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Supporting information for article:

Spin-resolved atomic orbital model refinement for combined charge and spin density analysis: application to the $YTiO_3$ perovskite

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S1. Representation of radial functions through expansion over Gaussian functions for titanium, yttrium and oxygen

The expansion parameters of GTO functions (eq. 7) which is used to describe the STO radial function of "valence" orbitals for titanium, yttrium and oxygen is presented in tables S1, S2, S3. The comparison of the radial functions described by STO and GTO functions for "valence" orbitals is presented on the figure S1 for corresponding atoms.

Table S1 "Valence" orbitals for titanium. Representation through Gaussian functions.

p_k (4S)	α_k (4s)	p_k (3d)	α_k (3d)
0.41318	0.10263	0.05680	0.26736
0.71920	0.26404	0.22987	0.74234
-0.47347	2.43669	0.40659	1.87259
-0.05144	17.56035	0.38758	5.10434
0.19515	28.28142	0.20989	14.17314
-0.02649	160.61295	0.05842	45.53364
		0.00735	184.02337

Table S2 "Valence" orbitals for yttrium. Representation through Gaussian functions.

p_k (5S)	α_k (5s)	p_k (4d)	α_k (4d)
0.35633	0.08021	0.02963	0.11163
0.79646	0.19808	0.17752	0.25542
-0.58090	1.66969	0.35183	0.58039
0.23182	15.36098	0.40549	1.34636
-0.09107	83.01756	0.27202	3.30473
-0.04154	2613.08849	-0.12671	27.15014
5.10332	3875.85660	-0.06503	91.91714
-6.52741	4007.46230	-0.00953	392.73275
1.48242	4419.97899		

Table S3 "Valence" orbitals for oxygen. Representation through Gaussian functions.

p_k (2S)	α_k (2s)	p_k (2p)	α_k (2p)
0.12234	0.54255	0.10074	0.39333
0.49402	1.33715	0.38465	1.14864
0.49227	3.45871	0.45020	3.42993
-0.25281	35.56531	0.25703	11.03848
0.26109	146.98360	0.06450	42.45348
-0.35469	154.77130	0.00675	237.74589
-0.01208	1854.08720		

