Volume-wise destruction of the antiferromagnetic Mott insulating state through quantum tuning

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RENiO₃ (RE = rare-earth element) and V₂O₃ are archetypal Mott insulator systems. When tuned by chemical substitution (RENiO₃) or pressure (V₂O₃), they exhibit a quantum phase transition (QPT) between an antiferromagnetic Mott insulating state and a paramagnetic metallic state. Because novel physics often appears near a Mott QPT, the details of this transition, such as whether it is first or second order, are important. Here, we demonstrate through muon spin relaxation/rotation (μSR) experiments that the QPT in RENiO₃ and V₂O₃ is first order: the magnetically ordered volume fraction decreases to zero at the QPT, resulting in a broad region of intrinsic phase separation, while the ordered magnetic moment retains its full value until it is suddenly destroyed at the QPT. These findings bring to light a surprising universality of the pressure-driven Mott transition, revealing the importance of phase separation and calling for further investigation into the nature of quantum fluctuations underlying the transition.
The Mott insulating phase (defined broadly as an insulating state induced by electron correlations) can often be suppressed by quantum tunneling, that is, varying a nonthermal parameter such as chemical composition or pressure, resulting in a zero-temperature quantum phase transition (QPT) to a metallic state driven by quantum fluctuations. Theories of exotic phenomena known to occur near the Mott QPT such as quantum criticality and high-temperature superconductivity often assume a second-order QPT, but direct experimental evidence for either first- or second-order behaviour at the magnetic QPT associated with the Mott transition has been scarce and further masked by the superconducting phase in unconventional superconductors.

In both materials, the QPT has received less attention than the thermal MIT, despite being vital for a full understanding of these materials and the pressure-driven Mott transition in general. The order of the QPT is significant. A second-order QPT leads to quantum criticality that may engender unusual properties and novel electronic phases. For a first-order QPT, the system would be expected to exhibit more typically first-order behaviour such as phase coexistence and abrupt changes in the ground state, not necessarily manifesting quantum criticality in the same way. Early numerical and analytical studies, scaling analysis and DMFT studies suggested first-order behaviour at the Mott QPT, but conclusive experiments on RENiO$_3$ and V$_2$O$_3$ have been lacking. Among the few experiments related to the QPT in these materials are a transport study of V$_2$O$_3$ under pressure revealing a gradual reduction of the low-temperature resistance with higher pressure, a neutron study suggesting quantum criticality and high-temperature superconductivity from numerical techniques like dynamical mean field theory (DMFT), modified the understanding of this system to include multiband, $S = 1$ models. This system remains a topic of active study.

Figure 1 | Phase diagrams for canonical Mott systems RENiO$_3$ and V$_2$O$_3$. (a) RENiO$_3$ phase diagram, with temperature along the vertical axis and rare-earth ionic radius along the horizontal axis. The red curve indicates a metallic–insulator transition on cooling, blue a paramagnet–antiferromagnetic transition, and yellow a structural transition. The coloured circles represent phase boundaries for the stoichiometric compounds determined by previous studies. Coloured arrows indicate compositions studied in the current work. The quantum phase transition (QPT) occurs at a radius of 1.175 Å, resulting in a QPT from an antiferromagnetic insulator to a paramagnetic metal. Varying the rare-earth ion leaves the electron count unchanged but alters the width of the relevant electron energy bands by changing the crystal structure; hence, this constitutes a bandwidth-controlled Mott QPT.

The mechanism of the MIT remains controversial. Various scenarios have been proposed, including the opening of a charge-transfer gap, orbital ordering and charge ordering, but experimental observations have been inconsistent with each of these scenarios.

