Structural and physical properties of trilayer nickelates \( R_4Ni_3O_{10} \) (\( R = \text{La}, \text{Pr} \) and \( \text{Nd} \))

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(Dated: July 16, 2020)

Here, we investigate in detail the low temperature structural and physical properties of the trilayer nickelates \( R_4Ni_3O_{10} \) (\( R = \text{La}, \text{Pr} \) and \( \text{Nd} \)) using resistivity, thermopower, thermal conductivity, specific heat, high-resolution synchrotron powder X-ray diffraction, and thermal expansion experiments. We show that all three compounds crystallize with a monoclinic symmetry (space group \( P21/a, Z = 4 \)), and undergo a metal-to-metal transition (MMT) near \( T_{\text{MMT}} \approx 135 \text{ K (La)}, 156 \text{ K (Pr)} \) and \( 160 \text{ K (Nd)} \). Upon cooling below MMT, the lattice parameters in each case show a distinct anomaly at \( T_{\text{MMT}} \), however, without any lowering of the lattice symmetry. Unambiguous signatures of MMT are also observed in magnetic and thermal measurements, suggesting that there is a strong coupling between the electronic, magnetic and structural degrees of freedom in these nickelates. Analysis of thermal expansion yields hydrostatic pressure dependence of MMT in close agreement with previous experimental results. In \( \text{Pr}_4\text{Ni}_3\text{O}_{10} \), we show that the 9-fold coordinated \( \text{Pr}^{3+} \) ions in the rocksalt (RS) layers have a crystal field (CF) split doublet ground state with possible antiferromagnetic ordering near 5 K. In contrast to this, the \( \text{Pr}^{3+} \) ions in the perovskite-block (PB) layers with a 12-fold coordination seems to exhibit a non-magnetic singlet ground state. In \( \text{Nd}_4\text{Ni}_3\text{O}_{10} \), on the other hand, the CF ground state of \( \text{Nd}^{3+} \) ions in both RS and PB layers is a Kramers doublet. The heat capacity of \( \text{Nd}_4\text{Ni}_3\text{O}_{10} \) shows a pronounced Schottky-like anomaly near \( T = 35 \text{ K} \); and, an upturn below 10 K due to the presence of short-range correlations between the Nd moments. However, no signs of long-range ordering could be found down to 2 K despite a sizeable value of \( \theta g \sim -40 \text{ K} \). The strongly suppressed magnetic long-range ordering in both \( R = \text{Pr} \) and \( \text{Nd} \) suggests the presence of strong magnetic frustration in these compounds. The low-temperature resistivity shows a \( -\sqrt{T} \) dependence, and the electronic term in the specific heat of \( \text{Nd}_4\text{Ni}_3\text{O}_{10} \) is falsely inflated due to the overwhelming Schottky contribution. These observations rule out the alleged heavy fermion behavior recently reported for \( \text{Nd}_4\text{Ni}_3\text{O}_{10} \).

PACS numbers:

I. INTRODUCTION

The transition metal oxides based on nickel, or the nickelates for short, have witnessed a resurgence of interest in the last few years. Several recent papers have shown that nickelates are unique due to their strongly coupled charge, spin and lattice degrees of freedom, which can be manipulated to engineer novel electronic and magnetic phases (see for example Ref. 1–3). Another reason for this resurgence could be attributed to the discovery of superconductivity in \( \text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2 \) by Li et al. in the year 2019, which, in fact, led to the fulfillment of a long-sought-after quest for superconductivity in the nickelates\(^4\). Nearly two years before this momentous discovery, an ARPES study on single crystals of \( \text{La}_4\text{Ni}_3\text{O}_{10} \), which is the \( n = 3 \) member of the Ruddlesden Popper (RP) \( \text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1} \) (\( n = 1, 2, 3 \ldots \infty \)) series, revealed a large hole Fermi surface that closely resembles the Fermi surface of optimally hole-doped cuprates\(^5\) (see also Ref. 6). This discovery is important since the infinite layer \( \text{NdNiO}_2 \) (called the \( T' \) phase) is related to the perovskite \( \text{NdNiO}_3 \) (\( n = \infty \) member of RP series) from which it is obtained through the process of chemical reduction. In general, there is a whole range of infinite layer \( T' \) phases given by \( \text{R}_{n+1}\text{Ni}_n\text{O}_{2n+2} \) (\( n = 1, 2, 3 \ldots \infty \)), where \( R \) is usually an alkaline earth or rare-earth ion, that are analogously related to their corresponding RP \( \text{R}_{n+1}\text{Ni}_n\text{O}_{3n+1} \) phases. The nickelates of the RP series, therefore, constitute the primary phases with perovskite-type structure elements from which other nickelates, including the infinite layer \( T' \) variants, can be derived.

A survey of past literature reveals that the \( n = \infty \) member, namely, \( \text{R}_4\text{Ni}_3\text{O}_{10} \) (where \( R \) is a tripositive rare-earth ion) are amongst the most intensively investigated members of the RP series\(^7\). The \( \text{R}_4\text{Ni}_3\text{O}_{10} \) family has a rich phase diagram showing a sharp metal-to-insulator transition (MIT) for all the members except \( \text{La}_4\text{Ni}_3\text{O}_{10} \), which has an unconventional metallic and paramagnetic ground state\(^8\). The MIT in \( \text{R}_4\text{Ni}_3\text{O}_{10} \) is accompanied by a transition to a magnetically ordered phase and depending on the rare-earth ion occupying the \( R \) site the magnetic ordering is either concomitant with the MIT (for \( R = \text{Pr} \) and \( \text{Nd} \)) or occurs below the MIT (for \( R = \text{Eu}, \text{Gd}, \text{etc.} \) ). In contrast, the \( n = 1, 2, 3, \ldots \) members are relatively much less investigated – an exception to this being \( \text{La}_2\text{NiO}_4-\delta \) (\( n = 1 \)), which shows a very interesting and complex phase diagram as a function of the oxygen content\(^9\). The intermediate members between \( n = 1 \) and \( n = \infty \) of the RP series also exhibit a mixed-valent phase, ranging from \( 2+ \) for \( n = 1 \) to \( 3+ \) for \( n = \infty \). Such a mixed-valency is well-known to give rise to strongly coupled electronic and magnetic phases (see for example Ref. 10).

In this regard, the \( n = 3 \) member of the RP series would be an interesting family of compounds to investigate with an...
average Ni valence of 2.67. The compounds $R_4Ni_3O_{10}$ ($R = \text{La, Pr and Nd}$) are relatively easy to synthesize in pure form, and, if needed, can readily be reduced to their corresponding infinite layer $T^\prime$ analogs. Previous studies have shown that they undergo a metal-to-metal transition (MMT) in the temperature range 135 K to 160 K depending on the identity of the $R$ ion. While the exact nature of this transition is as yet unclear, it is generally believed to be associated with a charge-density-wave (CDW) like instability. The occurrence of CDW ordering at the MMT is favored by the ARPES study on $La_4Ni_3O_{10}$, which revealed a gap of about 20 meV opening up at the Fermi energy upon cooling the sample below $T_{\text{MMT}}$\(^5\). While writing this paper, we came across another recent report on the preprint server condmat arxiv where it has been proposed that this transition involves a very unusual incommensurate density wave having both charge and magnetic signatures\(^{11}\).

A theoretical study of the MMT has been recently done by Puggioni et al.\(^{12}\) who employed density functional theory to argue that at low temperatures $La_4Ni_3O_{10}$ should undergo "a hitherto unreported structural phase transition and transforms to a new monoclinic $P2_1/a$ phase". Experimentally, however, the exact symmetry of even the room-temperature phase of $La_4Ni_3O_{10}$ has been continuously debated as reviewed later in the manuscript (see section III). In contrast, the crystal structure and space group symmetry of both $Pr_4Ni_3O_{10}$ and $Nd_4Ni_3O_{10}$ is relatively less ambiguous. In these compounds, however, the presence of an additional magnetic sublattice of the rare-earth moments makes their magnetic behavior, both rich and complex, which is beginning to attract considerable attention recently. In a recent study, an isotropic but discontinuous change of lattice parameters has been reported across the MMT in $Nd_4Ni_3O_{10}$\(^{13}\). In the same report, the low-temperature upturn in resistivity, and a large value of electronic specific heat, have been interpreted as arising due to the Kondo effect in the Ni-sublattice. As for $Pr_4Ni_3O_{10}$, it has been shown recently that the $b$-axis of the unit cell undergoes a negative thermal expansion upon cooling below MMT\(^{14}\). In another very recent transport study employing single-crystalline samples, the MMT in $Pr_4Ni_3O_{10}$ has been argued to be of first-order type with a metal-to-metal transition in the in-plane resistivity, and a metal-to-insulator in the out-of-plane\(^{15}\) resistivity. However, the magnetic ground state of Pr or Nd sublattices in these compounds has remained poorly understood. Furthermore, the anomalies in the lattice parameters at the MMT recently uncovered invite further detailed, high-resolution, structural and thermal expansion studies.

