Giant coercivity and spin clusters in high pressure polymorphs of Mn₂LiReO₆.

Elena Solana-Madruga,^{*abc} Clemens Ritter,^d Olivier Mentré,^a J. Paul Attfield^b and Ángel M. Arévalo-López.^{*a}

Experimental details:

Stoichiometric proportions of $LiMn_2O_4$ and ReO_2 oxides were ground thoroughly and packed into Pt capsules, previous preparation of $LiMn_2O_4$ as reported in ref [1]. The precursors were heated at 1100 °C for 20 minutes under 5 (OIL) and 8 GPa (DPv), after what temperature was quenched and pressure was slowly released. X-ray diffraction confirmed single phase compounds (Fig S1) and further structural characterisation was performed in terms of neutron powder diffraction (NPD), much more sensitive to light elements as Li and O and with a good contrast between all cations (scattering lengths -3.73, -1.9 and 9.2 fm for Mn, Li and Re respectively) thus allowing determination of accurate cation distribution and oxygen positions. Degradation of Mn_2LiReO_6 phases with time was found from NPD for the DPv phase.

Bulk magnetic properties were measured on pure samples checked from XRD immediately after high pressure synthesis using a SQUID Quantum Design and a 9T PPMS-Dynacool magnetometers. Magnetisation was measured in zero field and field cooled modes for both samples. Field dependent magnetisation was measured at 2 K and every 20 K between 20 and 120 K for the DPv polymorph and at 2 K and 50 K for the OIL sample. Raw data showing the AFM matrix of the DPv sample are shown in Fig. S2 for selected temperatures. These data were treated to extract the FM component as shown in Fig. 3b in the main text. For that, the AFM contribution was linear fitted at high magnetic fields and subtracted from the full data. Fig. S3 compares the low temperature loop for both polymorphs, where a similar data analysis has been used for both to show the FM component only. The presence of a certain hysteresis in the OIL phase reflects the presence of FM clusters only ordered at a short range. Derivative curves for these data are included in the figure to confirm the high field feature is only observed in the DPv polymorph.

AC magnetisation was collected on fresh samples for the OIL polymorph between 30 and 60 K from 100 Hz to 10 kHz using an AC drive of 15 Oe to prove its cluster glass behaviour after no long-range magnetic order was observed from NPD. Additional AC data were measured in the same frequency range below 140 K for a fresh DPv sample. These data, depicted in Fig. S4, show the magnetic transition at 109 K and a plateau in the 20 - 70 K range, supporting the lower temperature anomaly reducing the magnetic moment as observed from the hysteresis loops. Slight mismatches in the magnetisation in the temperature range 35 - 50 K are due to the superposition of data sets collected at different experiments, with different sample centring.

The total and partial density of states calculated by DFT+U (U= 5 eV) in a spin-polarised ferromagnetic configuration of DPv-LiReMnO₆ is shown on the Figure 2 of the main text. Focusing on the highest part of the valence band (VB) between -7 eV and E_F, the mixed Re *d* and O *p* states occur between -6.5 and -4 eV, signing the dative covalent Re – O bonds from O²⁻ electron donors. This is far below the main occupied Mn *d* states, whose contribution range up to E_F and shows two maxima at -4 and -0.5 eV respectively. Such delocalised broad distribution of Mn *d* levels and O-p states is typical of the strongly distorted A-site MnO₆ polyhedra (2.1 Å < Mn – O < 2.8 Å) with the upper contribution assigned to axial σ^* Mn-O bondings. The absence of any spin down (\downarrow) Mn *d*, (not shown) validates the Mn²⁺ d⁵ high spin state. The lowest "pocket" of states in the conduction band (CB) starts at 0.65 eV above E_F. It has a minor Mn *d* contribution but essentially consists of empty mixed Re *d* and O *p* states is shifted by the on-site U repulsion in a higher CB second block, above 4 eV with prominent DOS above 6 eV. It hampers any easy Mn-Mn electronic hopping in this compound.