In the case of V$_2$O$_3$, hydrostatic pressure suppresses the MIT temperature from ~160 K at ambient pressure to 0 K at ~2.0 GPa (Fig. 1b), again resulting in a bandwidth-controlled QPT. The MIT is likewise accompanied by structural symmetry lowering (rhombohedral to monoclinic) in the insulating state. Replacing small amounts of V with either Ti or Cr produces similar effects as pressure, shown on the upper horizontal axis of Fig. 1b. Doping with Cr acts as negative pressure and leads to a first-order transition at high temperature between a paramagnetic metal and paramagnetic insulator, dividing the overall V$_2$O$_3$ phase diagram into three parts, similar to RENiO$_3$. However, the metallic phase produced by Ti doping orders magnetically unlike the pressure-induced metal, so these tuning methods are not equivalent.

The MIT in V$_2$O$_3$ was classified early on as a Mott–Hubbard transition, but experimental and theoretical developments in the 1990s and 2000s, particularly from numerical techniques like dynamical mean field theory (DMFT), modified the understanding of this system to include multiband, $S = 1$ models. This system remains a topic of active study.
Results

Composition-tuned QPT in RENiO$_3$.

The compositions of RENiO$_3$ studied in the present work include are indicated by the coloured arrows in Fig. 1a: RE = Y (cyan), Sm (purple), Sm$_{0.75}$Nd$_{0.25}$ (pink), Nd (blue), Pr (green), Nd$_{0.7}$La$_{0.3}$ (orange), Nd$_{0.6}$La$_{0.4}$ (red) and Nd$_{0.5}$La$_{0.5}$ (brown). μSR experiments in zero externally applied magnetic field (ZF) and a weak transverse field (wTF) applied perpendicular to the initial muon spin direction were performed for each sample on a temperature grid spanning the thermal magnetic phase transition, providing a detailed picture of the phase diagram near the QPT.

Representative ZF time spectra taken at 2 K on four compositions of RENiO$_3$ near the QPT are displayed in Fig. 2a. The spectrum for Nd$_{0.7}$La$_{0.3}$NiO$_3$ exhibits only slow relaxation with no oscillations, indicating an absence of magnetic order, as expected for this composition. In contrast, damped but coherent oscillations are seen for Nd$_{0.5}$La$_{0.5}$NiO$_3$, placing this composition just to the left of the QPT. Nd$_{0.7}$La$_{0.3}$NiO$_3$ and NdNiO$_3$, likewise show oscillations indicative of magnetic ordering.

For a given material, the ZF oscillation frequency and amplitude are directly proportional to the ordered moment size and the magnetically ordered volume fraction of the sample, respectively. From Fig. 2a, one clearly observes that the three ordered compounds have approximately the same oscillation frequency (hence moment size), but different oscillation amplitudes (hence OVs). To better illustrate the frequency behaviour, we plot in Fig. 2b the temperature dependence of the oscillation frequency for the compounds closest to the QPT. These frequencies were extracted from refinements described in the Methods section. The most striking feature of these results is that the two or three oscillation frequencies observed in each of the ordered compounds all lie along the same two frequency bands, illustrated by the shaded grey regions in Fig. 2b. This indicates that the saturated moment size is not changed by compositional tuning towards the QPT; rather, the full moment is destroyed abruptly and discontinuously at the QPT.

The compounds represented in Fig. 2b lie in the region of the phase diagram where the magnetic transition occurs simultaneously with the electronic and structural transitions. The temperature dependence of the frequency shows a discontinuous onset at the ordering temperature for these compounds, corresponding to a first-order thermal phase transition. We also measured several compounds located further away from the QPT where the magnetic transition is split from the electronic and structural transitions. Representative ZF spectra for YNiO$_3$ taken at several temperatures spanning the thermal phase transition are shown in Fig. 2c, revealing a gradual increase in the precession frequency as the temperature is lowered. This is further illustrated in Fig. 2d for RE = Lu, Y, Eu, Sm, and Sm$_{0.75}$Nd$_{0.25}$, with the continuous onset of the oscillation frequency suggesting second-order-like behaviour of the thermal phase transition. This is consistent with previous studies indicating a second-order magnetic transition for compounds with split electronic/structural and magnetic transitions, and first-order behaviour when the transitions occur simultaneously.

