Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting information to "Fundamentals of $NaMnO_2$, the cathode material for Na-ion rechargeable batteries"

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S1. MONOCLINIC α-NMO

In Figure S1 we show 3D isosurface plots of the magnetization density for monoclinic α-NMO, disentangled in contributions from the different groups of bands examined in the main text.

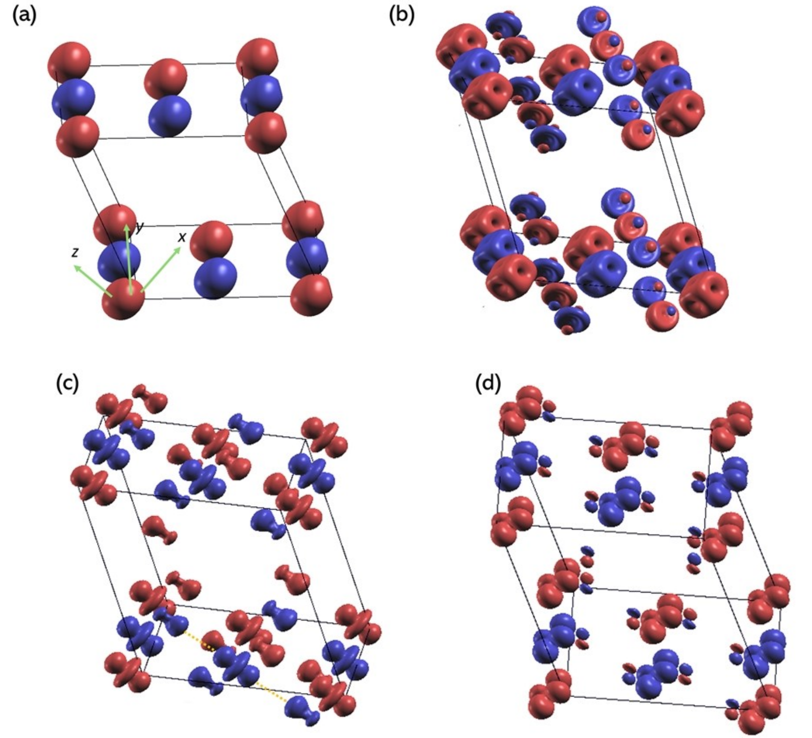

Figure S1: Calculated magnetization density isosurfaces for monoclinic α-NMO in the AF (1×2×1) unit cell. Red and blue surfaces indicate up-spin and down-spin magnetization, respectively. To describe the magnetization shape, it is useful to assume the cartesian reference drawn in green in (a), with x, y, and z axes oriented along [1,0,1], [0,1,0], and [-1,0,1] directions of the monoclinic cell, respectively. (a): magnetization derived from bands within the [-7 eV, -4.5 eV] energy interval. This magnetization only resides on Mn's and accounts for most of the local magnetic moments. (b) magnetization from bands within [-4.5 eV, -1 eV] range; in this region Mn and O are largely hybridized and we can recognize Mn d_{x2-y2} and O p_x, p_y orbital characters. (c) magnetization from the two energy highest valence bands, which derives from a combination of Mn d_{z2} and O p_z orbitals. The orange dotted line highlights the O-Mn-O trimer alignment, with spin-parallel orientation. (d) magnetization from the two hole bands at the conduction bottom. They derive from Mn d_{xy} orbitals, with tiny contributions from O p_y as well.

The bands within (-7 eV, -4.5 eV) are fully spin-polarized and weakly hybridized with oxygens; the corresponding magnetization (figure S1a) displays nearly spherical ellipsoids fully localized on the Mn's, and accounts for a large portion of the Mn magnetic moment. Figure S1b displays the contribution of bands from -4.5 eV to -1 eV; here we see features on both Mn and O; in particular, Mn's display a sort of holed cubes given by the combination of $d_{x^2-y^2}$, d_{xz} and d_{yz} orbitals (the x, y, z reference is shown in figure S1a). Figure S1c shows the magnetization associated with the two bands at the VBT, contributed by Mn d_{z^2} and O p_z orbitals; we notice that z is the [-1,0,1] direction of the aligned O-Mn-O segments (highlighted by the orange dotted line) thus the d_{z^2} - p_z coupling drives the spin-parallel Mn-O alignment along z. Finally, figure S1d displays the magnetization derived from the hole bands lying at the conduction bottom, which presents a $d_{xy} - p_y$ orbital character.

Table S1 : Mn 3*d* and O 2*p* orbital charges (per single atom) separated in majority-spin and minority-spin channels; total values (tot) are resolved in the 3 energy-disentangled band manifolds (G_1, G_2, G_3) which compose the valence bands (as described in the main text). Magnetic moments (M) per atom and per MnO_2 formula unit are also listed (in μ_B). Due to the AFM symmetry, Mn and O belonging to the oppositely polarized sublattice have same values but with majority-spin and minority-spin occupancy exchanged. For β-NMO there are two types of oxygens, O_1 and O_2, and the MnO_2 unit if formed by one O_1 and one O_2.