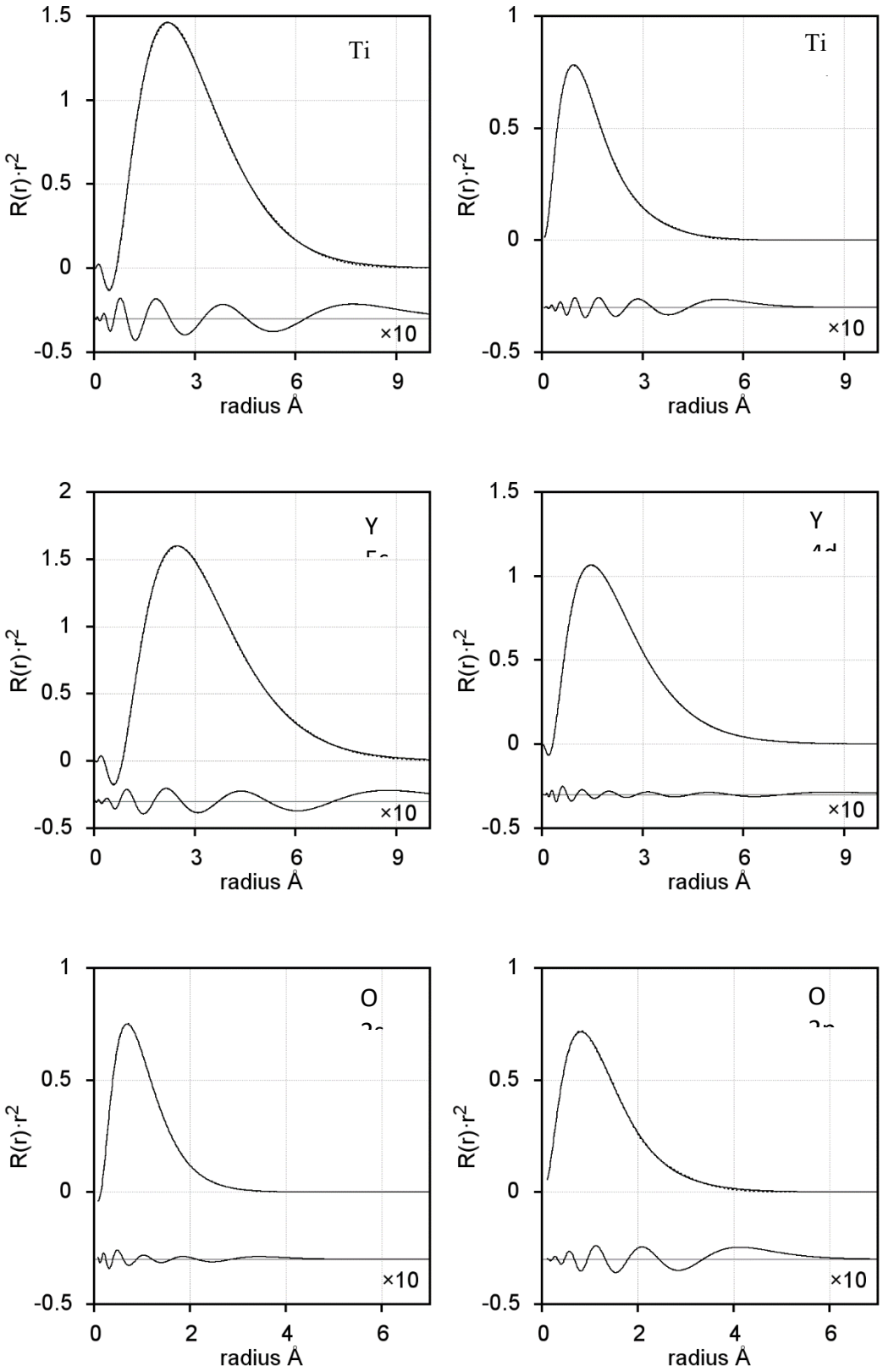

Figure S1 Radial function weighted on r^2 expressed through Slater (solid line) and Gaussian functions (dotted line) for titanium, yttrium and oxygen. Multiplied by ten the difference between models is shown below.

S2. Refinement in frame of orbital and multipole models

The figure S2 shows the definition of local Cartesian coordinate system for each atom in asymmetric unit cell. Y has axis "Y" to O1 (closest), axis "Z" along "b" axis; Ti has axis "Z" to O_2 (more distant), axis "X" to O_1 ; O_1 has axis "X" to Y (closest), axis "Z" along "b"; O_2 has axis "X" to Ti (more distant), axis "Y" to O_1.