The reduced ZF oscillation amplitudes observed in Fig. 2a for Nd$_{0.7}$La$_{0.3}$NiO$_3$ and Nd$_{0.6}$La$_{0.4}$NiO$_3$ suggest that even at 2 K, these compounds are not magnetically ordered throughout the full volume fraction, rather there are some paramagnetic regions remaining. To verify this, we performed wTF experiments at several temperatures for each compound. The results are summarized in Fig. 3a,b. Figure 3a displays the time spectra for Nd$_{0.7}$La$_{0.3}$NiO$_3$, Nd$_{0.6}$La$_{0.4}$NiO$_3$, and NdNiO$_3$ at 2 K and NdNiO$_3$ at 250 K. In wTF, the amplitude of the low-frequency oscillations is proportional to the non-magnetically ordered volume fraction; thus, a spectrum with no oscillation (such as NdNiO$_3$ at 2 K) corresponds to a fully ordered sample, while a spectrum with oscillation in the full asymmetry (such as NdNiO$_3$ at 250 K) indicates a completely disordered sample. The spectra for Nd$_{0.7}$La$_{0.3}$NiO$_3$ and Nd$_{0.6}$La$_{0.4}$NiO$_3$ show intermediate oscillation amplitudes, indicating that even at 2 K, these materials are only partially ordered. These compounds therefore exhibit intrinsic paramagnetic and antiferromagnetic phase separation.

The temperature dependence of the magnetic volume fraction extracted from the wTF data for several compounds spanning the phase diagram is displayed by the circles in Fig. 3b, along with the results determined from the ZF experiments shown as triangles. Nd$_{0.7}$La$_{0.3}$NiO$_3$ and Nd$_{0.6}$La$_{0.4}$NiO$_3$, the compounds that are closest to the QPT, show a significantly reduced ordered volume fraction, verifying that their ground state consists of phase-separated antiferromagnetic and paramagnetic regions. PrNiO$_3$ and NdNiO$_3$ also show phase separation over a broad temperature interval of about 50 K below the onset ordering temperature, although both are fully ordered at lower temperatures. The region of the phase diagram exhibiting phase-separated behaviour is indicated by the shaded area marked PS in Fig. 1. This magnetic phase separation may also be accompanied by phase separation between the high-temperature and low-temperature structural and electronic phases, but that is beyond the scope of this study. It is interesting to note that for the compounds exhibiting phase separation, the transition is stretched over a rather large temperature range. The hysteric differences between measurements taken in cooling and warming sequences (represented by open and filled symbols, respectively) confirms the first-order nature of thermal phase transition for NdNiO$_3$, PrNiO$_3$, Nd$_{0.7}$La$_{0.3}$NiO$_3$, and Nd$_{0.6}$La$_{0.4}$NiO$_3$.

Importantly, the reduced magnetic volume fraction in Nd$_{0.7}$La$_{0.3}$NiO$_3$ and Nd$_{0.6}$La$_{0.4}$NiO$_3$ cannot be attributed merely to an extrinsic effect of doping, since the doped compound Sm$_{0.75}$Nd$_{0.25}$NiO$_3$ shows a rapid magnetic transition...
in the full volume fraction. Furthermore, neutron diffraction of the Nd$_{0.6}$La$_{0.4}$NiO$_3$ sample at 70 K indicates that it is single-phase (Supplementary Fig. 2), excluding poor sample quality as a cause of this behaviour. Therefore, we attribute the reduced volume fraction to proximity to the QPT. X-ray diffraction measurements on NdNiO$_3$ also confirm that the expected structural response at the MIT occurs with hysteresis over a similar temperature range as that of the magnetic hysteresis, verifying the correlation between the magnetic and structural phases (Supplementary Fig. 1).

