 4f spins at the A-site [6, 10]. This is consistent with the negative Weiss temperature (figure 5(b)) and the decrease in $\chi T$ with decreasing temperature (figure 6(a)), which indicate the dominant magnetic interactions are antiferromagnetic. However, the Nd$^{3+}$ 4f spins continue to display paramagnetic behaviour, with an increase in susceptibility at lower temperatures. Previous studies have shown the rare-earth (RE) spins in Ru pyrochlores are slightly polarized by the weak RE–Ru exchange coupling, so the behaviour of the RE spins below ordering of the Ru sublattice is not truly paramagnetic [35–37]. Additionally, the history-dependence of the ZFC and FC measurements and the increased susceptibility at lower applied fields suggest there are weak uncompensated (i.e. ferromagnetic) moments (figure 5). The weak ferromagnetic interaction saturates at lower applied fields, so it has a diminished contribution to the field-normalized susceptibility at higher applied fields. Meanwhile, the ZFC–FC bifurcation of the magnetic susceptibility is consistent with weak ferromagnetism arising from spin canting, and is described later in more detail. Below $\approx 5$ K, there appears to be another transition, which causes a downturn in the $\chi T$ and an upturn in the $C_P$ (figure 6).

The specific heat contains a corresponding $\lambda$-type anomaly with a maximum at 142 K (figure 6(b)), consistent with a second-order phase transition. Additionally, the electrical resistivity near the magnetic ordering temperature displays anomalous behaviour. An Arrhenius-style plot shows a change in slope at the magnetic ordering temperature (figure 7). Electrical conduction in $A_2\text{Ru}_2\text{O}_7$ materials involves Ru 4d states, and magnetic ordering of Ru 4d spins causes a subtle change in electrical transport due to changes in scattering, as shown in the derivative of figure 7. Low-temperature electrical resistivity follows a 3D variable-range hopping model with

$$\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^{1/4}$$

[39, 40], with a change in the hopping barrier at the magnetic ordering temperature ($T_N = 143$ K). Fitting the entire dataset yields $\rho_0 = 5.64 \times 10^{-10} \Omega \text{cm}$ and $T_0 = 6.89 \times 10^7$ K.

There has been considerable confusion in the literature about the nature of the ordering of the Ru 4d spins in Nd$_2$Ru$_2$O$_7$ and analogous Ru pyrochlores, in part due to the unusual field-dependent hysteresis present between the ZFC and FC susceptibility measurements, and also due to the many types of disorder and exotic phenomena that sometimes accompany geometric frustration in magnetic pyrochlores. In particular, several reports have mentioned that the glassy nature of the ordering of Ru 4d spins is evident in bulk magnetic susceptibility measurements [8–10, 41, 37]. However, neutron diffraction experiments below the ordering temperature show that Ru spins order with a long correlation length [9, 10]. This is incompatible with a glassy-state, where there is no long-range magnetic order.

This is not the only signature of a spin-glass that is violated by

Figure 7. (a) Low-temperature electrical resistivity follows a Mott 3D variable-range hopping model, but deviates at the magnetic ordering temperature ($T_N = 143$ K). Magnetic ordering of the Ru 4d conduction electrons leads to a change in the electrical transport, as shown in the derivative (b).
experimental evidence. Notably, the temperature-dependence of the specific heat should vary smoothly near the magnetic ordering temperature [42], a stark contrast with the $\lambda$-type anomaly at 143 K, shown in figure 6(b).

Ac magnetic susceptibility measurements were also conducted, as another signature of a spin-glass is a magnetic ordering temperature that varies with the frequency of the applied magnetic field [42, 43]. The real, in-phase, component of the ac susceptibility ($\chi'$) is shown in figure 8(a), while the imaginary, out of phase, component of the complex susceptibility ($\chi''$) was below the instrumental detection limit (not shown). Because the response of the Nd$^{3+}$ dominates the total susceptibility, a paramagnetic background was fit using the Curie–Weiss equation and subtracted to obtain the change in susceptibility due to antiferromagnetic ordering of Ru 4d spins (figure 8(b)). The antiferromagnetic ordering temperature associated with the Ru 4d spins is independent of frequency, which is inconsistent with canonical spin-glass behaviour [42, 43].