Here, we use very high-resolution synchrotron based powder X-ray diffraction data to investigate the structure of $R_4Ni_3O_{10}$ ($R = \text{La, Pr and Nd}$) in the temperature range from $T = 300$ K to 90 K, which adequately spans the MMT in all three compounds. High-resolution thermal expansion measurements are carried out in the temperature range from $T = 200$ K to 2 K, which are used to examine the structural changes at $T_{\text{MMT}}$, the variation of Grüneisen parameter ($\Gamma$) across the MMT and to derive the hydrostatic pressure dependence of $T_{\text{MMT}}$. The thermal conductivity ($\kappa$), ther-
intergrowth, which greatly influences the physical properties of the compounds. Hence, we adopted a wet chemical method (citrate route) to synthesize pure phase of the $R_4\text{Ni}_3\text{O}_{10}$ ($R = \text{La, Pr and Nd}$) compounds. Stoichiometric amounts of $R_2\text{O}_3$ ($R = \text{La, and Nd}$) or Pr$_5\text{O}_{11}$ (Sigma Aldrich, 99.99\%, preheated at 1000 °C prior to use in each case), and $\text{NiO}$ (Sigma Aldrich, 99.999\%) were added to 15M nitric acid solvent. The solution was heated till the precursors dissolved and formed a clear, transparent, light green solution. Then an equimolar amount of anhydrous citric acid powder (ACS reagent, ≥ 99.5\%) was added and this solution was slowly heated up to 280 °C, whereby reddish brown vapours of nitrous oxide evolved and the solution attained a green gel-like texture. The gel was further dried by heating it up to 300 °C till it turned off-white with a yellowish tinge. At around 350 °C, the citrates were decomposed by auto-ignition process and this yielded very fine grey powder of the oxide precursors. The resultant powders were cold pressed into pellets and heated in flowing oxygen for 24 h with intermediate grinding and pelletizing. The sinterings were carried out at 1100 °C for La$_4\text{Ni}_3\text{O}_{10}$, 1050 °C for Pr$_4\text{Ni}_3\text{O}_{10}$ and 1000 °C for Nd$_4\text{Ni}_3\text{O}_{10}$. The pure phase of the samples was obtained after four sinterings. The phase purity after each sintering was monitored using a Bruker D8 Advance powder X-ray diffractometer. The chemical composition of the samples was analyzed using the energy dispersive X-ray analysis (EDX) technique in a Zeiss Ultra Plus scanning electron microscope.

Since the structural and electronic properties of R phases often show strong dependence on the oxygen stoichiometry, we carried out complete decomposition of our samples under 10% Ar-H$_2$ atmosphere employing a heating rate of 5 K/min in a high resolution TGA setup (Netzsch STA 449 F1). Using these experiments, we inferred the oxygen stoichiometry to lie in the range 97 % to 98 % of the ideal value for all the samples.

The high-resolution synchrotron powder X-ray diffraction experiments were carried out at the MSPD-BLO4 beamline of the ALBA synchrotron center, Barcelona, Spain. The samples were prepared in the form of finely ground powders that were placed in a borosilicate capillary tube of 0.5 mm inner diameter. The sample was cooled using an Oxford Cryostream 700 series nitrogen blower, and the diffractograms were collected in the range 0° ≤ 2θ ≤ 30° with a step size of 0.003°. The incident beam energy was set at 38 keV ($\lambda = 0.3263$ Å) and a high resolution detector (MAD26) was used to resolve any subtle structural modifications. The structural refinement was done by the Rietveld method using the FULLPROF suite. For the refinement of our synchrotron data, we adopted the following procedure: The occupancies of all the O–sites are fixed as fully occupied since X-Ray diffraction is not sensitive to the position of lighter elements. The Pseudo-Voigt function was used to model the line-profile. Linear interpolation method was used to define the background. To account for the anisotropic strain broadening of the peaks, we incorporated a strain model called as Broadening Model (quartic form). According to this model, only certain hkl dependent strain pa-

![FIG. 1: The crystal structure of trilayer $R_4\text{Ni}_3\text{O}_{10}$ ($R = \text{La, Pr and Nd}$) nickelates. Here PB represents the perovskite block and RS represents the rocksalt layer. R1 and R3 denote 9–fold and 12–fold coordinated rare-earth ions located in RS and PB, respectively.](image-url)
III. RESULTS AND DISCUSSION

A. Crystal structure

$L_{12} Ni_3 O_{10}$: There is a great deal of ambiguity in the literature regarding the space group that correctly defines the crystal structure of $La_4 Ni_3 O_{10}$. The earliest work by Seppänen et al. reported an orthorhombic space group $Fmmm^{20}$. However, Tkalić et al.\textsuperscript{21}, and Voronin et al.\textsuperscript{22} used the space group $Cmca$. Ling et al.\textsuperscript{23}, on the other hand, found the orthorhombic space group $Bmab$ (unconventional setting for $Cmca$) to be more suitable for refining their neutron powder diffraction data. Zhang et al. carried out structural refinement on the powders obtained by grinding floating-zone grown single crystalline specimens\textsuperscript{24}. They found the space group $Bmab$ as most suitable for their as-grown crystal specimen. However, they also noted that depending on the post-growth cooling conditions, the structure can transform to the space group $P2_1/a$. Finally, in a recent synchrotron based study, the symmetry of sintered $La_4 Ni_3 O_{10}$ is reported to be monoclinic $P2_1/a, Z = 4^{24}$.

In order to find the most appropriate space group from among those that were previously reported, we started by refining the structure using one space group at a time. To avoid biasing this procedure, every space group is tried till the refinement could not be improved any further. At the end of this rigorous exercise, whose results are detailed in the supplementary information (SI), we found that the monoclinic space group $P2_1/a$ (SG no. 14, $Z = 4$) best represents the experimental data. However, even with $P2_1/a$, the calculated profile around the high intensity peaks in the range $2\theta = 6^\circ$ to $7^\circ$, and those around $2\theta = 9.7^\circ$, remain far from perfect due to small differences between the measured and calculated intensities as shown in SI. In the paper by Kumar et al.\textsuperscript{24}, where the space group $P2_1/a$ was used, a similar difference between the calculated and measured intensities can be seen (see Fig. 2a and 2b of Ref. 24).

We therefore attempted a mixed phase refinement wherein, besides the principal $P2_1/a$ phase, two additional phases: (i) the orthorhombic $Bmab$ (SG no. 64) phase, and (ii) a lower ($n = 2$) member of the Ruddlesden Popper nickelate family, i.e., $La_3Ni_2 O_7$, with an orthorhombic space group $Cmcm$ (SG no. 63), are also incorporated. As shown in SI, inclusion of the orthorhombic $Bmab$ phase alone (2-phase refinement) improves the quality of fit significantly. In this 2-phase refinement we find $P2_1/a$ to $Bmab$ phases to be in the ratio 86.3 : 13.7. In order to see if we can get an even better match with the observed intensities, we also tried including $La_3Ni_2 O_7$ along with $Bmab$ (3-phase refinement). This lead to a slight improvement over the 2-phase refinement. In this case, whose results are shown in Fig. 2(a), we find the ratio $P2_1/a : Bmab : La_3Ni_2 O_7$ of three phases to be 85.6 : 7.8 : 6.6. Clearly, in both 2- and 3-phase refinements, the phase fraction of the primary phase $P2_1/a$ remains more or less unchanged. Since the Bragg peaks due to all three phases overlap considerably, it is difficult to say which of the two, 2- or 3-phase refinement, represents the actual scenario. Since the R-factors quantifying the quality of fit are marginally lower for the 3-phase refinement, here we have shown the results for the same. More details concerning these refinements can be sought from the supplementary information. The coexistence of $P2_1/a$ with a small amount...
of \(Bmab\) is in agreement with the work of Zhang et al. who show that \(La_4Ni_3O_{10}\) crystallizes in a mixture of \(Bmab\) and \(P2_1/\alpha\)—their relative phase fraction being a function of the cooling condition employed. For example, the phase \(Bmab\) transforms almost completely to \(P2_1/\alpha\) when annealed under flowing oxygen. Since, we synthesized our samples under flowing oxygen conditions, the presence of predominantly \(P2_1/\alpha\) phase is consistent with this report. However, it is possible that some amount of phase \(Bmab\) may have remained.

Finally, there is still some mismatch between the observed and calculated intensities around \(2\theta = 10^\circ\); this has been reported in the previous studies also and may arise from stacking faults\(^{25}\). It should also be remarked, that a small extra peak, \(\sim 1\%\) of the intensity of the main peak, near \(2\theta = 89.55^\circ\), is also observed (see, Fig. 3(b), 3(f) or 3(j)), which indicates the presence of a small unidentified parasitic phase.

Fig. 2(b-f) show the temperature variation of the lattice parameters of \(P2_1/\alpha\) phase. The lattice parameters decrease monotonically upon lowering the temperature down to \(T_{MMT}\) below which the \(b\)–axis expands upon further cooling; the lattice parameters along the \(a\)– and \(c\)–axis, on the other hand, continue to decrease, but they too exhibit clearly discernible anomalies at \(T_{MMT}\). The diffraction patterns recorded below MMT revealed neither any new or additional diffraction peaks nor any peak splitting, which suggests that the structural reorganization across the MMT, if any, is rather subtle (see, Fig. 3). The negative thermal expansion along the \(b\)–axis observed here agrees well with that reported by Kumar et al.\(^{24}\). The temperature variation of angle \(\beta\) is shown in panel (e). \(\beta\) increases with decrease in temperature showing a sudden dip near MMT. Additionally, a change of slope in the temperature variation of \(\beta\) is also observed around \(T = 250\) K. In the same temperature range even the lattice parameters show a slight change of slope, which might possibly suggest the presence of an additional subtle structural re-organization before the onset of MMT. For comparison, the normalized lattice parameters are shown in Fig. 2(g).

**Pr\(_4Ni_3O_{10}\):** Fig. 4 shows the results of Rietveld refinement performed on the room temperature synchrotron powder X-ray diffraction data for \(Pr_4Ni_3O_{10}\). In this case, the structural refinement was carried out using the monoclinic space group \(P2_1/\alpha\) (SG no. 14, \(Z = 4\)), which resulted in a satisfactory fit except near the highest intensity peak, where the calculated profile does not exactly match the observed data. Inclusion of a strain model helped to some extent but did not resolve the issue completely. Apparently, Zhang et al. also observed a similar inconsistency over the same \(2\theta\) range\(^{14}\). Whether the stacking faults or the intergrowth of lower RP members is the reason for this, however, could not be reliably ascertained. Also, analogous to \(La_4Ni_3O_{10}\), some intensity mismatch is observed near \(2\theta = 10^\circ\) (peak 221), which may be due to the stacking faults\(^{25}\). The room temperature lattice parameters obtained are \(a = 5.383\ \text{\AA},\ b = 5.472\ \text{\AA},\ c = 27.583\ \text{\AA}\) and \(\beta = 90.28^\circ\) which agree well with the values reported by Bassat et al.\(^{26}\).

