

ChemComm

Chemical Communications

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: E. Solana, K. Alharbi, M. Herz, P. Manuel and P. Attfield, *Chem. Commun.*, 2020, DOI: 10.1039/D0CC04756B.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Journal Name

COMMUNICATION

Unconventional magnetism in the high pressure 'all transition metal' double perovskite $\text{Mn}_2\text{NiReO}_6$

Elena Solana-Madruga,^a Khalid N. Alharbi,^a Maria Herz,^a Pascal Manuel^b and J. Paul Attfield^{*a}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

$\text{Mn}_2\text{NiReO}_6$, prepared at high pressure and temperature, has a highly-distorted double perovskite structure. Canted antiferromagnetic order is observed below $T_{\text{M1}} = 80$ K and an unusual continuous spin rotation of Mn spins occurs down to $T_{\text{M2}} = 42$ K where a collapse in weak ferromagnetism evidences an unprecedented switching of the weak ferromagnetic moment directions.

$\text{A}_2\text{BB}'\text{O}_6$ double perovskites with rocksalt-type order of the B/B' cations have been of great interest since the discovery of large magnetoresistances in $\text{Sr}_2\text{FeMoO}_6$.^{1,2} Double perovskites synthesised at ambient pressure typically have large, non-magnetic A-site cations like Ca^{2+} , Sr^{2+} , and Ba^{2+} , but a recent breakthrough has come from the discovery that Mn^{2+} analogues can be recovered from high pressures. Complex magnetic orders result from the $S = 5/2$ Mn^{2+} A-site cations in addition to transition metal B-cation spins. $\text{Mn}_2\text{FeSbO}_6$ ³ (and the basic ABO_3 -type perovskite MnVO_3 -II⁴) have incommensurate helimagnetic structures. The 'All Transition Metal' (ATM) double perovskite $\text{Mn}_2\text{FeReO}_6$ is ferrimagnetic with a high Curie temperature of 520 K and frustration switching of spin order and magnetoresistance on cooling.^{5,6} $\text{Mn}_2\text{MnReO}_6$ is also frustrated with perpendicular A and B site Mn^{2+} sublattices^{7,8} and $\text{Mn}_2\text{CoReO}_6$ is antiferromagnetically ordered below 94 K.⁹ Here we report the new double perovskite $\text{Mn}_2\text{NiReO}_6$ which shows remarkable Mn^{2+} spin rotation and weak ferromagnetic properties.

$\text{Mn}_2\text{NiReO}_6$ was synthesised at 8 GPa and 1573 K using a Walker-type multi-anvil press. Stoichiometric proportions of MnO , NiO and ReO_3 were ground in acetone and packed into a Pt capsule. The product was quenched to room temperature and slowly depressurized. Formation of a double perovskite

was confirmed using a powder X-ray diffraction (XRD) from a Bruker D2-Phaser instrument, and high resolution neutron powder diffraction (NPD) data were collected using the WISH instrument at ISIS. Long NPD scans were taken at 1.5, 75, and 150 K to determine crystal and magnetic structures, and shorter scans at intermediate temperatures were used to reveal their thermal evolutions. Diffraction data were fitted using the FullProf software suite.¹⁰ Magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) Quantum Design XL-MPMS magnetometer in the temperature range 2–300 K under zero-field cooling (ZFC) and field-cooling (FC) conditions in a magnetic field of 1000 Oe. Magnetisation-field hysteresis loops were collected at 2, 60, 75 and 150 K under applied magnetic fields up to 7 T.

$\text{Mn}_2\text{NiReO}_6$ was found to have a monoclinic $P2_1/n$ double perovskite crystal structure from refinements against XRD and NPD data (Fig. 1 and ESI F1). Secondary phases of ReO_2 , NiO and another rocksalt type phase, Ni_2MnO_3 ¹¹ (17.8(6) wt.%, 4.0(3) wt.% and 12.2(2) wt.% respectively), were also fitted. See ESI for further discussion. The large contrasts in neutron scattering lengths for Mn, Ni, Re and O (−3.73, 10.3, 9.2 and 5.8 fm respectively)¹² enable accurate determination of the cation distribution and oxygen positions. Structure refinement using the 150 K NPD data, summarized in ESI Table S1, reveals that the Mn and Re sites are fully occupied but 18% Mn substitutes for Ni, so the overall chemical composition $\text{Mn}_{2.18}\text{Ni}_{0.82}\text{ReO}_6$ is in keeping with the Ni-rich impurities observed.