**Pressure-tuned QPT in V$_2$O$_3**. To investigate whether the volume-wise destruction of the AF Mott phase at the QPT is a feature unique to RENiO$_3$ or is perhaps more generic, we performed corresponding ZF and wTF experiments on

### Figure 2 | Zero-field (ZF) muon spin relaxation (μSR) experiments on RENiO$_3$ and V$_2$O$_3$

#### a) ZF time spectra taken at 2 K for four compounds of RENiO$_3$ near the quantum phase transition. The coloured dots represent the data, the solid curves the fits. The three magnetically ordered compounds show nearly identical oscillation frequencies (hence identical moment sizes) but very different oscillation amplitudes (hence different ordered volume fractions).

#### b) Temperature dependence of the oscillation frequencies for RENiO$_3$ compounds with first-order thermal phase transitions. Filled (open) circles represent data taken in a cooling (warming) sequence. All magnetically ordered compounds have two or three frequencies lying along two common bands (shaded grey regions), indicating that the ordered moment size does not change along the horizontal axis of the phase diagram. The large grey circle with the neighbouring vertical bar indicates the average estimated standard deviation (ESD) of the refined frequency produced from the least-squares minimization compared to the symbol size. The coloured dashed lines are guides to the eye showing the approximate transition temperature for each composition.

#### c) ZF spectra for YNiO$_3$ taken at various temperatures through the thermal phase transition. 

#### d) Temperature dependence of the oscillation frequencies for RENiO$_3$ compounds with second-order-like thermal phase transitions, revealing the continuous development of the ordered moment size.

#### e, f) Plots for pressure-tuned V$_2$O$_3$ corresponding to (a,b).
pressure-tuned \(\text{V}_2\text{O}_3\). Hydrostatic pressure has the advantage of being a very clean tuning parameter, avoiding any possible complications of structural or chemical inhomogeneity often associated with chemical doping. The pressures at which we measured \(\text{V}_2\text{O}_3\) are indicated by coloured arrows in Fig. 1b: ambient pressure, 0.4, 1.29, 1.64, 1.73, 1.83, 1.96 and 2.43 GPa.

The key results for \(\text{V}_2\text{O}_3\) are identical to those for RENiO\(_3\): the AF state is destroyed by reduction of the ordered volume fraction while the moment size remains constant, with a significant region of ground-state phase separation near the QPT. The ZF \(\mu\text{SR}\) results for \(\text{V}_2\text{O}_3\) are summarized in Fig. 2e,f. From the ZF spectra displayed in Fig. 2e, it is clear that the oscillation frequencies at various pressures are virtually identical, while the oscillation amplitude shows a significant decrease as the critical pressure of 2.0 GPa is approached. As seen in Fig. 2f, all ZF oscillation frequencies lie along the same two frequency bands, demonstrating that pressure does not affect the ordered moment size. The lower-frequency band is in good agreement with an early \(\mu\text{SR}\) experiment\(^{31}\) on \(\text{V}_2\text{O}_3\). The ordered volume fraction obtained by both the ZF and wTF experiments is displayed in Fig. 3c, where we observe a gradual reduction in the low-temperature magnetic volume fraction beginning with the 1.64 GPa measurement. At 1.96 GPa, only about 15\% of the volume is magnetically ordered, and at 2.43 GPa, the magnetism is completely absent.

The phase separation between AF and paramagnetic regions is reminiscent of that observed in the charge sector by spatially resolved infrared spectroscopy in pure and Cr-doped \(\text{V}_2\text{O}_3\) (ref. 32). The curious stretching of the magnetic transition observed in RENiO\(_3\) is also seen in \(\text{V}_2\text{O}_3\) for larger applied pressures, in agreement with an earlier high-pressure NMR study\(^{33}\). This stretched transition is also somewhat similar to that observed in \(\text{V}_2\text{O}_3\) nanocrystals\(^{34}\), although surface area effects are likely the cause in that case. These results demonstrate that the AF phases in RENiO\(_3\) and \(\text{V}_2\text{O}_3\) have identical behaviour in all key aspects near the QPT.