We also carried out low temperature synchrotron XRD to capture structural modifications, if any, associated with the MMT. The low-temperature powder diffraction synchrotron data for \(Pr_4Ni_3O_{10}\) is shown in the supplementary information as Fig. S3. At low-temperatures, and specifically across \(T_{MMT}\), no unambiguous sign of new diffraction peak(s) emerging or splitting could be see. However, the relative intensity of the highest intensity peaks in the \(2\theta\)–range spanning \(6.5^\circ\) to \(7^\circ\) interchanges (see, Fig. S3 in SI). As shown in Fig. 4(b-e), in the temperature range around \(156\) K, where MMT is expected to occur, clear anomaly in all the lattice parameters is seen. The \(b\)–axis parameter shows an increase upon cooling below the MMT analogous to \(La_4Ni_3O_{10}\). Interestingly, a clearly discernible anomaly has also been observed above the MMT, near \(T = 200\) K. The presence of this anomaly is also reflected in the temperature variation of parameter \(\beta\), which exhibits a prominent dip at this temperature. Our data, therefore, suggest the presence of an additional subtle structural modification above the MMT near \(200\) K. Absence of any new X-ray diffraction peaks or splitting of any of the existing peaks across these transitions suggests that the overall symmetry of the structure remains unchanged over the temperature range examined here.

**Nd\(_4Ni_3O_{10}\):** Fig. 5 shows the results of Rietveld refinement performed on the room temperature synchrotron powder X-ray diffraction data for \(Nd_4Ni_3O_{10}\). The structural refinement was done using the monoclinic space group \(P2_1/\alpha\) (SG no. 14; \(Z = 4\)). The peak shape of the highest intensity peak was unusually broad and a strain model (2) was used to account for this anisotropic strain broadening. The room temperature lattice parameters obtained are \(a = 5.372\ \text{\AA},\ b = 5.460\ \text{\AA},\ c = 27.456\ \text{\AA}\) and \(\beta = 90.30^\circ\), which agree well with the values reported by Olafsen et al.\(^{27}\).

As shown in Fig. 5(b-e) the lattice parameters decrease...
monotonically upon decreasing the temperature with a weak anomaly in the temperature range from 106 K to 140 K. This anomaly is most prominent in the variation of the $b$-parameter where a kink is seen near $T = 150$ K, which coincides with $T_{MHT}$ previously reported for this compound. However, unlike the case of $\text{La}_4\text{Ni}_3\text{O}_{10}$ and $\text{Pr}_4\text{Ni}_3\text{O}_{10}$ the $b$-parameter for Nd continues to decrease upon cooling below this transition. The temperature variation of angle $\beta$ is shown in panel (e). Upon cooling below room temperature, $\beta$ first increases down to about $T = 200$ K. Thereafter, it decreases upon further cooling with a distinct anomaly near $T = 150$ K. This coincides with the anomalies in the lattice parameters. The non-monotonous behavior of $\beta$ with a broad
peak near $T = 200$ K suggests that while the lattice symmetry does not change the structure evolves gradually and subtly upon cooling below $T = 300$ K. The low-temperatures X-ray diffraction data, analogous to 3, are shown for Nd$_2$Ni$_3$O$_{10}$ as Fig. S4 in the supplementary information.

Table I summarizes the refinement details for the room temperature crystal structures of $R_2$Ni$_3$O$_{10}$, $R =$ La, Pr and Nd. The crystal structure of $R_2$Ni$_3$O$_{10}$ (monoclinic $P2_1/c$, $Z = 4$), shown in Fig. 1, comprises triple perovskite block (PB) layers ($RNiO_3$)$_3$, which consist of corner-linked NiO$_6$ octahedra. These triple PB layers are separated by RO layers with RS structure. There are four inequivalent $R-$atoms, two of which are located within the PB layers (labeled as $R_3$, $R_4$). They have a deformed 12-fold coordination analogous to the perovskites $RNiO_3$ as shown in Fig. 1. The remaining two $R-$atoms are located within the RS layers (labeled as $R1$, $R2$) and they exhibit a 9-fold coordination. Likewise, there are four distinct crystallographic sites for the Ni atoms. Borrowing the terminology used in Ref. 27, we shall label them as Ni1, Ni2: located in the inner layer (ILs), and Ni3, Ni4: located in the outer layer (OL), facing the RO layer on one side and PB layer on the other. The various R–O and Ni–O bond distances for all three samples are given in the SI. In all three cases, the elongated Ni–O bonds are apical, pointing towards the RS layer in agreement with Olafsen et al.27 who speculated that this may be a consequence of Ni$^{3+}$(OL)-Ni$^{2+}$(IL) charge ordering.

B. Electrical and thermal transport

Fig. 6 shows the temperature dependence of resistivity ($\rho$), thermopower ($S$), and thermal conductivity ($\kappa$) for all three samples. We first examine the electrical resistivity. Upon cooling below room temperature, $\rho(T)$ for all three samples decreases monotonically down to a temperature of approximately 136 K (La), 156 K (Pr) and 160 K (Nd). Upon further cooling, $\rho$ increases suddenly featuring a step in the $\rho$ versus $T$ plots at this temperature. The step is identified with the metal-to-metal transition in these samples, which agrees nicely with the temperature variation of lattice parameters discussed in the previous section. The resistivity discontinuity ($\Delta \rho$) at $T_{\text{MMT}}$ is found to be most pronounced for the Nd$_2$Ni$_3$O$_{10}$ and least for La$_4$Ni$_3$O$_{10}$. No measurable thermal hysteresis was observed between the heating and cooling data at $T_{\text{MMT}}$.

Below the MMT, the resistivity for La$_4$Ni$_3$O$_{10}$ and Pr$_4$Ni$_3$O$_{10}$ continues to decrease down to some temperature $T_0$, which is followed by an upturn or a region of negative $d\rho/dT$ that persists down to 2 K. $T_0$ is $\simeq$ 20 K and $\simeq$ 80 K for La$_4$Ni$_3$O$_{10}$ and Pr$_4$Ni$_3$O$_{10}$, respectively. In Nd$_2$Ni$_3$O$_{10}$, $d\rho/dT \simeq 0$ down to about 100 K, and $< 0$ upon further cooling. The upturn in this case is also more pronounced than for La and Pr. These observations concerning behavior of $\rho(T)$ in the three compounds are in good agreement with previous reports.$^{13,24,26,28}$

In previous studies, the low-temperature upturn has been variously interpreted. While it is attributed to the weak localization due to inelastic electron-electron interactions in Ref. 24, the Kondo effect was claimed to be the reason in Ref. 13. In order to resolve this issue, we replotted the low-temperature data for all three compounds on two different temperature scales: (i) $T^{0.5}$, and (ii) $\ln T$ scales. The results are shown in Fig. 7. Clearly, the data for all three samples is best described by a $\sqrt{T}$ dependence which persists almost down to the lowest temperature of 2 K. Very slight departure from this scaling for Pr$_4$Ni$_3$O$_{10}$ and Nd$_2$Ni$_3$O$_{10}$ near 10 K can be attributed to the short-range ordering of the rare-earth moments (vide infra). On the contrary, the $-\ln T$ behavior does not describe the upturn in $\rho$ satisfactorily or does so only over a narrow temperature range, with significant departure at low temperatures. Attempts to fit the low-temperature upturn to the Arrhenius or Variable Range Hopping (VRH) models (with or without interactions) also did not give satisfactory results (not shown).

The analysis above clearly favors a $\sqrt{T}$ dependence over other functional dependences commonly used to describe the low-temperature upturn in resistivity. The validity of the $T^{0.5}$ behavior suggests that at low-temperatures weak localization due to inelastic electron-electron scattering is possibly what
TABLE I: Refinement parameters obtained using the high-resolution synchrotron data for room the temperature crystal structure of $R_4Ni_3O_{10}$ ($R = La, Pr$ and $Nd$). The error bar in the lattice parameters is estimated to be of the order of $\pm0.0002$ in the fourth decimal place.

| Specimen      | Space group | SG No. | Phase Type | Phase % | a(Å)  | b(Å)  | c(Å)  | $\beta$ (°) | $\chi^2$ | $R_{WP}$ | $R_{EXP}$ | $R_p$ |
|---------------|-------------|--------|------------|---------|-------|-------|-------|-------------|---------|--------|----------|------|
| $La_4Ni_3O_{10}$ | $P2_1/a$  | 14     | M$^\dagger$| 85.6    | 5.4243| 5.4748| 28.0053| 90.192°     | 6.15   | 14.7   | 5.90     | 11.7 |
| $Bmab$       | 64         | O$^\dagger$ | 7.8    | 5.4040 | 5.4621 | 28.5542| 90°     |           |        |        |          |      |
| $Cmcm$       | 63         | O$^\dagger$ | 6.6    | 20.1250| 5.4638 | 5.4638| 90°     |           |        |        |          |      |
| $Pr_4Ni_3O_{10}$ | $P2_1/a$  | 14     | M$^\dagger$| 100    | 5.3826| 5.4717| 27.583| 90.284°     | 3.86   | 19.0   | 9.67     | 16   |
| $Nd_4Ni_3O_{10}$ | $P2_1/a$  | 14     | M$^\dagger$| 100    | 5.3719| 5.46  | 27.4560| 90.299°     | 4.57   | 15.8   | 7.41     | 12.7 |

M$^\dagger$: monoclinic and O$^\dagger$: orthorhombic

causes the resistivity upturn in all three compounds, which is typically observed for disordered metals and alloys$^{29}$. Here, the structural disorder might be in the form of stacking faults and intergrowth whose presence is reflected in the powder X-ray diffraction. This conclusion is also in agreement with Ref. 24. On the other hand, the evidence for the Kondo effect in our data is rather weak.