A spin-glass, by definition, must lack long-range order and display a frequency-dependent peak in the susceptibility [42, 43]; neither condition is satisfied in Nd$_2$Ru$_2$O$_7$. Moreover, owing to the weak exchange coupling between rare-earth 4f spins and Ru 4d spins, the nature of magnetic ordering of Ru 4d spins is not expected to differ as the identity of the rare-earth atom changes in the A$_2$Ru$_2$O$_7$ ($A = Pr, \ldots, Lu, Y$) series, so it is also unlikely that other members are spin-glasses.

Adding to the confusion regarding the magnetic behaviour of A$_2$Ru$_2$O$_7$ ($A = Pr, \ldots, Lu, Y$), previous studies of Nd$_2$Ru$_2$O$_7$ have claimed there is ferromagnetic ordering at 20 K, and reported a hysteresis in the low-temperature field-dependent magnetization [7], neither of which were observed here in samples of >99% purity. Additionally, a later study of the specific heat of Nd$_2$Ru$_2$O$_7$ showed multiple anomalies at 130 K and 20 K, in addition to the anomaly observed here at 142 K [8]. However, the ferromagnetic ordering at 20 K and the other specific heat anomalies are features of Nd$_3$Ru$_2$O$_7$, a secondary phase that is easily formed during preparation of Nd$_2$Ru$_2$O$_7$ and to which we attribute the ferromagnetic ordering and other specific heat anomalies. Extensive study of Nd$_3$Ru$_2$O$_7$ by neutron diffraction, magnetization, and specific heat measurements has shown the material undergoes a transition with a peak at 19 K due to ordering of both Ru$^{4+}$ and Nd$^{3+}$ spins [44]. Additionally, there is a peak in the specific heat at 130 K, corresponding to a first-order structural phase transition. Although preparation of A$_2$Ru$_2$O$_7$ ($A = Pr, \ldots, Lu, Y$) by a ceramic method appears straightforward, care must be taken at high temperatures in air to prevent slow decomposition of the product. To demonstrate this, Nd$_3$Ru$_2$O$_7$ was annealed in air at 1040°C and 1060°C for two weeks, and led to the formation of Nd$_3$Ru$_2$O$_7$ as a dominant, or single phase. In the literature, preparation of Nd$_3$Ru$_2$O$_7$ appears to consistently lead to appreciable amounts of Nd$_3$Ru$_2$O$_7$ as a secondary phase, with some studies showing up to 10 mol% [9]. Due to the similar properties and chemistry of analogous A$_2$Ru$_2$O$_7$ systems, it is not surprising to see similar features near 20 K in the magnetic susceptibility and the specific heat (e.g., ferromagnetic ordering and a $\lambda$-type anomaly) [8], as these features may originate from an A$_3$Ru$_2$O$_7$ secondary phase.

### 3.3. Electrical transport in Ru pyrochlores

The nature of the electrical transport behaviour in ruthenium pyrochlores (A$_2$Ru$_2$O$_7$) has been of considerable interest, as the nature of the A-site ion dictates whether the material will be insulating (e.g., $A = Pr, \ldots, Lu, Y$) or metallic (e.g., $A = Ti, Pb, Bi$) [3, 29, 45–47]. The most intuitive model has sought to explain the different behaviour strictly with the A-site ionic radius, as increasing the A-site radius increases the Ru–O–Ru bond angle. Electrical conduction takes place in the Ru$_2$O$_7$ network through overlap of Ru 4d and O 2p orbitals, so a larger Ru–O–Ru bond angle increases this overlap, the bandwidth, and the electrical conductivity [2, 3, 46].