**Discussion**

The two main results of these experiments are (1) that the saturated magnetic moment size is constant across the ordered region of the phase diagram before being abruptly destroyed at the QPT; and (2) that the magnetic volume fraction is heavily reduced near the QPT. We observed identical behaviour for RENiO\(_3\) and pressure-tuned \(\text{V}_2\text{O}_3\), both canonical bandwidth-controlled Mott insulators. These results unambiguously demonstrate that the QPT in these materials proceeds in a distinctly first-order fashion. The striking similarity between both of these canonical systems, along with experimental indications of structural phase separation in the archetypal Mott system NiS\(_2\).
tuned by pressure, indicates that this is a generic feature of the pressure-driven Mott QPT, supporting previous theoretical work. Further theoretical considerations regarding the surprisingly large region of parameter space exhibiting phase coexistence and additional details of this first-order QPT are provided in the Supplementary Note 1.

We note that similar phase separation between paramagnetic and magnetically ordered regions was observed by μSR/7 and nuclear magnetic resonance in the destruction of magnetic order in the itinerant helimagnet MnSi through pressure tuning, and by μSR/2 in the metallic ferromagnet (Sr,Ca)RuO3 through (Sr,Ca) chemical substitution. Signatures of first-order magnetic quantum evolution have also been observed in heavy fermion systems and many unconventional superconductors, accompanied by an inelastic resonance mode in the superconducting state. The magnetic resonance observed in tunnelling experiments on paramagnetic metallic Mott transition systems near the QPT as a signature of the magnetic order in the itinerant helimagnet MnSi through pressure cooling (2 K) indicates that this is a generic feature of the superconductors, accompanied by an inelastic resonance mode in the superconducting state. The magnetic resonance mode can be viewed as a soft mode towards the parent/competing magnetic order in the itinerant helimagnet MnSi through pressure tuning (2 K). Such a soft mode may also exist in the metallic superconducting Mott transition systems near the QPT as a signature of the magnetic phase boundary. The total initial asymmetry α(0) = α(0) + α(0) and the asymmetry baseline fixed to the values determined from a high-temperature measurement well above the magnetic ordering temperature. Both methods of analysis of the μSR data yielded essentially identical results for the magnetic volume fraction. The results from the first method of refinement are shown in Fig. 3.

The ZF asymmetry spectra were modelled by the function

\[ A(t) = \sum_{i} a_i^m \exp \left( -\frac{t}{\tau_i} \right) \cos \left( \frac{2\pi}{T_i} t + \phi_i \right), \]

where the \( a_i^m \) are the amplitudes of the precessing components, the \( T_i \) are the transverse damping rates due to a distribution of field strengths at the muon site(s), and the \( \phi_i \) are the precession frequencies. For the Nd moment, a damped Kubo-Toyabe component due to a combination of paramagnetic regions and the 1/3 non-oscillating component arising from the orientationally averaged magnetic regions of the sample, and \( \Lambda_t \) is the longitudinal relaxation rate (also known as 1/T1 when it applies to the 1/3 component from magnetically ordered regions). In all cases except for RE = Nd, there are 3 components: the magnetic volume fraction, with the lower-frequency component having roughly double the amplitude of the higher-frequency component. This may be understood as arising from two magnetically inequivalent muon stopping sites. For RE = Nd, a third frequency can be resolved at the lowest temperatures, perhaps due to ordering of the Nd moments. For the V2O3 experiments, a damped Kubo-Toyabe component due to a distribution of field strengths at the muon site(s), and the \( \phi_i \) are the precession frequencies. For the Nd moment, a damped Kubo-Toyabe component due to a distribution of field strengths at the muon site(s).