The thermopower of these samples, shown in panel (a), (b) and (c) of Fig. 6, also parallels the resistivity behavior in the sense that at $T_{MMT}$, $S(T)$ exhibits a sharp jump, which can be understood based on the Mott’s formula for thermopower, which is given by:

$$S = \frac{\pi^2 k_B^2 T}{3e} \left( \frac{\partial \ln \sigma(E)}{\partial E} \right)_{E=E_F}$$

(1)

where $k_B$ is the Boltzmann constant, $\sigma(E)$ is the electrical conductivity, $e$ the electronic charge, and $E_F$ is the Fermi energy.

Since, $\sigma$ can be expressed as: $\sigma = n(E)q\mu(E)$, where $n(E) = D(E)f(E)$: $D(E)$ is the density of states, and $f(E)$ the Fermi-Dirac distribution function, and $\mu$ is the carrier mobility, one can rewrite eq. 1 above as follows:

$$S = \frac{\pi^2 k_B^2 T}{3e} \left( \frac{1}{n} \frac{dn}{dE} + \frac{1}{\mu} \frac{d\mu}{dE} \right)_{E=E_F}$$

(2)

The mobility $\mu$ scales inversely with the effective mass of the charge carriers, which in turn is determined by the curvature of the electronic bands near $E_F$. While $\mu$ may undergo a small change below $T_{MMT}$, where the structural modification, if present, is very subtle, the quantity $dn/dE$, i.e., change in carrier concentration with respect to energy at $E_F$, is expected to vary drastically due to opening of a gap at $E_F$ below the MMT as shown in the previous ARPES studies$^{5}$.

FIG. 7: Temperature ($T$) variation of resistivity ($\rho$) of $La_4Ni_3O_{10}$ (a and b), $Pr_4Ni_3O_{10}$ (c and d) and $Nd_4Ni_3O_{10}$ (e and f) is shown on a $T^{0.5}$ scale (left panels), and a $\ln(T)$ scale (right panels).

We notice that, for $T > T_{MMT}$, $|S|$ increase almost linearly with increasing temperature as is typically seen for metals. Naively, one can use the single parabolic band model approximation to rewrite the Mott formula in eq. 1 in form:
\[ S = \frac{8\pi^2 k_B m^*}{3e\hbar^2} \left( \frac{\pi}{3n} \right)^2 T \]  

where \( m^* \) is the band effective mass of the charge carriers. By fitting \( S \) above \( T_{CMMT} \) using \( S = a_0 T \), where \( a_0 \) is the prefactor in eq. 3, one can estimate \( m^* \). For this purpose, we use \( n \) obtained from the Hall coefficient \( R_H \approx 10^{-3} \text{cm}^2/\text{C} \) at \( T = 300 \text{K} \). Following this procedure, we get \( m^* \approx 3.0 m_0 \) for \( \text{La}_4\text{Ni}_3\text{O}_{10} \), \( 3.7 m_0 \) for \( \text{Pr}_4\text{Ni}_3\text{O}_{10} \), and \( 2.7 m_0 \) for \( \text{Nd}_4\text{Ni}_3\text{O}_{10} \).

Below the MMT, the thermopower becomes rather small (\( |S| < 2 \mu \text{VK}^{-1} \)): positive for La and negative for Pr and Nd. The weak maximum in \(|S|\) below the MMT can be attributed to the phonon-drag. In the case of \( \text{La}_4\text{Ni}_3\text{O}_{10} \), in fact, there is a crossover from \( n^- \) to \( p^- \)-type near 130 K, and again from \( p^- \) to \( n^+ \)-type around 61 K. The overall behavior and the range of variation of \( S \) for the three samples is comparable to that previously reported. 

Coming now to \( \kappa \) which is not reported in any of the previous studies to the best of our knowledge. The temperature variation of \( \kappa \) is shown in panels (d), (e) and (f) of Fig. 6. Starting form the lowest temperature of \( T = 2 \text{K} \) in our experiments, \( \kappa \) for all three samples increases upon heating. The variation at low-temperatures is \( \sim T^3 \), which suggests that the contribution due to acoustic phonons is dominant in this temperature range. Upon heating further, a noticeable change in the temperature variation of \( \kappa \) takes place for \( T > 50 \text{ K} \): In \( \text{La}_4\text{Ni}_3\text{O}_{10} \) \( \kappa \) shows a broad peak in the interval 50 K to 100 K, attaining a peak value of 3 Wm\(^{-1}\)K\(^{-1}\) around 80 K; in \( \text{Pr}_4\text{Ni}_3\text{O}_{10} \) it shows an increasing behavior all the way up to 300 K, albeit with a much slower rate at high temperatures than for \( T < 50 \text{ K} \); and, in \( \text{Nd}_4\text{Ni}_3\text{O}_{10} \), \( \kappa \) gradually levels off above 50 K saturating at a value of \( \approx 1 \text{ Wm}^{-1}\text{K}^{-1} \) above \( T = 100 \text{ K} \). Thus, the behavior of \( \kappa \) in all three cases is rather similar for \( T \leq 50 \text{ K} \), but not above this temperature range. It is interesting to note that in spite of their reasonably high electrical conductivities (ranging from 100-1000 S cm\(^{-1}\)), the thermal conductivities of these compounds (ranging from 1-3 Wm\(^{-1}\)K\(^{-1}\)) is rather low, which, in turn, indicates that the phonon thermal conductivity in these nickelates is intrinsically very low. This may be related to their complex layered structure. Among other things, their low thermal conductivity and metal-like electrical conductivity above the MMT indicate their potential as oxide thermoelectrics.

Finally, it is reassuring to see that in all three samples MMT has been very clearly captured in the temperature variation of \( \kappa \). For each sample, this transition is manifested as a small, but clearly discernible, downward kink in \( \kappa(T) \) around the same temperature where \( \rho(T) \) or \( S(T) \) shows a jump. For \( R = \text{La} \) and \( \text{Pr} \), we measured the data, both, while heating and cooling and found some hysteresis around \( T_{CMMT} \). In fact, in \( \text{Nd}_4\text{Ni}_3\text{O}_{10} \) this feature is rather pronounced extending up to nearly 300 K. However, a lack of similar hysteresis in \( \rho \) versus \( T \), where the measurement uncertainties are less, does not allow us to make any definitive comment on the origin of this feature.

**C. Magnetic Susceptibility**

\( \text{La}_4\text{Ni}_3\text{O}_{10} \): Fig. 8 shows the temperature variation of the magnetic susceptibility \( \chi \) of \( \text{La}_4\text{Ni}_3\text{O}_{10} \), where Ni is the only magnetically active ion. This sample is therefore important to understand the magnetic behavior of the Ni sublattice which is otherwise masked in the \( \text{Pr}_4\text{Ni}_3\text{O}_{10} \) and \( \text{Nd}_4\text{Ni}_3\text{O}_{10} \) samples due to large local moments associated with Pr\(^{3+} \) and Nd\(^{5+} \) ions.

The temperature variation of \( \chi \) for the \( \text{La}_4\text{Ni}_3\text{O}_{10} \) sample is shown here in a fairly good agreement with previous reports. Upon cooling below room-temperature, \( \chi \) exhibits a decreasing behavior down to a temperature of about 136 K, followed by a sharp increase that persists down to \( T = 2 \text{ K} \) (lowest temperature in our measurement). A closer examination of \( \chi(T) \) indicates that a kink at \( T = 136 \text{ K} \), as shown in the inset, which coincides with \( T_{CMMT} \) in resistivity. This observation, which is new to our knowledge, is consistent with Ref. 11 where the MMT is described as an intertwined density wave with both charge and magnetic degrees of freedom at play.

The overall behavior of \( \chi \) in \( \text{La}_4\text{Ni}_3\text{O}_{10} \) is found to be rather peculiar for the following two reasons: First, the decreasing behavior with cooling at high temperatures \( (T > T_{CMMT}) \) is uncharacteristic of a local moment system in the paramagnetic regime. On the other hand, had it been Pauli paramagnetic due to a possible itinerant nature of Ni 3d electrons, the measured \( \chi(T) \) would have remained nearly temperature independent, which is not the case either. Kobayashi et al. measured \( \chi(T) \) of \( \text{La}_4\text{Ni}_3\text{O}_{10} \) up to higher-temperatures and found it to show a broad hump near \( T = 400 \text{ K} \). One may argue that this hump is a characteristic feature of low-dimensional spin systems; in \( \text{Pr}_4\text{Ni}_3\text{O}_{10} \), however, the superexchange pathways are not strictly lim-
ited to one or two dimensions. While it is true that these are layered structures and to that effect some degree of low-dimensionality may play a role, however, as pointed out by Zhang et al., the hybridization between Ni 3d and O 2p orbitals increases significantly with increasing thickness of the PB layer. As a result, the d_{3z^2-r^2} band, which is highly localized in La₃NiO₅, broadens considerably in La₃Ni₃O₁₀ leading to a delocalized or itinerant behavior. The second peculiar feature in χ(T) of La₃Ni₃O₁₀ concerns the sharp rise below 136 K, which has been, so far, overlooked in the previous literature or is interpreted as arising due to paramagnetic impurities. We fitted this upturn in the range 2 K ≤ T ≤ 10 K using the modified Curie-Weiss law:

\[ \chi = \chi_0 + \frac{C}{T - \theta_p}, \]

where treating \(\chi_0\), C and \(\theta_p\) as the fitting parameters. The best-fit value of \(\chi_0\) is 10⁻³ emu mol⁻¹ Oe⁻¹, the Curie-constant \(C = 1.7 \times 10^{-2}\) emu mol⁻¹ Oe⁻¹, and the paramagnetic Curie-temperature \(\theta_p \approx 2.7\) K. From the value of \(C\), we get a moment of about 0.3 µ_B/f.u., which is too large to be an impurity effect. The value of \(\chi_0\) is positive and also rather high (about one to two orders of magnitude higher than the Pauli paramagnetism due to free electrons). The value of \(\theta_p\) is positive, which indicates ferromagnetic interactions between the Ni spins. However, no long range magnetic ordering nor a tendency towards it has been observed even though short range AFM/FM correlations of the type Ni²⁺−O−Ni²⁺ and Ni³⁺−O−Ni³⁺ may have been present. As shown in the ARPES experiments, below the MMT, the d_{3z^2-r^2} band (or more precisely the γ band with d_{3z^2-r^2} character) develops a significant energy gap of ≈ 20 meV, which, upon cooling, would gradually lead to localization of d_{3z^2-r^2} electrons, which is possibly the reason for the observed increase in χ upon cooling below the MMT. In short, it seems that the overall magnetic behavior in La₃Ni₃O₁₀ is an interplay of itinerant and local moment behavior which gets more intriguing below MMT. Though not very significant, to some degree the low-dimensionality due to the layered structure may also play a role.

