– Electronic Supplementary Information –

Unexpected origin of the magnetism in monoclinic $Nb_{12}O_{29}$ from first-principles calculations

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Table S1. Calculated fractional coordinates of atoms at the Wyckoff sites in the unit cells listed in Table 1 of the main text. The interatomic distances (bonds lengths), bond-valences (V) and the number of 4d electrons in the Nb spheres (N(e)) of the Nb atoms are listed. The local magnetic moments (M) are also included. The doublet Nb-O bonds are along the *b*-axis (Figure S1).

Atom	site	x/a, y/b, z/c	Bond lengths (Å)	V(v.u.)/ N(e) / M (μ_B)
Orthorhombic phase				
Nb1	8f	0.0507, 0.0, 0.0362	-O: 1.79, 1.89, 2.00(×2), 2.30, 2.41	+4.77/ 1.22 /0.00
Nb2	8f	0.0505, 0.0, 0.6687	-O: 1.79, 1.85, 2.02(×2), 2.27, 2.34	+4.82/ 1.23 /0.00
Nb3	8f	0.0484, 0.0, 0.8514	-O: 1.76, 2.00, 2.00(×2), 2.14, 2.49	+4.68/ 1.23 /0.00
Nb4	8f	0.1849, 0.0, 0.0336	-O: 1.83, 1.91, 1.99 (×2), 2.14, 2.28	+4.88/ 1.18 /0.00
Nb5	8f	0.1845, 0.0, 0.6675	-O: 1.83, 1.92, 1.99(×2), 2.13, 2.28	+4.87/ 1.18 /0.00
Nb6	8f	0.1848, 0.0, 0.8508	-O: **1.91**, 1.94 (×2), 2.01, 2.02, 2.23	+4.92/ 1.13 /0.00
Monoclinic phase				
Nb1	4i	0.1019,0.0, 0.0667	-O: 1.79, 1.89, 2.00(×2), 2.30, 2.42	+4.77 / 1.22 / 0.01
Nb2	4i	0.3709, 0.0, 0.1445	-O: 1.83, 1.91, 1.99(×2), 2.15, 2.28	+4.87 / 1.18 / 0.05
Nb3	4i	0.0968, 0.0, 0.8804	-O: 1.76, 2.00, 2.01(×2), 2.14, 2.49	+4.72 / 1.23 / 0.02
Nb4	4i	0.3695, 0.0, 0.9613	-O: **1.91**, 1.94(×2), 2.01 2.02, 2.25	+4.90 / 1.14 / 0.10
Nb5	4i	0.1005, 0.0, 0.6988	-O: 1.80, 1.85, 2.02(×2), 2.27, 2.33	+4.82 / 1.22 / 0.02
Nb6	4i	0.3679, 0.0, 0.7774	-O: 1.83, 1.92, 1.99(×2), 2.12, 2.29	+4.88 / 1.18 / 0.06

Figure S1. Schematic coordinations of several NbO_6 octahedrons belonging to (a) the magnetic Nb4 atoms and (b) the non-spin-polarized Nb1 atoms in m-phase, and (c) the Nb6 atoms in the o-phase of $Nb_{12}O_{29}$.

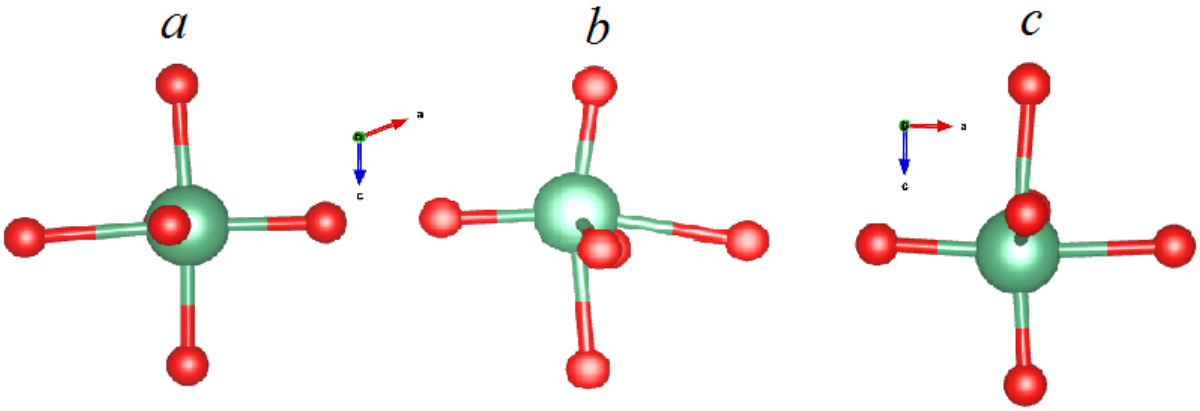

Figure S2. The isosurfaces of spin-density for m-$Nb_{12}O_{29}$ viewed along the (010) axis (a), and in perspective view (b). The green large spheres represent Nb atoms, and small red spheres O atoms. The spin-density for the Nb 4d orbitals is displayed in yellow.
[[[MvH: specify also the blue]]].