	α-NMO *C2/m*					β-NMO *Pmnm*			
	G_1	G_2	G_3	tot		G_1	G_2	G_3	tot
$Mn^{\uparrow}$	2.79	1.44	0.31	4.54	$Mn^{\uparrow}$	2.79	1.47	0.29	4.54
$Mn^{\downarrow}$	0.09	0.49	0.03	0.61	$Mn^{\downarrow}$	0.09	0.48	0.05	0.62
M_{Mn}	2.70	0.95	0.28	3.93	M_{Mn}	2.69	0.99	0.24	3.92
$O^{\uparrow}$	0.59	1.90	0.26	2.75	$O_1^{\uparrow}$	0.39	2.31	0.06	2.76
$O^{\downarrow}$	0.46	2.18	0.06	2.70	$O_1^{\downarrow}$	0.39	2.31	0.06	2.76
M_O	0.13	-0.28	0.20	0.05	M_{O1}	0	0	0	0
					$O_2^{\uparrow}$	0.57	1.93	0.23	2.74
					$O_2^{\downarrow}$	0.55	1.97	0.22	2.74
					M_{O2}	0.03	-0.04	0.01	0
M_{MnO2}	2.96	0.38	0.68	4.03	M_{MnO2}	2.72	0.95	0.25	3.92

Table S1 shows the calculated orbital occupancies for Mn 3*d* and O 2*p* states, resolved in majority-spin and minority-spin contributions; the partial values derived by each group of valence bands are also shown. For α-NMO the total magnetic moment on the oxygens is rather small, but it results from large compensating values associated to the different band groups.

To examine in detail the J_2 frustration, in figure S2 we compare the magnetization density derived from the (-4.5, -1) eV range for the AF ground state (fig.S2a) and for the AF1 phase (fig.S2b). Considering the AF phase, it is easy to see that the four J_2 couplings for each Mn are actually non-equivalent, since the orbital orientation of the intermediate oxygens generates two distinct path: the spin-parallel J_2 (made by two orange-dashed Mn-O bonds) and the spin-antiparallel J_2‘ (one orange- and one green-dashed Mn-O bond); thus, the magnetic frustration due to the structural equivalence of the four inter-stripe Mn-Mn neighbors is actually relieved by the orbital-order of the oxygens. On the other hand, no magnetic frustration is present in the AF1 phase, and inf fact no orbital-order is present on the oxygens: they are magnetically ordered but all equal from the orbital viewpoint.

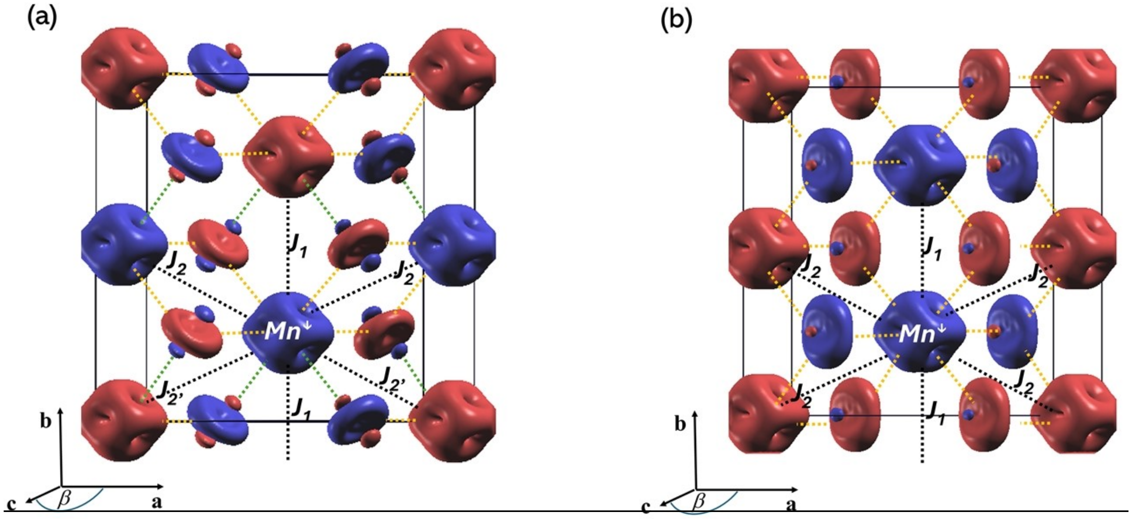

Figure S2: (a) View of the (*a*,*b*) plane magnetization density derived from the [-4.5 eV, -1 eV] bands (same as in Figure S5b). for monoclinic α-NMO in the AF (1×2×1) unit cell. Red and blue surfaces indicate up-spin and down-spin magnetization, respectively. Mn-Mn bonds are shown as black dashed lines, Mn-O bonds as orange-dashed or green-dashed lines to distinguish their different orbital orientation. Orbital order on the oxygens allows to distinguish the exchange interactions between spin-parallel Mn (J_2) from that of spin-antiparallel Mn ($J_{2'}$). (b) Same (*a*,*b*) plane view but for the AF1 phase. In this configuration, the J_2 exchange interactions are not frustrated and oxygens are still magnetically-ordered but orbital order disappear. Notice that this calculation is done in the AF1 (1×1×1) unit cell, thus no orbital order can arise to relieve frustration on J_1.