The precession frequencies were determined from refinements performed over the first 5 s of the asymmetry time spectra. Additional refinements over a larger time window (0-8 μs) and a larger time-channel binning size were performed to more accurately determine \( a_i^m \) and \( T_i \). For a magnetically ordered sample with domains distributed isotropically overall solid angles, 2/3 of the asymmetry will exhibit oscillations and 1/3 will not. This is because magnetic field components along the Cartesian direction defined by the initial muon spin do not contribute to the precession of the muon spin, while the other two Cartesian directions do. In RENiO3 and V2O3, as in many other magnetic materials, the 2/3 oscillating component is strongly damped, and is manifested only as a residual component when the spectrum is viewed over a large time window with relatively large time-channel binning. The total asymmetry arising from magnetically ordered regions of the sample can therefore be estimated as 3/2 multiplied by the missing asymmetry, with the magnetic volume fraction then given by 3/2 ÷ \( \frac{1}{2} \sum_{i} a_i^m \exp \left( -\frac{t}{\tau_i} \right) \cos \left( \frac{2\pi}{T_i} t + \phi_i \right) \).

For RENiO3, the magnetic volume fraction determined from ZF data in this way agreed quite well with the volume fraction determined by the μSR experiments. For V2O3, this resulted in a slight overestimation of the magnetic volume fraction. Therefore, we multiplied by 4/3 instead of 3/2 (corresponding to a 1/4 non-oscillating component rather than 1/3), which then gave close agreement with the μSR results. Such a deviation from the ideal 2/3 versus 1/3 division of the magnetic volume fraction has been done elsewhere.

The μSR spectra were analysed using the least-squares minimization routines in the MuisFit software package. The μSR asymmetry spectra were modelled by the function

\[ A(t) = a_p \exp \left( -\frac{t}{\tau} \right) \cos (\omega t + \phi), \]

where \( t \) is time after muon implantation, \( A(t) \) is the time-dependent asymmetry, \( a_p \) is the amplitude of the oscillating component (related to the paramagnetic volume fraction), \( \tau \) is an exponential damping rate due to paramagnetic spin fluctuations and/or nuclear dipolar moments, \( \omega \) is the Larmor precession frequency set by the strength of the transverse magnetic field, and \( \phi \) is a phase offset. In the case of \( V_2O_3 \), a second slowly-damped oscillating component was included to account for muons stopping in the pressure cell. The zero for \( A(t) \) was allowed to vary for each temperature to deal with the asymmetry baseline shift known to occur for magnetically ordered samples, as has been done elsewhere. From these refinements, the magnetically ordered volume fraction at each temperature \( T \) was estimated as 1 - \( \frac{A(t)}{A(T_{max})} \) where \( A(T_{max}) \) is the amplitude in the paramagnetic phase at high temperature. We performed a second set of refinements of the μSR data using a two-component model for the asymmetry, an oscillating component with asymmetry \( a_p \) representing the paramagnetic fraction and a non-oscillating component decay parameter \( \tau \) is the half-oscillating component of the magnetically ordered fraction. The total initial asymmetry \( a_p = a_p + a_0 \) and the asymmetry baseline fixed to the values determined from a high-temperature measurement well above the magnetic ordering temperature. Both methods of analysis of the μSR data yielded essentially identical results for the magnetic volume fraction. The results from the first method of refinement are shown in Fig. 3.

The ZF asymmetry spectra were modelled by the function

\[ A(t) = \sum_{i} a_i^m \exp \left( -\frac{t}{\tau_i} \right) \cos \left( \frac{2\pi}{T_i} t + \phi_i \right) + a_0 \exp \left( -\frac{t}{\tau_0} \right), \]
magnetic transition, even though the true low-temperature structure has monoclinic symmetry. Supplementary Fig. 2 displays the temperature dependence of the cell volume in panel (a) and the isotropic atomic displacement parameter for Ni in panel (b), both obtained from PDF modelling. In both cases, a deviation from the high-temperature trend is observed at 200 K, with substantial differences between the warming and cooling sequences over a similar temperature range as the magnetic volume fraction hysteresis observed by µSR. The results of the previous structural studies were very similar. These observations are consistent with previous structural studies of NaNiO$_3$.