Neutron powder diffraction (NPD) data were collected at D20 at the Institut Laue-Langevin using wavelength λ = 1.54 Å for accurate structural characterisation at 300 K in high resolution mode in the

angular range 0 ° – 150 ° with a 0.05 ° step size. Data for magnetic structure determination were collected at 3 K and 140 K for the DPv polymorph and at 2 K and 150 K for the OIL phase using wavelength λ = 2.41 Å. The small amounts of sample, 30 mg and 40 mg respectively, required the use of difference data sets for reliable refinements, where the signal of the empty sample holder was also subtracted. Magnetic symmetry analysis was performed using BasIreps tool implemented in FullProf software. ^[2] For the DPv polymorph, allowed irreducible representations (Irreps) and their basis vectors are summarised in Table S1. All magnetic peaks can be indexed using propagation vector [0 0 0] and Mn²⁺ spins follow Irrep Γ_1 , with AFM collinear alignment into the *ac* plane and a FM contribution below the detection limit of our D20 data allowed along *b*. Magnetic moments at 3 K refine to 2.4(1) μ_B with m_x and m_z contributions 2.27 μ_B and 0.87 μ_B respectively. No magnetic signal was observed in the low temperature data of the OIL polymorph, as shown in the raw 2 and 150 K data (top panel) and their difference pattern (bottom panel) shown in Fig. S5.



Fig. S1. Rietveld fits of the OIL (top) and DPv (bottom) structures against laboratory XRD data. 5% of secondary MnO, not observed in magnetisation or NPD, is refined from these data in the DPv sample.



Fig. S2. Raw hysteresis loops of OIL (left) and DPv_Mn₂LiReO₆ (right).



Fig. S3. 2 K hysteresis loops after AFM contribution subtracted for OIL (red) and DPv (black) Mn_2LiReO_6 . Derivative curves are plotted in the same respective colours.



Fig. S4. Real (up) and Imaginary (middle) AC magnetisation of the OIL (left) and $DPv_Mn_2LiReO_6$ (right). The cluster glass behaviour of the OIL phase is clear from the frequency dependency and Vogel-Fulcher fit as described in the main text. The magnetic transition of the DPv is clearly observed as a non-frequency dependent signal at 109 K. A plateau in the 20 – 70 K temperature range with a further decrease at lower temperatures supports the spin reorientation and the decreasing magnetic moment observed at 2K from DC hysteresis measurements. Bottom, $d\chi''/dT$ vs T for OIL_Mn_2LiReO₆.



Fig. S5. NPD data collected at 3 K (red) and 150 K / 140 K (green) for the OIL (left) / DPv_Mn₂LiReO₆ (right) at D20, using λ = 2.14 Å. Their difference patterns (blue) are shown in the bottom panel. No magnetic peaks are observed for the OIL, but only evidence for short range order as background undulation.

Table S1. Irreducible representations (Irrep) and basis vectors from the magnetic symmetry analysis of DPv_Mn₂LiReO₆ (*P21/n*) with propagation vector [0 0 0]. Only real components are shown, since imaginary components are 0 for all basis vectors. Magnetic moments at 3 K refine to 2.4(1) μ_B with m_x and m_z contributions of 2.3 μ_B and 0.9 μ_B respectively using Γ_1 .

Symm	Γ_1	Γ_2	Γ_3	Γ_4
x, y, z	100 010 001	100 010 001	100 010 001	100 010 001
$-x^{+1/2}, y^{+1/2}, -z^{+1/2}$	-100 010 00-1	-100 010 00-1	100 0-10 001	100 0-10 001
-x, -y, -z	100 010 001	-100 0-10 00-1	100 010 001	-100 0-10 00-1
x+1/2, -y+1/2, z+1/2	-100 010 00-1	100 0-10 001	100 0-10 001	-100 010 00-1

Table S2. Magnetic frustration index, calculated as $f = |\theta| / T_N$, for all reported Mn₂BB'O₆ ordered corundum derivatives.