The isothermal magnetization \(M(H)\) at \(T = 150\) K, 100 K and 3 K is shown in the inset of Fig. 8. \(M(H)\) at 150 K and 100 K is linear with \(M(H)\) at 3 K is non-linear. We fitted this upturn in the range 2 K ≤ T ≤ 10 K using the modified Curie-Weiss law (equation 4) which results in the following values of the best-fit parameters: \(\chi_0 \approx 2.8 \times 10^{-3}\) emu mol⁻¹ Oe⁻¹, \(C \approx 6.3\) emu mol⁻¹ Oe⁻¹ K⁻¹, and \(\theta_p \approx 36\) K. These values are in good agreement with those previously reported by Bassat et al. The value of \(\chi_0\) is positive and comparable in magnitude to that for La₃Ni₃O₁₀. The negative sign of \(\theta_p\) indicates that the exchange interaction between the neighboring Pr³⁺ moments is of antiferromagnetic nature. If we attribute the \(T \approx 5\) K anomaly to the magnetic ordering of Pr moments, it would be fair to conclude that the ordering has been significantly suppressed. The ratio \(\theta_p/T_N\), which is known as the frustration index, is close to 7, which is a fairly high value suggesting the presence of strong frustration.

The experimental effective magnetic moment per formula unit can be calculated from the Curie constant C using the formula:

\[ \mu_{eff} = \sqrt{8C} \]

which comes out to be ≈ 7.2 µ_B/f.u.. Theoretically, \(\mu_{eff}/f.u..\) is given by \([4\mu_{eff}(Pr) + 3\mu_{eff}(Ni)]\). Substituting the theoretical value of \(\mu_{eff} = 3.58\) µ_B per Pr³⁺ ion results in a relatively much smaller, if any, contribution arising from the Ni sublattice.

\(M(H)\) at \(T = 2\) K and 5 K is shown in the inset of Fig. 9. The magnetization increases almost linearly with increasing field reaching a value of ≈ 2µ_B/f.u. or ≈ 0.5 µ_B/Pr³⁺, which is significantly smaller than the theoretical saturation moment of 3.13 µ_B/Pr³⁺, which is partly due to the fact that 1/2 of the Pr-moments have a singlet ground state (vide infra), the remaining 1/2 are antiferromagnetically ordered.
near $T = 5$ K.

$Nd_4Ni_3O_{10}$: In $Nd_4Ni_3O_{10}$ (Fig. 10), $\chi(T)$ also exhibits an increasing behavior upon cooling. Even though the effective magnetic moment mon Nd- and Pr-ions is nearly the same, the low-temperature $\chi$ in $Nd_4Ni_3O_{10}$ is almost four times larger than for Pr$_3Ni_2O_{10}$. As we shall see later, it is due to the crystal field splitting, which renders one-half of the Pr-moment ineffective at low-temperature due to their singlet ground state. On the other hand, Nd$^{3+}$ is a Kramers ion, and therefore the Nd ions in both PB and RS layers have a doublet ground state. Interestingly, a closer examination of the data near 160 K reveals the presence of a small kink that can be attributed to the MMT.

A modified Curie-Weiss fit (eq. 4) in the range 175 K to 300 K gives the following values of the best-fit parameters: $\chi_0 \approx 3.8 \times 10^{-3}$ emu mol$^{-1}$ Oe$^{-1}$, $C \approx 6.3$ mol$^{-1}$ Oe$^{-1}$ K$^{-1}$, and $\theta_p = -46.5$ K. These values are in close agreement with those recently reported by Li et al. The value of $\chi_0$ is consistent with that obtained for La$_4Ni_3O_{10}$. From $C$, the experimental $\mu_{eff}$ turns out to be $\approx 7.1 \mu_B$ / f.u.. The effective moment of $7.1 \mu_B$ per f.u. is practically due to the Nd$^{3+}$ moments alone whose theoretical $\mu_{eff}$ is $3.62 \mu_B$, which amounts to $7.2 \mu_B$ / f.u., suggesting that the local moment associated with Ni, if any, is comparatively very small. The value of $\theta_p$ is high given the absence of any magnetic ordering down to a temperature of $T = 2$ K, suggesting the presence of a rather strong magnetic frustration surpassing even that of the Pr compound. It should, however, be pointed out that near $T = 2.5$ K, the susceptibility exhibits a very weak anomaly, as shown in the inset of Fig. 10. As we shall see further, in the specific heat of Nd$_4Ni_3O_{10}$ no clear peak is found in this temperature range. However, $c_p$ increases upon cooling. with a very slight blip in this temperature range. Since magnetic ordering in Nd$_2O_3$ sets in only below $T = 0.5$ K, this feature cannot be due to some small quantity of unreacted Nd$_2O_3$ that may have possibly gone undetected in the powder X-ray diffraction. The possibility of lower member Nd$_3Ni_2O_5$ ordering at this temperature however cannot be ruled out, though it should be stressed that in our X-ray diffraction we did not find any evidence of the presence of this phase. Hence, at this stage it is difficult to point out the exact origin of this feature, but even if it is due to partial ordering of Nd moments, the statement concerning strong magnetic frustration remains valid.

Before advancing further, it will be useful to comment on the nature of the Curie-Weiss fit at lower temperatures. First, we find that upon changing the lower temperature limit of the fitting range, the fit remains satisfactory with fitting parameters unchanged provided either $C$ or $\chi_0$ is fixed to its high-temperature value. This remains valid down to $\approx 120$ K, which is below MMT but the kink at MMT is minor which does not alter the nature of fit. Second, a satisfactory fit to the low-temperature data by means of the Curie-Weiss law resulted in a considerably enhanced value of $\chi_0$, which simultaneously resulted in a reduction in the value of $C$. For example, fitting in the temperature range 5 K to 50 K gives $\chi_0 = 2.7 \times 10^{-2}$ emu mol$^{-1}$ Oe$^{-1}$, $C = 2.85$ mol$^{-1}$ Oe$^{-1}$ K$^{-1}$, and $\theta_p = -3.2$ K. In this range, fixing $\chi_0$ (or $C$) to its high-temperature value and varying only $C$ (or $\chi_0$) and $\theta_p$ did not yield a satisfactory fit. This behavior, present only at low-temperatures, may be attributed to the crystal field splitting of the lowest $J-$ multiplet of the Nd$^{3+}$ ions.

$M(H)$ at $T = 2$ K (inset of Fig. 10), shows a Brillouin function dependence; however, the saturation moment ($\approx 5 \mu_B$ / f.u. or 1.25 $\mu_B$ / Nd) is appreciably smaller than the theoretical value ($g_J J = 3.3 \mu_B$ / Nd), which is, once again, a possible manifestation of the crystal field splitting. At $T = 100$ K, and 250 K, $M(H)$ increases in a linear manner with $M(H)_{100K} > M(H)_{250K}$, which is in line with the paramagnetic nature of the Nd$^{3+}$ moments in this temperature range.

D. Specific heat

The specific heat ($c_p$) data of $R_4Ni_3O_{10}$ samples exhibits a sharp anomaly at their respective metal-to-metal transitions. This anomaly is particularly pronounced for Pr$_3Ni_2O_{10}$ and Nd$_3Ni_2O_{10}$. These samples also show additional anomalies at low temperatures, associated with the rare-earth sublattices. However, before coming to that we first look at the specific heat of La$_4Ni_3O_{10}$ where these low-temperature anomalies are not present.

La$_4Ni_3O_{10}$: In La$_4Ni_3O_{10}$ the specific heat anomaly occurs at 136 K as shown in Fig. 11. It should be emphasized that in a La$_4Ni_3O_{10}$ crystallizing in the Bmab space group the specific heat anomaly occurs at a temperature of $\approx 150$ K, and it is near 136 K for the $P2_1/a$ phase. This is consistent...
bare electron mass, which is comparable to the effective mass of states higher than the band effective mass by a constant which makes the effective mass derived from the density of states to be zero. Also, the small difference between the two can be due to the electronic and lattice contributions, respectively (see inset in Fig. 11). The best-fit yields: \( \gamma \approx 15 \text{ mJ Ni-mol}^{-1} \text{K}^{-2}, \beta \approx 0.43 \text{ mJ mol}^{-1} \text{K}^{-4}. \) The Debye temperature \( (\Theta_D) \) is calculated from \( \beta \) using the relation: \( \beta = 12\pi^4 N k_B / 5 \Theta_D, \) which gives a value of \( \Theta_D \approx 450 \text{ K}. \) The values of \( \Theta_D \) and \( \gamma \) obtained here are comparable to those previously reported\(^\text{16}\). As shown in the inset of Fig. 11, a weak field dependence is observed when a magnetic field of 50 kOe is applied. From the value of \( \gamma \) one can readily estimate the density of states at the Fermi energy, \( D(E_F) \), using the expression: \( D(E_F) = 3\gamma / 2\pi^2 k_B^2, \) which gives a value of \( \approx 3.0 \times 10^{22} \) states \( \text{eV}^{-1} \text{cm}^{-3}. \) Now, using the carrier density \( n, \) one can estimate the corresponding density of states \( D^\ast(E_F) \) at \( E_F \) using the free-electron model. Taking \( n \approx 6.3 \times 10^{21} \text{ cm}^{-3}, \) one gets \( D^\ast(E_F) \approx 7.6 \times 10^{21} \) states \( \text{eV}^{-1} \text{cm}^{-3}. \) From the ratio \( D(E_F)/D^\ast(E_F) = m^\ast / n, \) we estimate the effective mass \( (m^\ast) \) for \( \text{La}_3 \text{Ni}_3 \text{O}_{10} \) to be \( m^\ast \approx 3.9 m_e, \) where \( m_e \) is the bare electron mass, which is comparable to the effective mass obtained from the high-temperature thermopower \( (\approx 3.0 m_e). \) The small difference between the two can be due to the possible Fermi surface reconstruction below the MMT. Also, we have not accounted for the valley degeneracy, if any, which makes the effective mass derived from the density of states higher than the band effective mass by a constant factor \( N^{2/3} \) where \( N \) is the valley degeneracy. In any case, the important point is that from the value of \( m^\ast \) one can conclude that the electronic correlations in \( \text{La}_3 \text{Ni}_3 \text{O}_{10} \) are only modestly enhanced.

