Supporting information

$NaMoO_2$: a layered oxide with molybdenum clusters

Laura Vitoux, Marie Guignard, Nicolas Penin, Dany Carlier, Jacques Darriet, Claude Delmas

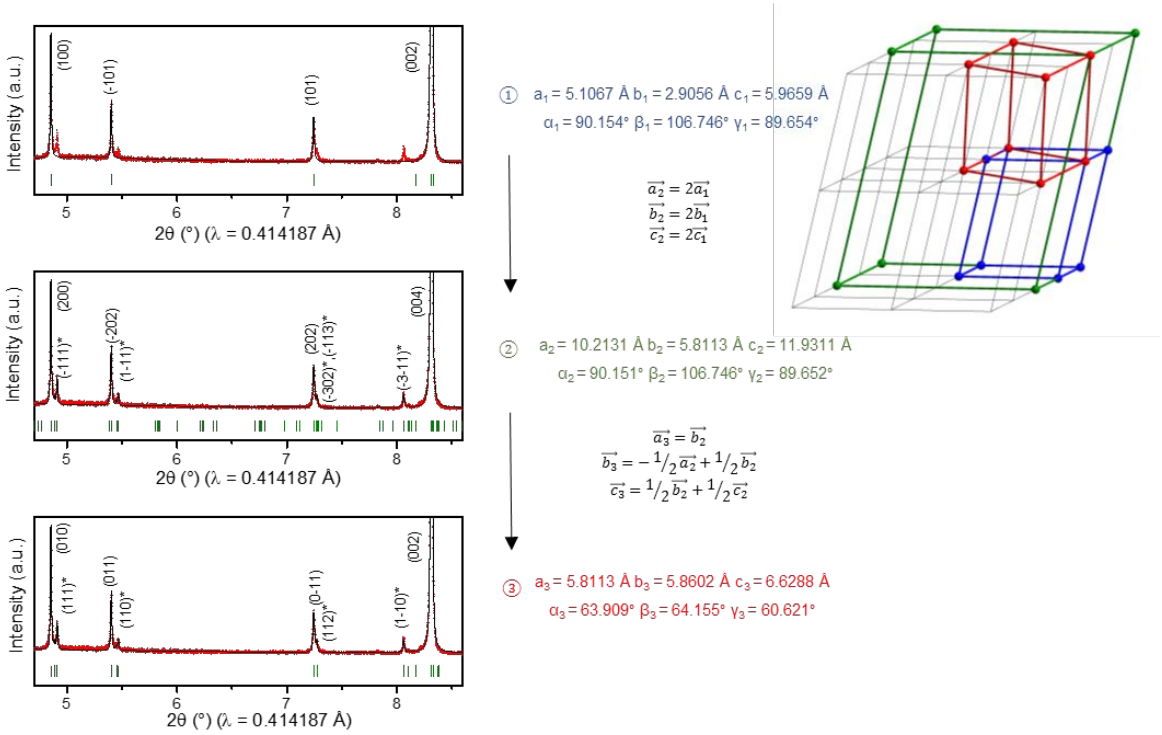

Figure S1: An enlargement in the 2θ-range of the synchrotron diffraction pattern of O''3-$NaMoO_2$ (well-crystallized) show the characteristic peaks of the superstructure marked by stars. The calculated diffraction pattern by the Lebail method (black line) is superimposed to the experimental pattern (red filled diamonds). Bragg peaks are indexed considering the triclinic cells indicated next to each pattern and represented on the right side. Bragg peak positions are marked by green ticks.

Table S1. Structural parameters of $NaMoO_2$ (ex $Na_{2/3}MoO_2$) determined from the Rietveld refinement.

Source: Synchrotron
Chemical formula: $NaMoO_2$
Formula Weight: 150.948 $g.mol^{-1}$
Temperature: 300 K
Pressure: 1 atm
Wavelength for constant wavelength or TOF: 0.4142 Å
Crystal system: Triclinic
Space group (No.): P-1 (N° 2)
a = 5.8115(2) Å, b = 5.6803(3) Å, c = 6.6291(4) Å, α = 63.607(3)°, β = 64.154(3)°, γ = 60.620(3)°
V = 169.54(2) $Å^3$
Z = 4
d-space range: 0.65 – 11.87 Å
$\chi^2 = 2.75$
$R_p = 9.81$ %
$R_{wp} = 14.12$ %
Definition of R factors:

$\chi^2 = \Sigma_i w_i (y_{C,i} - y_{O,i})^2 / N$ Profile factor Rp: $R_p^2 = \Sigma_i (y_{C,i} - y_{O,i})^2 / \Sigma_i (y_{O,i})^2$ Weighted Profile Factor Rwp : $R_{wp}^2 = \Sigma_i w_i (y_{C,i} - y_{O,i})^2 / \Sigma_i w_i (y_{O,i})^2$				
Atom	x	y	z	Biso (Å^2)
Mo1	0.4945(1)	0.2219(1)	0.5012(1)	0.41(1)
Mo2	0.0362(1)	0.2061(1)	0.5087(1)	0.50(1)
Na1	0.0074(6)	0.2567(5)	0.9922(6)	0.78(1)
Na2	0.4887(6)	0.2724(5)	0.9846(5)	0.67(1)
O1	0.269(1)	0.979(1)	0.751(1)	0.32(1)
O2	0.223(1)	0.495(1)	0.293(1)	0.28(1)
O3	0.262(1)	0.985(1)	0.261(1)	0.73(1)
O4	0.265(1)	0.527(1)	0.687(1)	0.67(1)