Time-of-flight neutron diffraction measurements of NaNiO$_3$ were performed at the Spallation Neutron Source of Oak Ridge National Laboratory on the NQ-3D instrument. Rietveld refinements were performed using GSAS$^5$ on the EXPGUI platform$^{50}$. Supplementary Fig. 3 displays the results of refining the Pbnm model against the measured diffraction pattern at 70 K, which is above the MIT in this compound. The measured pattern is shown by blue crosses, the calculated pattern in red, and the difference curve in green. The fit is of good quality, ruling out the presence of any significant impurity phase in this compound.

Data availability. All relevant data are available from the authors upon request.

References

1. Imada, M., Fujimori, A. & Tokura, Y. Metal-insulator transitions. Rev. Mod. Phys. 70, 1039–1263 (1998).
2. Volta, J. Quantum phase transitions. Rep. Prog. Phys. 66, 2069–2110 (2003).
3. Keimer, B., Kivelson, S. A., Norman, M. R., Uchida, S. & Zaanen, J. From quantum matter to high-temperature superconductivity in copper oxides. Nature 518, 179–186 (2015).
4. Torrance, J. B., Lacorre, P., Nazzal, A. I., Ansaldo, E. J. & Niedermayer, C. Systematic study of insulator-metal transitions in perovskites RNiO$_3$ (R = Pr, Nd, Sm, Eu) due to closing of charge-transfer gap. Phys. Rev. B 45, 8209–8212 (1992).
5. McWhan, D. B., Rice, T. M. & Remeika, J. P. Mott transition in Cr-doped V$_2$O$_5$. Phys. Rev. Lett. 33, 1348–1347 (1969).
6. Alonso, J. A. Charge disproportionation in RNiO$_3$ perovskites: simultaneous metallic-insulator and structural transition in YNiO$_3$. Phys. Rev. Lett. 82, 3871–3874 (1999).
7. García Muñoz, J. L., Rodríguez Carvajal, J. & Lacorre, P. Sudden appearance of an unusual spin density wave at the metal-insulator transition in the Perovskites RNiO$_3$ (R = Pr, Nd). Europhys. Lett. 20, 241–247 (1994).
8. García Muñoz, J. L., Aranda, M. A. G., Alonso, J. A. & Martínez-Lope, M. J. Structure and charge order in the antiferromagnetic band-insulating phase of NaNiO$_3$. Phys. Rev. B 79, 134342 (2009).
9. Barman, S. R., Chainani, A. & Sarma, D. D. Covalency-driven unusual collective spin and charge order in perovskite oxides. Phys. Rev. B 90, 100102 (2014).
10. Pickett, W. T., Fishkin, T. F. & Kamlah, M. Site-specific magnetic and electronic properties of NaNiO$_3$ (R = Pr, Nd, Eu, Ho) and RCoO$_3$ (R = Pr, Nd) investigated by resonant soft magnetic powder neutron diffraction. Phys. Rev. B 70, 132405 (2004).
11. Alonso, J. A. Charge disproportionation in R$_2$NiO$_4$$_{2–x}$ studied by photoemission and X-ray absorption spectroscopy: band gap and orbital ordering. Phys. Rev. B 52, 13865–13873 (1995).
12. Abbate, M. et al. Electronic structure and metal-insulator transition in NaLaNiO$_3$. Phys. Rev. B 65, 155101 (2002).
13. Lorenzo, J. E. et al. Resonant X-ray scattering experiments on electronic orderings in NaNiO$_3$ single crystals. Phys. Rev. B 71, 045128 (2005).
14. Bodenthin, Y. et al. Magnetic and electronic properties of NaNiO$_3$ (R = Pr, Nd, Eu, Ho, and Y) perovskites studied by resonant soft magnetic powder diffraction. J. Phys.: Condens. Matter 23, 036002 (2011).
15. Park, H., Mills, A. J. & Marianetti, C. A. Total energy calculations using DFT + DMFT: computing the pressure phase diagram of the rare earth nickelates. Phys. Rev. B 89, 245133 (2014).