\( \text{Pr}_3 \text{Ni}_3 \text{O}_{10}: \) Fig. 12 shows the specific heat of \( \text{Pr}_3 \text{Ni}_3 \text{O}_{10} \) where a sharp transition is observed at 156 K, which agrees nicely with the anomaly associated with the MMT in the transport data. In this case, too, the position and shape of the anomaly remains unaffected by the application of an external magnetic field. Apart from this, a broad anomaly is seen in the low temperature regime centered around \( T_1 \approx 5 \text{ K}, \) which coincides with the anomaly in \( \chi \) at the same temperature. Interestingly, even this low-temperature anomaly is not significantly perturbed by an applied field of up to 50 kOe.
To examine the contribution of 4f electrons associated with Pr to the specific heat (designated as $c_{sf}^{Pr}$ in the following) at low temperatures, we subtracted the specific heat data of La$_3$Ni$_3$O$_{10}$ from that of Pr$_3$Ni$_3$O$_{10}$, since both are isostructural, with very similar molecular weights. It is, therefore, reasonable to approximate the lattice specific heat of Pr$_3$Ni$_3$O$_{10}$ with that of La$_3$Ni$_3$O$_{10}$. Furthermore, we have assumed that the Ni sub-lattice contributes equally to the specific heat of both compounds in the low-temperature regime, well below the MMT, which is a reasonable assumption given that $T_{MMT}$ for the two compounds lies in the same temperature range.

$c_{sf}^{Pr}$ obtained using this procedure is shown in Fig. 12 (lower panel) over the temperature range 2 K $\leq T \leq 120$ K. Interestingly, in addition to the peak centered around $T_1 = 5$ K, $c_{sf}^{Pr}$ shows an additional broad peak around $T_2 = 36$ K. This new feature is likely a Schottky anomaly arising due to the crystal field splitting of the lowest $J = 4$ multiplet of the Pr$^{3+}$ ions. To understand this further, we estimate the magnetic entropy ($s_{sf}$) using the formula:

$$s_{sf} = \int_0^T \left( \frac{c_{sf}}{T} \right) dT.$$  

For the purpose of a rough estimate, we extrapolate $c_{sf}^{Pr}$ below $T = 2$ K linearly to $T = 0$ K. The calculated $s_{sf}$ is shown as an inset in the lower panel of Fig. 12. It shows a relatively steep rise below 10 K, but continues to increase, albeit at a slower rate, upon heating beyond 15 K. The region between 10 K and 15 K is where the crossover from higher ($T < 10$ K) to slower ($T > 15$ K) happens. The increase in $s_{sf}$ beyond 15 K can be attributed to the higher lying crystal field levels as discussed further.

The magnetic entropy released in the temperature range $T \leq 15$ K ($\approx 3T_1$) is $\approx 11.5$ J mol$^{-1}$K$^{-1}$, i.e., $\approx 2.9$ J Pr-mol$^{-1}$K$^{-1}$, which is approximately $\frac{1}{7}$ of $R \ln 2$. What this suggests is that the peak at $T_1$ is likely due to the magnetic ordering of $\frac{1}{2}$ of the Pr$^{3+}$ ions per Pr$_3$Ni$_3$O$_{10}$ formula unit, which is plausible since there are 2 types of Pr coordinations in this structure: 9-fold (RS layers) and 12-fold (PB layers). Incidentally, the Pr$^{3+}$ ions in the perovskite compound PrNiO$_3$ have a singlet ground state with no magnetic ordering at any temperature$^{33}$. Since the coordination of Pr$^{3+}$ ions in the PB layers of Pr$_3$Ni$_3$O$_{10}$ is analogous to that in the compound PrNiO$_3$, it is reasonable to assume that they, too, have a singlet ground state with no magnetic ordering. Therefore, we can tentatively associate the broad peak in the specific heat at $T_1$ to the magnetic ordering of the 9-fold coordinated Pr$^{3+}$ ions. A similar scenario has been previously reported for the compounds Pr$_3$RuO$_7$ which has two types of Pr coordinations, namely, eightfold and sevenfold, with Pr ions in the sevenfold coordination having a crystal field split singlet ground state, and those in the eightfold coordination a doublet$^{34}$.

However, the question arises as to why the peak associated with the magnetic ordering of Pr$^{3+}$ ions in the RS layer is not as sharp as it is typically seen at a long-range ordered magnetic transitions. For the 9-fold coordinated Pr$^{3+}$ ions there are two crystallographically inequivalent Pr sites (Pr1 and Pr2). Due to minor differences in bond angles and bond lengths around Pr1 and Pr2, the exchange integrals $J_{11}$ (within the Pr1 sublattice), $J_{22}$ (within the Pr2 sublattice), and intersite $J_{12}$ may differ slightly, which could be one of the reasons for the $c_p$ anomaly at $T_1$, associated with ordering of Pr1 and Pr2, to be broad. The other reason could be related to the fact that a $R^{3+}$ moment in a RS layer is only weakly coupled to the $R^{3+}$ moment in the adjacent RS layer, leading to a quasi-two-dimensional behavior.

Let us now turn our attention to the peak at $T_2$ which seems to arise due to the crystal field splitting of the lowest J-multiplet of Pr$^{3+}$ ions. In a previous inelastic neutron scattering study on the perovskite compound PrNiO$_3^{33}$, it was found that the 9-fold degenerate J-multiplet of the $P_{y}^{3+}$ ion splits into 9 singlets due to the crystal field effect. The energy difference between the ground state singlet ($E_{1}^{\text{g}}$) and the first excited state ($E_{1}^{\text{e}}$) is $6.4$ meV or approximately $70$ K.

In the first order approximation, the crystal field splitting of Pr ions in the PB layers of Pr$_3$Ni$_3$O$_{10}$ can be assumed to be similar to that in the compound PrNiO$_3$. Within this assumption, the Schottky anomaly due to the ground and first excited singlet is expected to be centered slightly below $T = (E_{1}^{\text{g}} - E_{1}^{\text{e}})/2k_B \approx 35$ K, which is remarkably close to the position of the peak at $T_2$. Since the second excited singlet is located around $E_{2}^{\text{e}} = 15$ meV ($\approx 165$ K), it is too high up to have any significant effect on the Schottky anomaly arising due to the $E_{1}^{\text{g}}/E_{1}^{\text{e}}$ pair.

It can therefore be concluded that the Pr ions in the PB layer have a singlet ground state due to a crystal field effect, with a broad Schottky anomaly associated with ground and first excited singlet pair. On the other hand, Pr ions in the RS layers have a crystal field split doublet as their ground state, and undergo magnetic ordering around $T_1$. The observed increase in $s_{sf}$ above $2T_1$ is partly due to $E_{0}/E_{1}$ excitations associated with Pr-ions in the PB layer, and partly due to the higher lying crystal field split levels of Pr ions in the RS layers. In the absence of a detailed crystal field splitting scheme for the Pr ions in the RS layers, a quantitative analysis of the low-temperature specific heat is left as a future exercise.

Fig. 13 shows the specific heat of Nd$_4$Ni$_3$O$_{10}$, which is characterized by a sharp anomaly at $T = 160$ K. The position of this anomaly is in a fairly good agreement with the MMT inferred from the transport data, and is found to be independent of an applied magnetic field at least up to $50$ kOe. The low temperature $c_p$ is characterized by an upturn below about $T = 10$ K. Upon application of a magnetic field, this upturn evolves to take the shape of a broad peak, which progressively shifts to higher temperatures as the magnetic field increases – centered around 4 K under $H = 50$ kOe. This behavior is reminiscent of a Schottky-like anomaly, which often arises in the rare-earth based compounds due to the crystal field splitting.

To investigate this further, we estimate the specific heat associated with 4f electrons of Nd, labeled $c_{sf}^{Nd}$. The specific heat of La$_3$Ni$_3$O$_{10}$ is used as a lattice template, and also to
FIG. 13: Top panel: Temperature ($T$) variation of specific heat ($c_p$) of Nd$_4$Ni$_2$O$_{10}$ from 2 K to 300 K; lower inset shows $c_p$ in the low-temperature range for an applied field of 0 kOe, 30 kOe and 50 kOe; upper inset gives a zoomed-in view of the anomaly at MMT. Bottom panel: low-temperature specific heat associated with the 4f electrons of Nd$_4$Ni$_2$O$_{10}$ is plotted as $c_{4f}/T$ versus $T^2$; inset shows $c_{4f}$ versus $T$ up to $T = 120$ K to show the presence of a pronounced Schottky anomaly near $T = 40$ K. The modified Schottky fitting results for three cases: $g(1) = 1, g(2) = 1$ (red), $g(1) = 1, g(2) = 2$ (blue), and $g(1) = 1, g(2) = 0.5$ (khaki) (see text for details).