В	B'	Structure	T_N	f	ref
Fe	Sb	IL	260	1.8	[3]
Cr		IL	60	3.3	[4]
Sc		NTO	42	3.3	[5]
In		OIL	38	4.2	[6]
Mn	W	NTO	58	4.8	[7]
Fe		NTO	75	*	[8]
Fe	Nb	LN	90	*	[9]
	Та	LN	80	2.6	[9]
	Мо	NTO	337	0.7	[10]
	Мо	OIL	229	*	[11]
Li	Re	OIL	46	4.3	This work

* No θ value reported.

References:

^[1] M. M. Thackeray, W. I. F. David, P. G. Bruce, J. B. Goodenough, *Mat. Res. Bull.*, 1983, 18, 461-472. ^[2] J. Rodriguez-Carvajal, *Physica B*, 1993, 192, 55.

^[3] A. J. Dos santos-García, E. Solana-Madruga, C. Ritter, A. Andrada-Chacón, J. Sánchez-Benítez, F. J. Mompean, M. Garcia-Hernandez, R. Sáez-Puche, R. Schmidt, *Angew. Chem. Int. Ed.* 2017, 56, 4438 – 4442.

^[4] A. J. Dos santos-García, E. Solana-Madruga, C. Ritter, D. Ávila-Brande, O. Fabelo, R. Sáez-Puche, *Dalton Trans.* 2015, 44, 10665-10672.

^[5] E. Solana-Madruga, Á.J. Dos santos-García, A.M. Arévalo-López, D. Ávila-Brande, C. Ritter, J.P. Attfield, R. Sáez-Puche, *Dalton Trans.* 2015, 44, 20441-20448.

^[6] Á. M. Arévalo-López, E. Solana-Madruga, E. P. Arévalo-López, D. Khalyavin, M. Kepa, A. J. Dos santos-García, R. Sáez-Puche, J. P. Attfield, *Phys. Rev. B*, 2018, 98, 214403.

^[7] M.-R. Li, E. E. McCabe, P. W. Stephens, M. Croft, L. Collins, S. V. Kalinin, Z. Deng, M. Retuerto, A. S. Gupta, H. Padmanabhan, V. Gopalan, C. P. Grams, J. Hemberger, F. Orlandi, P. Manuel, W.-M. Li, C.-Q. Jin, D. Walker, M. Greenblatt, *Nat. Commun.* 2017, 8, 2037.

^[8] M.-R Li, M. Croft, P. W. Stephens, M. Ye, D. Vanderbilt, M. Retuerto, Z. Deng, C. P. Grams, J. Hemberger, J. Hadermann, W.-M. Li, C.-Q. Jin, F. O. Saouma, J. I. Jang, H. Akamatsu, V. Gopalan, D. Walker, M. Greenblatt, *Adv. Mater.* 2015, 27, 2177–2181.

^[9] M.-R. Li, D. Walker, M. Retuerto, T. Sarkar, J. Hadermann, P. W. Stephens, M. Croft, A. Ignatov, C. P. Grams, J. Hemberger, I. Nowik, P. S. Halasyamani, T. T. Tran, S. Mukherjee, T. S. Dasgupta, M. Greenblatt, *Angew. Chem. Int. Ed.* 2013, 52, 1–6.

^[10] M.-R. Li, M. Retuerto, D. Walker, T. Sarkar, P. W. Stephens, S. Mukherjee, T. S. Dasgupta, J. P. Hodges, M. Croft, C. P. Grams, J. Hemberger, J. Sánchez-Benítez, A. Huq, F. O. Saouma, J. I. Jang, M. Greenblatt, *Angew. Chem. Int. Ed.* 2014, 53, 10774 –10778.

^[11] M.-R. Li, M. Retuerto, P. W. Stephens, M. Croft, D. Sheptyakov, V. Pomjakushin, Z. Deng, H. Akamatsu, V. Gopalan, J. Sánchez-Benítez, F. O. Saouma, J. I. Jang, D. Walker, M. Greenblatt, *Angew. Chem. Int. Ed.* 2016, 55, 9862 –9867.