S2. TRICLINIC α-NMO

In Fig.S3 we display band structure and magnetization density calculated by VPSIC for triclinic α-NMO in the (1×2×1) supercell. The band gap of 2.24 eV is direct at the M point; the band structure can be disentangled in the same manifolds seen for the monoclinic structure, indicated by the different colors in figure S3a; the magnetization densities derived from each group of bands are shown in figure S3b (black bands), S3c (red), S3d (magenta), S3e (orange).

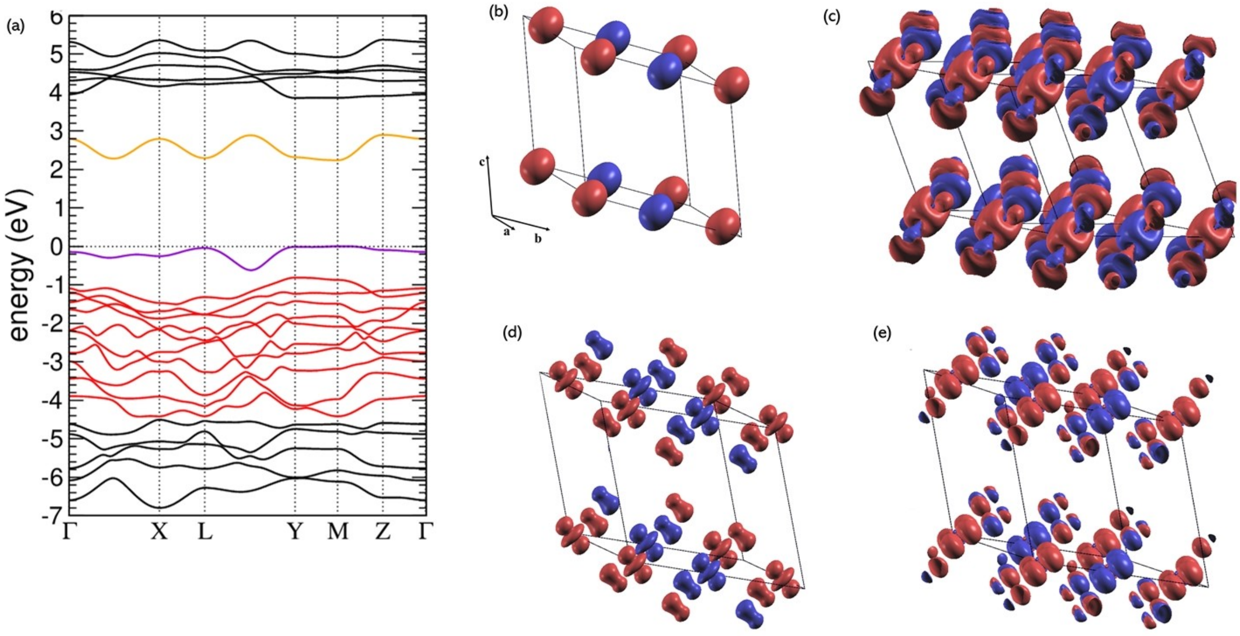

Figure S3: (a) band energies of triclinic α-NMO in the AF2 (1×2×1) unit cell. Different band groups are drawn in different colors, analogously to the monoclinic structure (see main text). (a): magnetization derived from the black bands within the [-7, -4.5]eV energy interval. This magnetization mainly resides on Mn's and accounts for most of the local magnetic moments. (b) magnetization from red bands within [-4.5, -1]eV range; in this region Mn and O are largely hybridized and we can recognize Mn $d_{x2\text{-}y2}$ and O p_x, p_y orbital characters. (c) magnetization from the energy highest valence band, which derives from a combination of Mn d_{z2} and O p_z orbitals. (d) magnetization from the hole band at the conduction bottom, which derives from Mn d_{xy} and O p_y orbitals. Red and blue surfaces indicate up-spin and down-spin magnetization, respectively.

The characteristics of magnetization density are analogous to those shown by the monoclinic structure; in particular, the same stripe-like behavior is obtained for the (-4.5, -1) eV bands: MnO_2 stripes carry zig-zag AFM superexchange interactions along the stripes. In the triclinic symmetry the stripe is along ($\bar{1}$, 1, 0) and parallel to the ($\bar{1}$, $\bar{1}$, 0) plane.