Let us now turn our attention to the increase in $c_{4f}^{Nd}$ upon cooling below $T = 10$ K. In NdNiO$_3$ a similar upturn leading to a broad peak around $T = 1.7$ K had been previously reported$^7$. It was argued to arise from the exchange splitting of the ground state doublet. However, unlike NdNiO$_3$, in Nd$_4$Ni$_2$O$_{10}$ the Ni moments are not ordered and hence the Ni–Nd exchange field in this case is almost non-existent. On the other hand, it might be that this upturn is precursory to an impending magnetic ordering of the Nd moments at further low-temperatures. After all, the Nd-Nd exchange, as inferred from the high temperature Curie-Weiss fit, is about $-45$ K, which is rather high. This could be analogous to the case of Nd$_2$O$_3$ recently reported, which also exhibits a high $\theta_p \approx -24$ K, but with long-range order setting in only below $T = 0.55$ K. Surprisingly, $c_p$ of Nd$_2$O$_3$ shows not only a sharp peak at 0.55 K corresponding to the long-range ordering of Nd moments but also a broader feature centered around 1.5 K. The authors report that the entropy associated with this broad peak should be considered in order to account for the $R\ln 2$ entropy expected from a ground state doublet. In Ref. 13, $c_p$ of Nd$_4$Ni$_2$O$_{10}$ is given down to 0.5 K, which indeed shows a broad peak in zero-field at $T \approx 1.8$ K. Further studies down to much lower temperatures would be

\[
c_{Sch}^{(i)} = 2R \left( \frac{\Delta_i}{T} \right)^2 \frac{g(1) \exp(-\Delta_i/T)}{1 + g(1) \exp(-\Delta_i/T)}^2
\]
interesting to explore this analogy further and to understand the true ground state of the Nd sublattice.

Finally, $c_p^{Nd}/T$ versus $T^2$ is plotted in the lower panel of Fig. 13. The data from 12 K to 20 K can be fitted to a straight line whose intercept on the $y$-axis is $\sim 150$ mJ mol$^{-1}$K$^{-2}$. Indeed, in Ref. 13, a high $\gamma$ value of 146 mJ mol$^{-1}$K$^{-2}$ is reported by fitting $c_p/T$ versus $T^2$ to $\gamma + \beta T^2$ in this temperature range. However, caution must be exercised while interpreting the intercept value in such cases since $c_p$ in this temperature range, as shown in the inset of Fig. 13b, is overwhelmed by the Schottky contribution arising from the crystal field split lowest $J$–multiplet of Nd$^{3+}$ ions. It is for this reason we believe that the high $\gamma$ value in Ref. 13, which led the authors of this study to conclude a "novel" heavy-electron behavior in Nd$_4$Ni$_3$O$_{10}$, is a gross overestimation. As is well documented in the heavy fermion-literature, if the electronic specific heat $\gamma$ in such cases is derived by extrapolating the high-temperature specific heat data to $T = 0$ K using $\gamma T + \beta T^2$ unusually large values are obtained, which can be falsely interpreted as arising due to the heavy fermion behavior.

E. Thermal Expansion and Grüneisen analysis

The temperature dependence of length changes studied by capacitive dilatometry, presented in Figs. 14 to 16, follows the volume dependence as measured using synchrotron powder X-ray diffraction (see Fig. 2-4(f)). However, while there is quantitative agreement for Pr$_4$Ni$_3$O$_{10}$, we find discrepancies for La$_4$Ni$_3$O$_{10}$ and Nd$_4$Ni$_3$O$_{10}$. Specifically, the dilatometric length changes are about 25 % and 45 % larger than suggested by X-ray diffraction, respectively. The data are isotropic, i.e., we find the behavior to be the same when measuring along different directions of the polycrystalline cuboids, which excludes a simple non-random orientation effect to cause this discrepancy. Instead, the data suggest a non-uniform internal stress distribution within the polycrystalline samples which can lead, in porous materials, to larger thermal expansion than in the bulk$^{35}$. The length changes in Pr$_4$Ni$_3$O$_{10}$ evidence significant coupling of electronic and structural degrees of freedom. Specifically, there are pronounced anomalies at $T_{MMT}$ in all studied materials. In La$_4$Ni$_3$O$_{10}$, the data in Fig. 14 display a broad feature which signals shrinking of the sample volume upon exiting the MMT phase while heating the sample. Qualitatively, this implies negative hydrostatic pressure dependence $dT_{MMT}/dp < 0$. The minimum of the thermal expansion anomaly appears at $T_{MMT} = 134$ K, suggesting either a weak first-order character of the transition or a somehow truncated $\lambda$-like behavior similar to what is indicated by the specific heat anomaly (cf. Fig. 11).

In order to estimate the background contribution to the thermal expansion coefficient, a polynomial was fitted to the data well below and above the thermal expansion anomaly as shown in Fig. 14$^{36}$. The background $\alpha^{bg}$ mainly reflects the phonon contribution. Due to the large size of the anomaly, using different temperature ranges for the determination of the background and/or choosing different fit functions does not change the result significantly. Subtracting $\alpha^{bg}$ from the data yields the anomaly contribution to the thermal expansion coefficient $\Delta \alpha$ as shown in Fig. 17a. Recalling the discrepancy of dilatometric and XRD length changes mentioned above for La$_4$Ni$_3$O$_{10}$ and Nd$_4$Ni$_3$O$_{10}$, for the following quantitative analysis of both we have scaled the dilatometric data to the XRD results. Quantitatively, our analysis then yields total anomalous length changes $\Delta L/L = \int \Delta \alpha dT = -4.2(9) \cdot 10^{-5}$.

FIG. 14: Temperature dependence of the thermal expansion coefficient $\alpha$ of La$_4$Ni$_3$O$_{10}$. The red line shows a polynomial estimate of the background (see text for details). The arrows mark $T_{MMT}$ and the asterisk indicates an experimental artifact. The inset shows the length changes $dL/L$ around $T_{MMT}$; the dotted line is a guide to the eye.

FIG. 15: Temperature dependence of the thermal expansion coefficient $\alpha$ of Pr$_4$Ni$_3$O$_{10}$. The red line shows a polynomial estimate of the background (see the text). The shaded regions indicate the regions where anomalies in $\alpha$ are observed. The anomalies are marked with arrows. Inset: Relative length changes $dL/L$ around $T_{MMT}$. The dotted lines are guides to the eye.
TABLE II: Total anomalous length and entropy changes \( \Delta_l/L = \int \alpha dT \) and \( \Delta s = \int \Delta c_p^{\text{MMT}} / dT \), discontinuous length changes \( \Delta_dL/L \), Gr"uneisen parameter \( \Gamma \) and hydrostatic pressure dependence of \( T_{\text{MMT}} \) of LaNi\textsubscript{3}O\textsubscript{10} (see the text).

| Composition     | \( \Delta_l/L \) | \( \Delta_dL/L \) | \( \Delta s \)   | \( \Gamma \)  | \( dT_{\text{MMT}}/dp \) |
|-----------------|------------------|------------------|-----------------|----------------|----------------|
| LaNi\textsubscript{3}O\textsubscript{10} | -4(1) \cdot 10^{-5} | - | 1.0(3) J/(mol K) | -8.2(2) K/GPa | - |
| PrNi\textsubscript{3}O\textsubscript{10}  | -5(1) \cdot 10^{-5} | -3.1(6) \cdot 10^{-5} | 3.1(6) J/(mol K) | -4.1(1) K/GPa | - |
| NdNi\textsubscript{3}O\textsubscript{10}  | -5.1(4) \cdot 10^{-5} | -2.6(2) \cdot 10^{-5} | 3.5(9) J/(mol K) | -1.5(4) \cdot 10^{-7} mol/J | -3(1) K/GPa |

FIG. 16: Temperature dependence of the thermal expansion coefficient \( \alpha \) of NdNi\textsubscript{3}O\textsubscript{10}. The dash-dot red line shows a polynomial estimate of the background (see text for details). The shaded regions indicate the regions where anomalies in \( \alpha \) are observed. The anomalies are marked with arrows. Inset: Relative length changes \( dL/L \) around \( T_{\text{MMT}} \). The dotted lines are guides to the eye.

When replacing La by Pr and Nd in \( R_4\text{Ni}_3\text{O}_{10} \), the anomalies in the thermal expansion at \( T_{\text{MMT}} \) become significantly sharper and evidence rather discontinuous behavior (see Figs. 15 and 16). In addition, there are pronounced features at low temperatures (marked by arrows) that are associated with rare-earth sublattice. In particular, the data clearly confirm negative volume expansion in \( \text{Nd}_4\text{Ni}_3\text{O}_{10} \) below \( \sim 20 \) K. At higher temperatures, the sharp anomalies at \( 156 \) K (\( R = \text{Pr} \)) and \( 160 \) K (\( R = \text{Nd} \)) at \( T_{\text{MMT}} \) are accompanied by a regime of rather continuous length changes which extends from \( T_{\text{MMT}} \) down to about \( 110 \) K, i.e., it is significantly larger than the anomaly regime in La\textsubscript{4}Ni\textsubscript{3}O\textsubscript{10}. Applying the procedure described above for determining the background yields the thermal expansion anomalies as displayed in Fig. 17b and 17c for the two compounds.

The anomalies \( \Delta \alpha \) in the thermal expansion coefficients at the MMT are presented in Fig. 17 together with the respective anomalies of the specific heat. The latter have been derived by estimating the background specific heat analogously to the procedure used for the thermal expansion data and using the same fitting regimes in both cases\textsuperscript{36}. For each composition, scaling of \( \Delta c_p \) and \( \Delta \alpha \) has been chosen to obtain the best overlap of the specific heat and thermal expansion data around \( T_{\text{MMT}} \) and above. The fact that the thermal expansion coefficient of \( R_4\text{Ni}_3\text{O}_{10} \) with \( R = \text{La}, \text{Pr}, \) and \( \text{Nd} \) has been rescaled according to the X-ray diffraction results (see the text). Note the same scale of the thermal expansion ordinate in all graphs.

FIG. 17: Anomalies in the specific heat and the negative thermal expansion coefficient of \( R_4\text{Ni}_3\text{O}_{10} \) with \( R = \text{La}, \text{Pr}, \) and \( \text{Nd} \). The anomaly size in (a) and (c) has been rescaled according to the X-ray diffraction results (see the text). Note the same scale of the thermal expansion ordinate in all graphs.