The interatomic distances, as summarized in Fig. 2 and Table S1, show that the structure of $\text{Mn}_2\text{NiReO}_6$ is highly distorted from the ideal double perovskite arrangement. The A-site Mn coordination is reduced from the ideal perovskite 12-fold environment to an irregular 7-coordinate polyhedron, with Mn–O distances ranging from 1.70 to 2.83 Å (and other distances >3.10 Å, see ESI Table S5). This differs from other $\text{Mn}_2\text{BB}'\text{O}_6$ double perovskites where 8-coordination of Mn up to a similar distance limit was reported.^{3,5–9,13–15} $\text{Mn}_2\text{NiReO}_6$ also has a very short Mn–O distance of 1.70 Å showing that the structure is highly distorted. (Short Mn^{2+} –O distances have also

^a Centre for Science at Extreme Conditions (CSEC) and School of Chemistry, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, United Kingdom.

*j.p.attfield@ed.ac.uk

^b ISIS Facility, Rutherford Appleton, Laboratory, Harwell, Oxford, Didcot OX11 0QX, United Kingdom.

† Data that support the findings of this study have been deposited at <https://datashare.is.ed.ac.uk/handle/10283/838>.

‡ Electronic Supplementary Information (ESI) available: supporting figures and tables. See DOI: 10.1039/x0xx00000x



been reported in high pressure Mn_3O_4 .¹⁶⁾ A comparison against other $\text{Mn}_2\text{BB}'\text{O}_6$ double perovskites in ESI shows that $\text{Mn}_2\text{NiReO}_6$ has the largest octahedral tilt angles and distortion parameters reported in this family to date. Although bond distances and derived Bond Valence Sums in ESI do not distinguish clearly between $\text{Ni}^{2+}/\text{Re}^{6+}$ and $\text{Ni}^{3+}/\text{Re}^{5+}$ charge distributions¹⁷, magnetic moments refined against 1.5 K NPD data indicate $\text{Ni}^{2+}/\text{Re}^{6+}$, as also found in $\text{Sr}_2\text{NiReO}_6$.^{18,19}

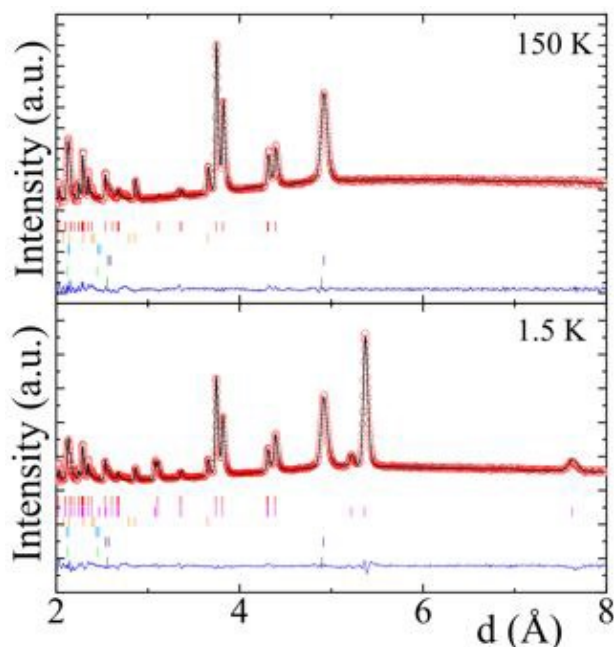


Figure 1. Rietveld fits to 150 and 1.5 K NPD data of $\text{Mn}_2\text{NiReO}_6$. Bragg phase markers at 1.5 K from top to bottom are; $\text{Mn}_2\text{NiReO}_6$ nuclear and magnetic, ReO_2 , NiO nuclear and magnetic, and $(\text{Ni,Mn})\text{O}$ nuclear and magnetic.