Table S2 : Optimized structure parameters by ab initio calculation for the O''3-$NaMoO_2$ material

Space Group P-1 a = 5.8212 Å, b = 5.8803 Å, c = 6.6372 Å α = 63.94°, β = 64.22°, γ = 60.80° V = 171 Å^3, Z = 4						
Atom	**Wyckoff**	**Occ.**	**x**	**y**	**z**	**Biso (Å²)**
Mo1	2i	1	0.4930	0.2198	0.5019	1
Mo2	2i	1	0.0387	0.2037	0.5074	1
Na1	2i	1	0.0085	0.2563	0.9912	1
Na2	2i	1	0.4913	0.2715	0.9813	1
O1	2i	1	0.2635	0.9796	0.7575	1
O2	2i	1	0.2262	0.4957	0.2873	1
O3	2i	1	0.2259	0.9873	0.2616	1
O4	2i	1	0.2603	0.5277	0.6901	1

Table S3 : Interatomic distances measured in the optimized structure of O''3-NaMoO2. Long distances are written in grey.

	distance (Å)		distance (Å)
Mo1-Mo1	2.5572	Na1-Na1	2.8714
	3.3247		3.0134
Mo1-Mo2	2.6461	Na1-Na2	2.8267
	2.6761		2.8825
	3.1473		2.9969
	3.2894		3.0481
Mo2-Mo2	2.6926	Na2-Na2	2.8578
	3.2498		3.0458
Mo1-O1	2.0923	Na1-O1	2.2419
	2.1029		2.2616
Mo1-O2	2.1233	Na1-O2	2.3009
Mo1-O3	2.1552	Na1-O3	2.312

Mo1-O4	2.1719	Na1-O4	2.3710
	2.1899		2.4655
Mo2-O1	2.1188	Na2-O1	2.2517
Mo2-O2	2.1240	Na2-O2	2.2932
	2.2334		2.4260
Mo2-O3	2.0829	Na2-O3	2.2332
	2.1566		2.3240
Mo2 – O4	2.1738	Na2 – O4	2.3535

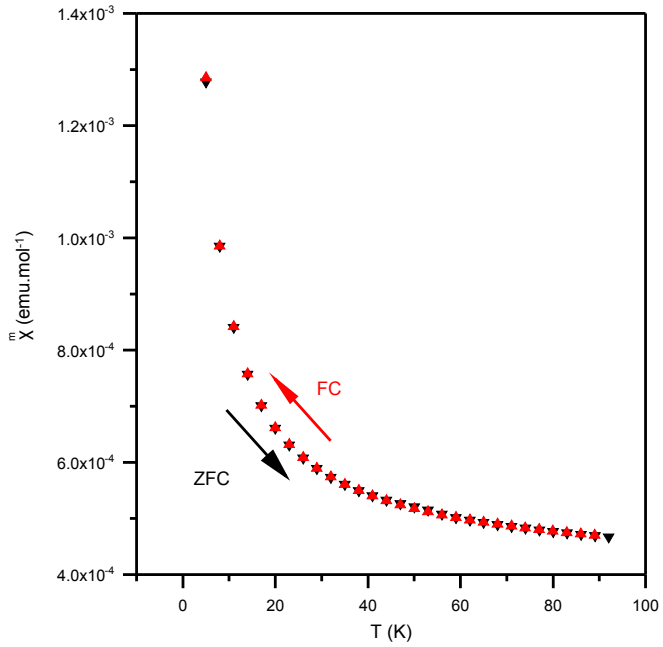

Figure S2 : Thermal evolution of the magnetic susceptibility between 5K and 100K, zero field-cooled (ZFC) in black, Field Cooled (FC) in red.

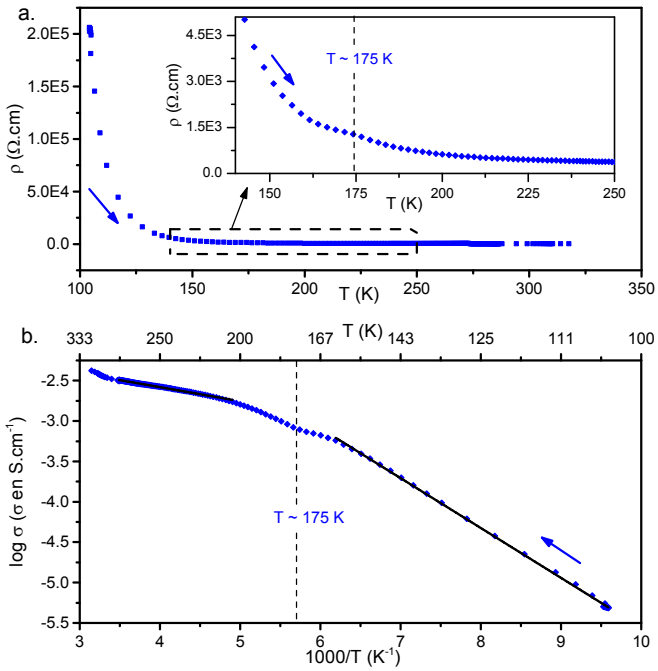

Figure S3 : a. Low temperature (100 K – 318 K) resistivity measurement on well-crystallized $NaMoO_2$ pellets. In the insert is shown a thermally activated charge density wave at 175 K. b. Linear refinement of log σ = 1000/T using Arrhenius Law for 286 K < T < 204 K (R^2 = 0.997, Ea = 0.123 eV) and 162 K < T < 104 K (R^2 = 0.999, Ea = 0.035 eV).