Unfortunately, testing this relationship is not straightforward, as no lanthanide leads to metallic behaviour. Although the La$^{3+}$ radius is similar to Bi$^{3+}$ and should thus be large enough to induce metallic behaviour, La$_2$Ru$_2$O$_7$ is outside the pyrochlore stability-field [1, 6, 48]. Several studies interested in the electrical conductivity of these systems have examined solid solutions with Bi or Pb to overcome this hurdle and increase the average ionic radius to the point at which the system becomes metallic [3, 20, 25, 26, 29, 49]. However, it is not appropriate to compare rare-earth Ru pyrochlores with those containing Pb or Bi [e.g., Pb$_2$Ru$_2$O$_7$, Tl$_2$Ru$_2$O$_7$], as these contain either A-site ions of different formal charge in the case of Pb$^{2+}$, or have contributions from overlap between empty 6s states and filled states, as in the case of Tl$^{3+}$. Even an isovalent substitution of Ln$^{3+}$ by Bi$^{3+}$ may not allow straightforward comparison; structural studies of Bi$_2$Ru$_2$O$_7$ have shown that Bi$^{3+}$ atoms are off-centred due...
Figure 9. Room-temperature electrical resistivity of $A_2\text{Bi}_2\text{Ru}_2\text{O}_7$ ($A = \text{Pr}, \ldots, \text{Lu}, \text{Y}$) solid solutions decrease smoothly with increasing average cation radius. Introduction of Bi drastically changes the behaviour (circles); the materials become metallic near a typical substitution of $x = 0.5$. Dotted lines are guides to the eye, and the thin dashed line at $\rho = 0.01 \Omega \text{ cm}$ represents the Mott minimum metallic conductivity at room temperature. Ionic radii of 8-coordinate 3+ cations were taken from Shannon [50]. Values of electrical resistivity were taken from [1, 3, 20, 26, 51–54].

Casual examination of figure 9 suggests a monotonic decrease in the room-temperature resistivity as the ionic radius of the $A$-site increases, when only the rare-earth-containing pyrochlores ($A_2\text{Bi}_2\text{Ru}_2\text{O}_7$, $A = \text{Pr}, \ldots, \text{Lu}, \text{Y}$) are considered. However, placing a small amount of Bi on the $A$-site dramatically changes the electrical transport; the onset of metallic behaviour occurs at a typical substitution of $x = 0.5$ in $A_2\text{Bi}_2\text{Ru}_2\text{O}_7$. The difference in electrical resistivity is striking, and suggests there is more than the effect of ionic radius when Bi is incorporated into the material. We argue that local distortion of Bi centres in Ru pyrochlores is responsible for the metallic behaviour and the distinct behaviour of $\text{Bi}_2\text{Ru}_2\text{O}_7$ and $A_2\text{Bi}_2\text{Ru}_2\text{O}_7$ when contrasted with Bi-free samples. Other researchers have pointed to the presence of additional oxygen vacancies (other than the ordered vacancy dictated by the pyrochlore structure) and decreased Ru–O bond distance that accompany metallic behaviour [3, 29], though these are a result, rather than the cause, of metallic bonding.