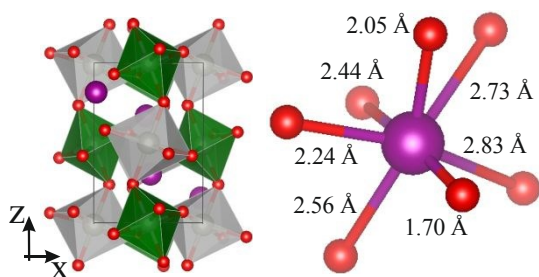


Figure 2. Structure of the double perovskite $\text{Mn}_2\text{NiReO}_6$, as refined from 150 K NPD data. Mn is shown as purple spheres and Ni and Re octahedra are green and grey respectively. The coordination of Mn^{2+} in the A site is depicted on the right.

Temperature variation of magnetic susceptibility is shown in Fig. 3a. The Curie-Weiss fit shown gives an effective paramagnetic moment of $8.16 \mu_B \text{ f.u.}^{-1}$ which is comparable to the spin-only estimate of $9.0 \mu_B$ per unit $\text{Mn}_2\text{NiReO}_6$, given the presence of secondary phases. The fitted Weiss constant is $\theta = 1.8 \text{ K}$ but this may not be meaningful given the presence of

impurities and extrapolation from a small fitting range. A sharp ferro- or ferrimagnetic transition with divergence of ZFC and FC data is observed at $T_{M1} = 80 \text{ K}$, and a discontinuity reveals a second magnetic transition at $T_{M2} = 42 \text{ K}$. Magnetic hysteresis loops at 60 and 75 K in Fig. 3b show a small net moment of $0.17 \mu_B \text{ f.u.}^{-1}$, indicating that a weak ferromagnetic order is present below T_{M1} . However, at 2 K, below the second magnetic transition, the loop has almost collapsed with a residual moment of $0.02 \mu_B \text{ f.u.}^{-1}$ although the coercive field of 51 mT is comparable to the 60 K value of 63 mT.

Magnetic peaks from $\text{Mn}_2\text{NiReO}_6$ are observed in neutron powder diffraction (NPD) patterns below $T_{M1} = 80 \text{ K}$, as shown in Figs. 1 and 4. All magnetic peaks are indexed by propagation vector $k = [0 \ 0 \ 0]$ and fits of different models from magnetic symmetry analysis¹⁰ showed that the Mn, Ni, and Re spins all follow the same irreducible representation corresponding to antiferromagnetic order of spins in the ac -plane, as shown in Fig. 4a. All moments are ordered below 80 K. Ni^{2+} and Re^{6+} site moments were found to have magnitudes in a ratio near 2:1 and were constrained to this ratio following their ideal S values for stability of the magnetic fits. Full refinement of the crystal and magnetic structures at 1.5 K gave respective moments of $3.98(3)$, $1.25(1)$ and $0.62 \mu_B$ for Mn^{2+} , Ni^{2+} and Re^{6+} . These are lower than their ideal 5, 2 and $1 \mu_B$ values evidencing the magnetic frustration within the highly connected networks of the three magnetic cations as well as the Ni/Mn disorder. Magnetic moments for 5d cations are also known to be reduced by effects of large spin-orbit coupling and strong hybridization with oxygen.²⁰⁻²²

The magnetic structure of $\text{Mn}_2\text{NiReO}_6$ has moments coupled parallel in the c -direction but antiparallel in the ab -plane through Ni-O-Re and Mn-O-Mn linkages, demonstrating the presence of competing ferro- and anti-ferromagnetic interactions, in keeping with the small Weiss temperature. In an ideal, undistorted, double perovskite, 180° M-O-M' superexchange interactions between $t_{2g}^1 \text{Re}^{6+}$ and $t_{2g}^6 e_g^2 \text{Ni}^{2+}$ are expected to be ferromagnetic whereas couplings between $t_{2g}^3 e_g^2 \text{Mn}^{2+}$ ions would be antiferromagnetic, and a variety of 90° M-O-M' interactions are also present.