16. Uemura, Y. J., Yamazaki, T., Kitaoka, Y., Takigawa, M. & Uemura, H. Positive muon spin precession in magnetic oxides MnO and V$_2$O$_3$: local fields and phase transition. Hyperfine Interact. 17-19, 339–344 (1984).
17. Lüpi, S. et al. A microscopic view on the Mott transition in chromium-doped V$_2$O$_5$. Nat. Commun. 1, 105 (2010).
18. Takigawa, M., Ahrens, E. T. & Ueda, Y. Anomalous magnetic properties of metallic V$_2$O$_3$ under pressure. Phys. Rev. Lett. 76, 283–286 (1996).
19. Blagovec, V. A. et al. Magnetic phase transition in V$_2$O$_3$ nanocrystals. Phys. Rev. B 82, 094543 (2010).
20. Feng, Y., Jaramillo, R., Banerjee, A., Honig, J. M. & Rosenbaum, T. F. Magnetism, structure, and charge correlation at a pressure-induced Mott-Hubbard metal-insulator transition. Phys. Rev. B 83, 035106 (2011).
21. Blagovec, V. A. et al. Magnetic phase transitions in V$_2$O$_3$ nanocrystals. Phys. Rev. B 82, 094543 (2010).
22. Suter, A. & Wöjak, B. Musfr: a free platform-independent framework for xas data analysis. Phys. Procedia 30, 69–73 (2012). 12th International Conference on Muon Spin Rotation, Relaxation and Resonance (μSR2011).
23. Deng, Z. et al. Lui(Zn,Mn)as as a new generation ferromagnet based on a I-IV-V semiconductor. Nat. Commun. 2, 422 (2011).
24. Wang, K. et al. Enhanced ferromagnetic and electric correlations in RuSe$_2$. APL Mater. 3, 041513 (2015).
25. Jensen, K. M. et al. Demonstration of thin film pair distribution function analysis (tpDF) for the study of local structure in amorphous and crystalline thin films. IUCrJ 2, 481–489 (2015).
26. Rietveld, H. A. Profile reﬁnement, method for nuclear and magnetic structures. J. Appl. Crystallogr. 2, 65–71 (1969).
27. Rodríguez Carvajal, J. Recent advances in magnetic structure determination by neutron powder diffraction. Physica B 192, 55–69 (1993).
28. Yang, X., Juhás, P., Farrow, C. & Billinge, S. J. L. xPDFsuite: an end-to-end software solution for high throughput pair distribution function transformation, visualization and analysis. Preprint at http://arxiv.org/abs/1402.3163 (2015).
29. Farrow, C. L. et al. PDFit2 and PDFgui: Computer programs for studying nanostructures in crystals. J. Phys. Condens. Matter 19, 335219 (2007).
30. Larson, A. C. & Von Dreele, R. B. General structure analysis system. Report No. LAUR-86-748, (Los Alamos National Laboratory, Los Alamos, 1994).
31. Tobi, B. H. EXPGUI, a graphical user interface for GSAS. J. Appl. Crystallogr. 34, 201–213 (2001).

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Author contributions
This project was proposed and coordinated by Y.J.U. µSR data were taken by B.A.F., L.L., S.C.C., T.J.S.M., A.M.H., M.N.W., Y.C., G.L., B.C., C.D., S.G., E.N., T.U.I., W.H., S.S., A.F. and Y.J.U. for RENiO3 and by B.A.F., S.C.C., Z.G., R.K., E.M. and Y.J.U. for V2O3. The µSR data analysis was carried out by B.A.F. and Y.J.U. The neutron and X-ray scattering studies were performed by B.A.F. and S.J.L.B. J.A., C.J. and W.M.L. provided the RENiO3 samples. H.K. and T.M. provided the V2O3 sample. M.I. and G.K. provided theoretical considerations. The manuscript was drafted by B.A.F. and Y.J.U., and has been completed with input from all authors. This work is part of the PhD thesis project of B.A.F. at Columbia University.

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