3.4. High-temperature thermoelectric properties

The electrical transport properties of rare-earth $A_2\text{Ru}_2\text{O}_7$ ($A = \text{Pr}, \ldots, \text{Lu}, \text{Y}$) members are near the onset of metallic behaviour. This unique position is a good place to examine thermoelectric properties, where there is a balance between a high Seebeck coefficient and low electrical resistivity. Electrical resistivity and Seebeck coefficient of $\text{Nd}_2\text{Ru}_2\text{O}_7$ are presented from 300 K to 900 K (figure 10). The thermoelectric properties of $\text{Nd}_2\text{Ru}_2\text{O}_7$ do not change over three measurement cycles, despite the low oxygen partial pressure and high temperature during measurements. The room-temperature electrical resistivity is 2.0 $\Omega$ cm, and decreases with increasing temperature, as expected for a non-metal. The room-temperature Seebeck is promising ($=220 \mu \text{V K}^{-1}$), but quickly decreases with increasing temperature, and $\approx20 \mu \text{V K}^{-1}$ above 420 K. $\kappa z T$ is also presented (figure 10(b)), as a proxy for the thermoelectric figure of merit, and is several orders of magnitude too small for $\text{Nd}_2\text{Ru}_2\text{O}_7$ to be a competitive thermoelectric material. The thermoelectric figure of merit, $z T$, is given by $z T = S^2 T / (\rho \kappa)$ and is a function of the Seebeck coefficient $S$, electrical resistivity $\rho$, thermal conductivity $\kappa$, and temperature $T$. Many materials exhibit a thermal conductivity between 1 and 10 W m$^{-1}$K$^{-1}$, so $z T$ is a useful proxy to compare the electrical performance of thermoelectric materials and estimate $z T$ within an order of magnitude.

Following our investigation of $\text{Nd}_2\text{Ru}_2\text{O}_7$ and learning of its low $\kappa z T$ at high temperatures, we realized that a simple analytical method for estimating the competitiveness of a thermoelectric at high temperatures would be useful for identifying new candidate materials. Such a method would be especially helpful if it did not require high-temperature measurements, as this would save time and resources. Many materials are currently being screened for high-temperature thermoelectric performance, but measurements at elevated temperatures require specialized instrumentation that is not widely available. Room-temperature Seebeck measurements...
small and leads to a vanishingly small point, it is represented by the symbol × in figure 10(c).

This type of analysis is particularly useful in establishing that the performance of a particular class of materials may be ineffectual due to a key property being outside the useful range. The choice of axes is similar to a Jonker plot, in which the Seebeck coefficient is plotted versus electrical conductivity. However, Jonker plots are used to examine the effect of changing the carrier concentration of a single material rather than looking at a field of candidate thermoelectrics [59, 60]. Also, while Zhu et al have shown that Jonker plots could be used to estimate the peak thermoelectric power factor ($S^2\rho^{-1}$) of a material [61], other analyses are involved, and the approach is distinct from the one employed here.

4. Conclusion

Pyrochlore Nd$_2$Ru$_2$O$_7$ has been prepared and examined using a combination of structural, magnetic, and electrical and thermal transport studies. Some substitutional disorder on the A-site is proposed from the structural studies, but is not anticipated to strongly influence the physical properties. The magnetic behaviour of Nd$_2$Ru$_2$O$_7$ has been clarified through a combination of dc and ac magnetic measurements, and heat capacity studies. Despite the potential for geometric frustration of magnetism in the pyrochlore structure type, we find no such exotic behaviour or glassiness in Nd$_2$Ru$_2$O$_7$ above 5 K, and instead tentatively suggest Nd$_2$Ru$_2$O$_7$ is a canted antiferromagnet that displays weak ferromagnetism. When the electrical transport properties are regarded in light of published data on rare-earth substituted A$_2$Ru$_2$O$_7$ pyrochlores, it is clear that ionic radius plays a key role in determining electrical behaviour. However, the metallic electrical properties that accompany incorporation of Bi$^{3+}$ on the A-site lie outside this description, and we suggest Bi$^{3+}$ off-centring may drive this anomalous behaviour. High-temperature measurements of the thermoelectric properties indicate that Nd$_2$Ru$_2$O$_7$ has excessively high electrical resistivity for it to be a useful thermoelectric, despite displaying a promising Seebeck coefficient at room temperature. We propose a modified version of the Jonker plot as a powerful tool to screen candidate thermoelectric materials. We find that it is particularly useful in establishing that a particular class of materials may be ineffectual due to a key property being outside the useful range.

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