Magnetic peaks intensities from $\text{Mn}_2\text{NiReO}_6$ are found to evolve differently on cooling, for example, the (100) peak shown in Fig. 4b is essentially saturated below $\sim 50 \text{ K}$, while the (010) intensity continues to grow down to 10 K. This demonstrates that spin components parallel to these planes grow at different rates, and refinements showed that spin rotation occurs in the ac -plane as the spin order saturates. Initial fits showed that the spin direction for Ni (and Re) sites does not change significantly with temperature, and so in the final fits, the Ni (and Re) spin direction was fixed while the Mn x - and z - components were refined independently (see ESI for details). The resulting moments and rotation angles ϕ (defined as the angle of rotation from $+c$ towards $+a$ in the xz -plane) are shown in Fig. 4c. The monoclinic symmetry of $\text{Mn}_2\text{NiReO}_6$ enables the sign of the rotation angles ϕ to be determined. The thermal variation of spin angles in Fig. 4c shows that Mn spins initially order with $\phi_{\text{Mn}} \approx 30^\circ$ just below $T_{M1} = 80 \text{ K}$. This is within error of the constant $\phi_B = 36^\circ$ tilt angle that the ordered



Ni and Re site moments exhibit at all temperatures, so all spins are essentially collinear just below T_{M1} . The tilts of the NiO_6 and ReO_6 octahedra are respectively $\psi_{\text{Ni}} = -\psi$ and $\psi_{\text{Re}} = +\psi$, following the same sign convention as for the spin rotation angles ϕ , where the octahedral tilt angle is $\psi = 23^\circ$ as shown in ESI. The opposite signs of ψ_{Ni} and ψ_{Re} result from their out-of-phase tilting in the z-direction (Fig. 2). Hence all ordered spins are near parallel to the tilted axis of the ReO_6 octahedra immediately below T_{M1} . This likely results from the strong electronic anisotropy of $5d^1$ Re^{6+} , as $3d^8$ Ni^{2+} and high spin $3d^5$ Mn^{2+} both have non-degenerate ground states.

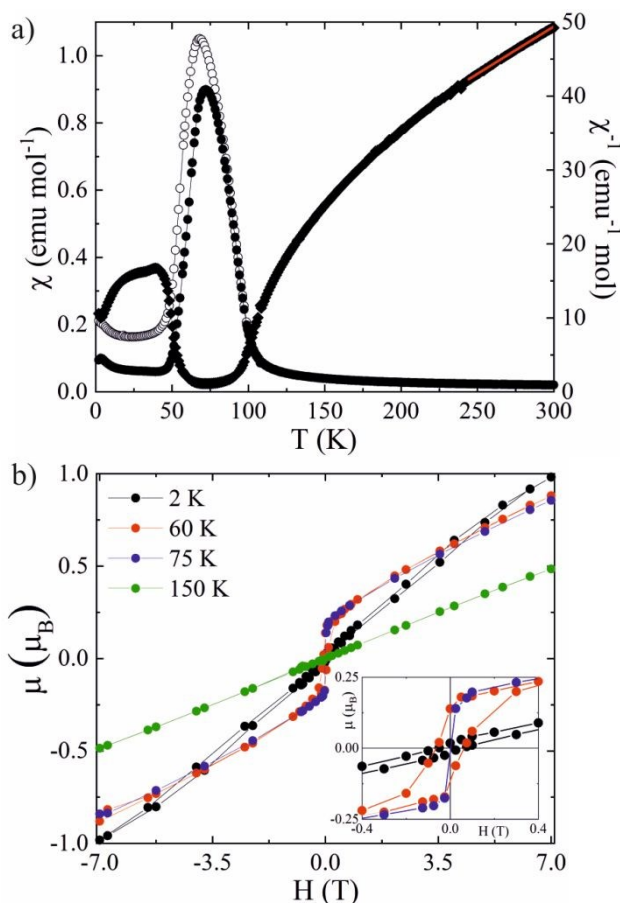


Figure 3. a) Magnetic susceptibility of $\text{Mn}_2\text{NiReO}_6$ (ZFC/FC = closed/open symbols) and the reciprocal ZFC data with Curie-Weiss fit shown. b) Magnetisation-field hysteresis loops at several temperatures with the low field region of the spin-ordered regime in the inset.