Our analysis yields the \( \Gamma \) values summarized in table II. Using the Ehrenfest relation, the obtained values of \( \Gamma \) yield the hydrostatic pressure dependencies of the ordering temperature at vanishing pressure, i.e., \( dT_{\text{MMT}}/dp = T_{\text{MMT}} V_m \Gamma \). The results deduced using the molar volume \( V_m \) are shown in table II.

The obtained initial slopes of hydrostatic pressure dependencies of \( T_{\text{MMT}} \) are comparable to values reported from measurements of the electrical resistivity under pressure. Specifically, Wu \textit{et al.} report \(-6.9\) K/GPa for La\textsubscript{4}Ni\textsubscript{3}O\textsubscript{10}.
which nicely agrees to the results of the Grüneisen analysis presented above. The comparison with Nd₄Ni₃O₁₀ studied in Ref. 13 is, however, ambiguous. On the one hand, Li et al. ¹³ report discontinuous shrinking of the unit cell volume at $T_{\text{MMT}}$ by 0.08% while cooling, which, both, qualitatively and quantitatively, contrasts our data (cf. inset of Fig. 16). In particular, this value implies a positive hydrostatic pressure dependence of about $+35$ K/GPa.¹⁴ However, at the same time an initial negative hydrostatic pressure dependence of about $-8$ K/GPa is reported in Ref. 13 which thermodynamically contradicts the reported volume changes at $T_{\text{MMT}}$ but is reasonably consistent with the results of our Grüneisen analysis.

The broad region of anomalous length changes between $T_{\text{MMT}}$ and $\sim 100$ K signals clear temperature variation of the Grüneisen ratio, in this temperature regime, the reason of which is not fully clear. In general, the fact that capacitance dilatometry is obtained under small but finite pressure, which in the case at hand is estimated to about 0.6(1) MPa, may affect measurements in particular on polycrystalline samples. The fact that the dilatometer detects volume increase however renders a scenario as observed in recent studies of electronic nematicity of LaFeAsO rather unlikely, where the shear modulus $C_{66}$ is the elastic soft mode of the associated nematic transition so that dilatometry under finite pressure results in associated volume decrease.³⁹,⁴⁰ We also exclude that variation of $T$ is associated with incompletely resolved strain from the discontinuous transition at $T_{\text{MMT}}$ because the measurements have been performed upon heating and the temperature regime of the observed anomaly is very large. Instead, we conclude the presence of a competing ordering phenomenon as suggested by the failure of Grüneisen scaling.³⁷ Intriguingly, a temperature regime of unexpected behavior has also been detected in the out-of-plane resistivity $\rho_{\perp}$ in Pr₄Ni₃O₁₀ single crystal where, in contrast to the in-plane resistivity, an increase of $\rho_{\perp}$ upon cooling, i.e., insulating behavior, is observed in a large temperature regime.¹⁵ It is tempting to trace back this intermediate temperature regime of $d\rho_{\perp}/dT < 0$, i.e., a metal-to-insulator-like behavior of $\rho_{\perp}$ at $T_{\text{MMT}}$, to the competing degree of freedom which manifests in the thermal expansion coefficient and change of Grüneisen parameter shown in Fig. 17b.

IV. SUMMARY & CONCLUSIONS

We investigated the trilayered nickelates $R_4Ni_3O_{10}$ ($R = \text{La, Pr and Nd}$) that are $n = 3$ members of the RP series. We focused our investigations on understanding the following important aspects concerning the physical properties of these compounds: (i) what is the correct space group characterizing the room-temperature crystal structure of these compounds, (ii) is there a structural phase transition at $T_{\text{MMT}}$, (iii) how do various thermodynamic quantities, including resistivity, magnetic susceptibility, specific heat, thermopower, thermal conductivity and thermal expansion coefficient vary across MMT, and (iv) to understand the magnetic behavior of the rare-earth sublattices in Pr₄Ni₃O₁₀ and Nd₄Ni₃O₁₀.

In order to address these questions, we synthesized high-quality samples using the sol-gel method, which is known from previous studies to produce phase pure samples as opposed to the solid-state synthesis where considerable intergrowth of other lower members of the RP series also takes place. These samples were then subject to a high-resolution synchrotron powder X-ray diffraction at the ALBA synchrotron source, both, at 300 K and lower temperatures down to 90 K, which easily spans $T_{\text{MMT}}$ in all three compounds. A thorough analysis of the data collected confirmed that La₄Ni₃O₁₀ crystallizes in the monoclinic $P2_1/a$, $Z = 4$ phase with a slight admixture of the $Bmab$ phase. On the other hand, in Pr₄Ni₃O₁₀ and Nd₄Ni₃O₁₀, monoclinic $P2_1/a$, $Z = 4$ phase was found to be fully consistent with the observed data. Below $T_{\text{MMT}}$, we neither found new peaks emerging nor did we see any of the peaks splitting in the powder X-ray diffraction ruling out any lowering of the lattice symmetry accompanying this transition. On the other hand, we did find appreciable changes in the lattice parameters of all three compounds at $T_{\text{MMT}}$ which is estimated to be near $135$ K, $156$ K and $160$ K for $R = \text{La, Pr and Nd}$, respectively. More specifically, in La₄Ni₃O₁₀ and Pr₄Ni₃O₁₀ the $b$—parameter is found to exhibit an anomalous expansion upon heating. Interestingly, there are indications of a subtle structural modification not involving any symmetry change occurring over a broad temperature range between $T_{\text{MMT}}$ and room-temperature, centered around $250$ K—this feature is most abundantly visible in the temperature variation of angle $\beta$ of the unit cell. The thermal expansion coefficient also captured the anomaly at $T_{\text{MMT}}$ rather vividly. Since our capacitance dilatometer data are limited only to temperatures below $200$ K, the continuous change in $\beta$ with temperature above the MMT could not, however, be corroborated by the thermal expansion. From the analysis of $\Delta\alpha$, we conclude that the MMT anomaly becomes more first order-like as we go to smaller lanthanide ionic radii (and thereby larger distortions from the perovskite structure). Findings from resistivity, specific heat and thermopower measurements summarized below also corroborate this behavior.

Resistivity data of all samples exhibit sharp jump or discontinuity at their respective $T_{\text{MMT}}$ in agreement with previous reports — the jump gets sharper upon going from La to Nd. No sign of hysteresis between the cooling and heating data could be recorded for any of three samples. The resistivity of all three samples shows an upturn, i.e., $\rho/T < 0$, at low-temperatures. An analysis of $\rho$ in the region of negative $\rho/T$ suggests that this upturn likely results from weak-localization arising due to inelastic electron-electron interactions. This result is in agreement with Ref. 24 where the data for La₄Ni₃O₁₀ has been analyzed in considerable details. In particular, we exclude a Kondo-like mechanism in the Ni-sublattice leading to $\rho/T < 0$ as has been proposed recently.¹³ This result is further strengthened by thermopower and specific heat experiments. From thermopower, we found the band effective mass of the charge carriers to range from $3m_e - 4m_e$, and the specific heat of Pr₄Ni₃O₁₀
and Nd$_4$Ni$_3$O$_{10}$ is found to be overwhelmed by the crystal field excitations associated with the lowest $J$-multiplet, which tends to falsely inflate the value of $\gamma$ for these compounds. In La$_4$Ni$_3$O$_{10}$, where these complications are not present, $\gamma \approx 15$ mJ mol$^{-1}$K$^{-2}$ or 5 mJ mol$^{-1}$K$^{-2}$ is found to be only moderately enhanced, yielding an effective mass of about 3.9$m_0$ in close agreement with the effective mass deduced from the high-temperature thermopower. These findings negate the recent claims of a "novel" heavy fermion ground state in Nd$_4$Ni$_3$O$_{10}$.  

As for the magnetic ground state of the $R-$sublattice in Pr$_4$Ni$_3$O$_{10}$ and Nd$_4$Ni$_3$O$_{10}$, rather intriguing behaviors were found. First, the Curie-Weiss temperature ($\theta_p$) for both these compounds is of the order of $-40$ K; however the long-range ordering remains suppressed down to temperatures as low as 5 K for Pr$_4$Ni$_3$O$_{10}$ and less than 2 K for Nd$_4$Ni$_3$O$_{10}$ suggesting the presence of strong magnetic frustration, which may be related to the layered structure, which renders the $R^{3+}$ moments located in the RS layers quasi-two-dimensional. From the analysis of $\gamma$ and $\chi$, we inferred that in Pr$_4$Ni$_3$O$_{10}$, 1/2 of the Pr$^{3+}$ ions – located in the PB layers – exhibit a crystal field split non-magnetic singlet ground state, while the remaining 1/2 – located in the RS layers – show a ground state doublet with an antiferromagnetic ordering below about 5 K. In Nd$_4$Ni$_3$O$_{10}$, on the other hand, all four Nd-ions in the formula unit exhibit a Kramers doublet ground state with first excited state as doublet for one-half of the Nd ions and quartet for the remaining half, giving rise to a pronounced Schottky-type anomaly centered around $T = 35$ K. In summary, the rare-earth sublattice in $R_4$Ni$_3$O$_{10}$ compounds with $R =$ Pr and Nd, exhibit very intriguing behavior which should be subject to further examination using specific heat down to much lower temperatures, and inelastic and elastic neutron scattering. With the possibility of single-crystal growth, the interesting low-temperature behavior of these compounds as shown here should attract significant further interest.

Acknowledgments

These experiments were performed at MSPD - BLO4 beamline at ALBA Synchrotron with the collaboration of ALBA staff. The authors thank the Department of Science and Technology, India (SR/NM/Z-07/2015) for the financial support and Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) for managing the project. SS acknowledges financial support form SERB (WMR/2016/003792). RK acknowledges support by Deutsche Forschungsgemeinschaft (DFG) through KL 1824/13-1 and by BMBF via Spin-Fun (no. 13XP5088).

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