Although spin reorientation transitions, where spin directions switch from one fixed direction to another, are known in double perovskites, e.g. $\text{Sr}_2\text{CoOsO}_6$ ²⁰, continuous changes of spin direction over a broad temperature range do not usually occur. Spin directions remain fixed in all of the previously reported $\text{Mn}_2\text{BB'O}_6$ double perovskites shown in ESI except for the reorientation transition in $\text{Mn}_2\text{FeReO}_6$ ⁶. However, the Mn spin angle ϕ_{Mn} in $\text{Mn}_2\text{NiReO}_6$ increases continuously from $\phi_{\text{Mn}} \approx 30^\circ$ just below $T_{M1} = 80$ K to $\phi_{\text{Mn}} = 55^\circ$ at $T_{M2} = 42$ K. ϕ_{Mn} is effectively constant below T_{M2} , so the second transition marks

a change between rotating and non-rotating Mn^{2+} spin phases. This is most likely driven by frustration between the spin orders. Each Mn spin is surrounded by two 'up' and two 'down' Ni and Re spins, and each Ni or Re spin has four 'up' and four 'down' Mn spin neighbours. The monoclinic lattice distortion breaks the equivalence of spin-spin interactions and couples the spin orders, as evidenced by discontinuities at T_{M1} and T_{M2} in lattice strains $e_{ac} = 1 - \sqrt{2}a/c$ and $e_b = \cos\theta$ measured from the refined cell parameters (see ESI) observed in Fig. 4a.

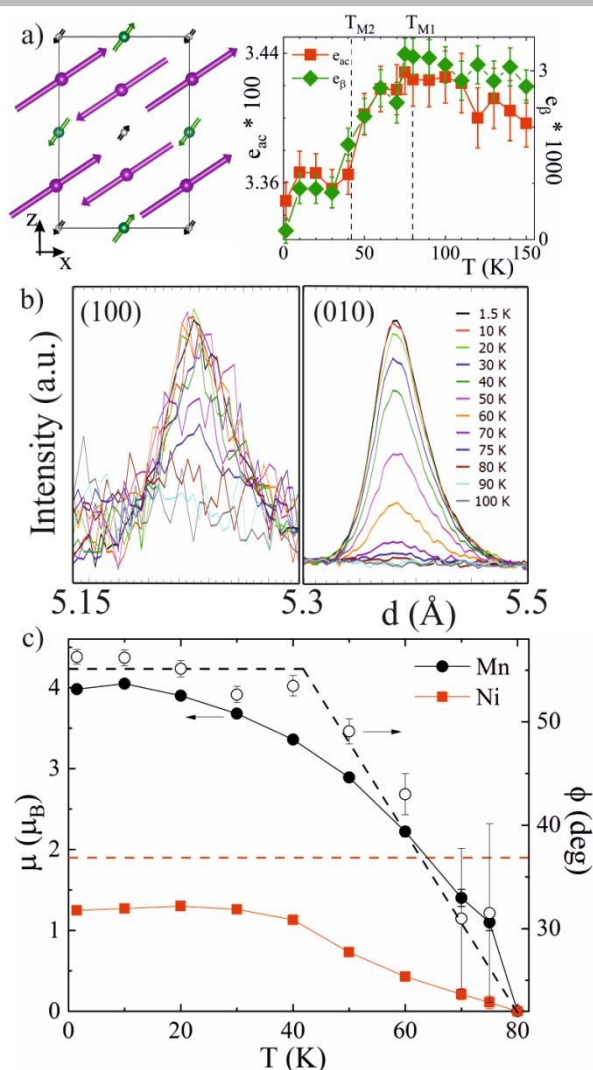


Figure 4. a) Magnetic structure of $\text{Mn}_2\text{NiReO}_6$ at 1.5 K. The right panel shows the thermal variation strain of the e_{ac} and e_b parameters. b) Plots of (100) and (010) magnetic peaks showing their different thermal evolutions. c) Thermal evolution of the refined magnetic moments and angles ϕ (closed and open symbols, respectively) for Mn^{2+} and Ni^{2+} site spins. Re^{6+} moments were constrained to take half the value of those for Ni^{2+} .

Neutron diffraction reveals antiferromagnetic ordering of the Mn, Ni, and Re spins in $\text{Mn}_2\text{NiReO}_6$, but the magnetisation data in Fig. 3 show that a small ferromagnetic component is



also present. This is explained by the presence of non-zero antisymmetric Dzyaloshinskii–Moriya exchange interactions leading to canting of the moments. Symmetry analysis in ESI shows that the irreducible representation describing the observed antiferromagnetic orders of spins in the *ac*-plane also permits ferromagnetic components in the *b* direction, although these are too small to be detected by NPD. Such weak ferromagnetism is common in perovskites where octahedral tilting lowers symmetry and can be used to generate electrical polarisation and hence multiferroic properties.²³

All three of the antiferromagnetic Mn, Ni, and Re sublattices in $\text{Mn}_2\text{NiReO}_6$ give rise to ferromagnetic components. It is notable that the net ferromagnetic moment takes a relatively large value $\sim 0.17 \mu_B \text{ f.u.}^{-1}$ in the rotating-spin phase on cooling below $T_{M1} = 80 \text{ K}$, but collapses to a much smaller value $\sim 0.02 \mu_B \text{ f.u.}^{-1}$ approaching $T_{M2} = 42 \text{ K}$ below which spin directions are fixed. A possible explanation for this is that the relative directions of some of the ferromagnetic components switch at the T_{M2} transition. A switch from +++ directions of the respective weak ferromagnetic moments of Mn, Ni and Re spins above T_{M2} , aligned with the applied field, to +-- below, driven by antiferromagnetic coupling between the ferromagnetic *y*-components at the A and at the B, B' sublattices as the spins become more fully ordered, accounts for the observed sharp magnetisation change at T_{M2} . Such a transition based on switching of weak ferromagnetic moments from a ferro- to a ferri-magnetic order is unprecedented and demonstrates a further new possibility generated by having magnetic A and B sublattices in 'all transition metal' perovskites.

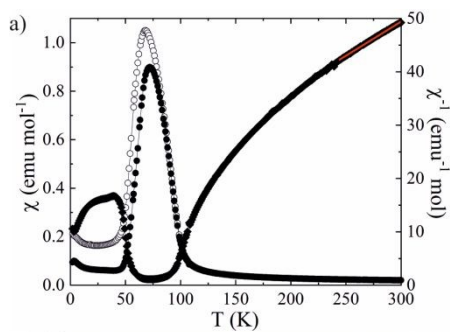
In conclusion, the double perovskite $\text{Mn}_2\text{NiReO}_6$ prepared under high pressure and high temperature conditions shows a high degree of $\text{Mn}^{2+}/\text{Ni}^{2+}/\text{Re}^{6+}$ cation order although 18% excess of Mn^{2+} substitutes for Ni. The monoclinic structure of $\text{Mn}_2\text{NiReO}_6$ is highly distorted with the largest octahedral tilt angles and distortion parameters reported for in the $\text{Mn}_2\text{BB'O}_6$ family to date. All three magnetic sublattices order simultaneously at $T_{M1} = 80 \text{ K}$ with antiferromagnetically-oriented spins, and an unusual change between rotating and non-rotating Mn^{2+} spin phases at $T_{M2} = 42 \text{ K}$. Weak ferromagnetism due to spin canting is observed but the net magnetisation undergoes a collapse at T_{M2} , consistent with switching of the relative directions of the weak ferromagnetic moments at the different sublattices from a ferro- to a ferri-magnetic arrangement. The unusual spin rotation, not seen in other $\text{Mn}_2\text{BB'O}_6$ analogues, and the novel switching of weak ferromagnetic states demonstrate further new possibilities that arise from interacting magnetic A and B sublattices in highly distorted 'all transition metal' double perovskite lattices.

We acknowledge EPSRC for funding and STFC for beamtime allocation at ISIS. K.N.A. acknowledges funding from King Abdulaziz City Science and Technology (KACST).

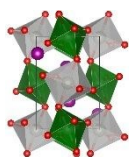
Notes and references

1. K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, Y. Tokura. *Nature*, 1998, **395**, 677–680. DOI: 10.1039/D0CC04756B
2. S. Vasala, M. Karppinen, *Progress in Solid State Chemistry*, 2015, **43**, 1–36.
3. A. J. Dos santos-García, C. Ritter, E. Solana-Madruga, R. Sáez-Puche, *J. Phys. Condens. Matter.*, 2013, **25**, 206004.
4. M. Markkula, A. M. Arevalo-Lopez, A. Kusmartseva, J. A. Rodgers, C. Ritter, H. Wu, J. P. Attfield, *Phys. Rev. B*, 2011, **84**, 094450.
5. M.-R. Li, M. Retuerto, Z. Deng, P. W. Stephens, M. Croft, Q. Huang, H. Wu, X. Deng, G. Kotliar, J. Sánchez-Benítez, J. Hadermann, D. Walker, M. Greenblatt, *Angew. Chem. Int. Ed.* 2015, **54**, 12069–12073.
6. A. M. Arévalo-López, G. M. McNally, J. P. Attfield, *Angew. Chem. Int. Ed.* 2015, **54**, 12074–12077.
7. M.-R. Li, J. P. Hodges, M. Retuerto, Z. Deng, P. W. Stephens, M. C. Croft, X. Deng, G. Kotliar, J. Sánchez-Benítez, D. Walker, M. Greenblatt, *Chem. Mater.*, 2016, **28**, 3148–3158.
8. A. M. Arévalo-López, F. Stegemann, J. P. Attfield, *Chem. Commun.*, 2016, **52**, 5558.
9. C. E. Frank, E. E. McCabe, F. Orlandi, P. Manuel, X. Tan, Z. Deng, M. Croft, V. Cascos, T. Emge, H. L. Feng, S. Lapidus, C. Jin, M. X. Wu, M. R. Li, S. Ehrlich, S. Khalid, N. Quackenbush, S. Yu, D. Walker, M. Greenblatt, *Chem. Commun.*, 2019, **55**, 3331.
10. J. Rodriguez-Carvajal, *Physica B*, 1993, **192**, 55.
11. E. Solana-Madruga, Y. Sun, A. M. Arévalo-López, J. P. Attfield, *Chem. Commun.*, 2019, **55**, 2605–2608.
12. V. F. Sears, *Neutron News*, 1992, **3**, 26–37.
13. E. Solana-Madruga, A. J. Dos santos-García, A. M. Arévalo-López, D. Ávila-Brandé, C. Ritter, J. P. Attfield, R. Sáez-Puche. *Dalton Trans.* 2015, **44**, 20441–20448.
14. A. J. Dos santos-García, E. Solana-Madruga, C. Ritter, D. Ávila-Brandé, O. Fabelo, R. Sáez-Puche. *Dalton Trans.* 2015, **44**, 10665–10672.
15. A. M. Arévalo-López, E. Solana-Madruga, C. Aguilar-Maldonado, C. Ritter, O. Mentré, J. P. Attfield. *Chem. Comm.* 2019, **55**, 14470–14473.
16. S. Hirai, A. M. dos Santos, M. C. Shapiro, J. J. Molaison, N. Pradhan, M. Guthrie, C. A. Tulk, I. R. Fisher, W. L. Mao, *Phys. Rev. B*, 2013, **87**, 014417. Distances are shown in ICSD CIF file 188903.
17. T. Stoyanova-Lyubenova, A. J. Dos santos-García, E. Urones-Garrote, M. J. Torralvo, M. Á. Alario-Franco. *Dalton Trans.*, 2014, **43**, 1117.
18. H. Kato, T. Okuda, Y. Okimoto, and Y. Tomioka, *Phys. Rev. B* 2004, **69**, 184412.
19. M. Retuerto, M. J. Martínez-Lope, M. García-Hernández, M. T. Fernández-Díaz, J. A. Alonso. *Eur. J. Inorg. Chem.* 2008, **4**, 588.
20. R. Morrow, R. Mishra, O. D. Restrepo, M. R. Ball, W. Windl, S. Wurmehl, U. Stockert, B. Büchner, P. M. Woodward. *J. Am. Chem. Soc.* 2013, **135**, 18824–18830.
21. R. Morrow, J. W. Freeland, P. M. Woodward. *Inorg. Chem.* 2014, **53**, 7983–7992.
22. P. Kayser, S. Injac, B. J. Kennedy, T. Vogt, M. Avdeev, H. E. Maynard-Casely. *Inorganic Chemistry* 2017, **56** (11), 6565–6575.
23. N. A. Spaldin, R. Ramesh. *Nature Mats.* 2019, **18**, 203–212.





$_{12}\text{NiReO}_6$ has an unusual rotation of Mn spins from 80 down to 42 K where a collapse in weak ferromagnetism evidences switching of the canted components.



View Article Online
DOI: 10.1039/D0CC04756B