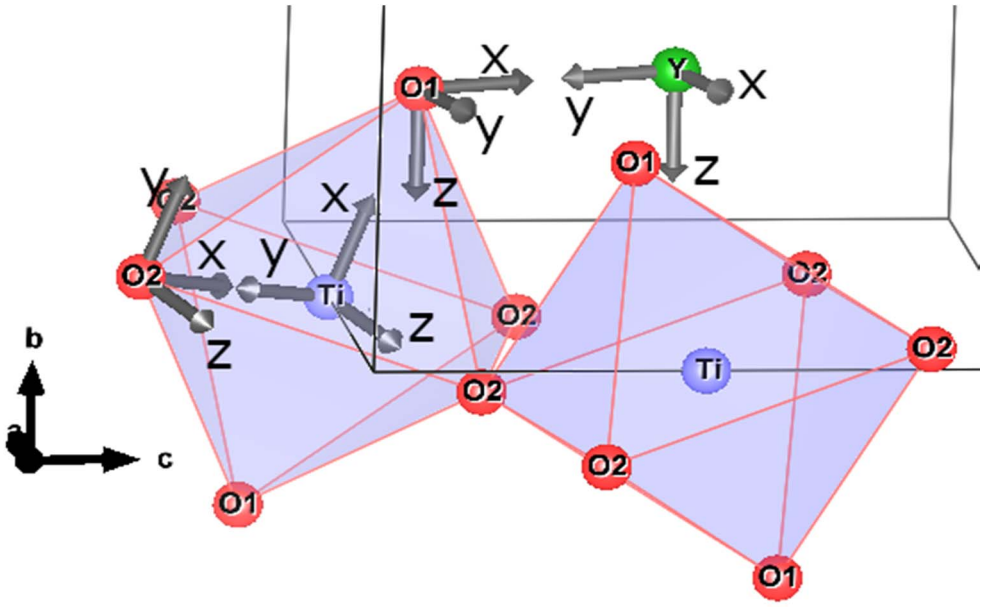

Figure S2 Definition of Cartesian local coordinate system for each atom in asymmetric unit cell.

Table S4 Coordinates and harmonic vibration parameters for each atom after refinement in frame of multipole and orbital models.

	Multipole model			
	Ti	Y	O_1	O_2
x	0.5	0.574144(3)	0.457507(26)	0.309438(18)
y	0.0	0.25	0.25	0.057899(14)
z	0.0	0.522086(3)	0.121074(29)	-0.309518(20)
U_{11}, Å	0.001994(9)	0.001883(5)	0.003884(33)	0.003632(25)
U_{22}, Å	0.001444(8)	0.002137(4)	0.002624(32)	0.004072(25)
U_{33}, Å	0.002498(7)	0.002112(4)	0.003743(37)	0.003676(26)
U_{12}, Å	-0.000120(6)	0	0	-0.000622(20)
U_{13}, Å	-0.000157(6)	0.000064(3)	-0.000633(28)	-0.000627(19)
U_{23}, Å	-0.000005(5)	0	0	0.000430(20)
			Orbital model	
	Ti	Y	O_1	O_2
x	0.5	0.574147(3)	0.457512(27)	0.309449(18)
y	0	0.25	0.25	0.057893(14)
z	0	0.522075(4)	0.121029(30)	-0.309529(21)
U_{11}, Å	0.002116(9)	0.001938(5)	0.003845(34)	0.003614(26)
U_{22}, Å	0.001474(8)	0.002007(4)	0.002602(33)	0.004061(26)
U_{33}, Å	0.002401(8)	0.002154(4)	0.003775(38)	0.003650(27)
U_{12}, Å	0.000091(7)	0	0	-0.000613(21)
U_{13}, Å	-0.000059(6)	0.000054(3)	-0.000661(29)	-0.000629(19)
U_{23}, Å	0.000020(6)	0	0	0.000422(21)

Table S5 Parameters of anharmonicity for titanium atom.

4th order (the parameters are multiplied by 10^5)

name	orbital	multipole	name	orbital	multipole	name	orbital	multipole
1111	2(3)	-6(3)	1122	5(5)	-7(5)	1233	-4(10)	-29(10)
2222	1.4(7)	0.9(7)	1123	-8(9)	14(8)	1333	-12(7)	-44(7)
3333	31(3)	43(2)	1133	-11(9)	-2(9)	2223	11(2)	-3(2)
1112	12(6)	-1(5)	1222	9(3)	-15(3)	2233	-8(5)	-2(5)
1113	-1(6)	-26(6)	1223	6(6)	25(6)	2333	4(5)	12(5)

6th order (the parameters are multiplied by 10^5)

name	orbital	multipole	name	orbital	multipole	name	orbital	multipole
111111	-1.0(9)	-2.2(8)	111233	7(5)	2(5)	122333	-4(3)	-1(3)
222222	0.4(1)	0.3(1)	111333	-2(4)	-14(3)	123333	-1(4)	-5(4)
333333	3(1)	5(1)	112222	3(1)	2(1)	133333	-2(3)	-9(3)
111112	3(2)	2(2)	112223	2(2)	3(2)	222223	1.1(4)	0.1(4)
111113	1(2)	-4(2)	112233	-14(4)	-13(4)	222233	-2.5(9)	-1.9(9)
111122	8(2)	5(2)	112333	-3(5)	6(4)	222333	3(1)	2(1)
111123	-3(4)	3(3)	113333	9(4)	14(3)	223333	6(2)	9(2)
111133	5(4)	6(3)	122222	1.3(5)	-1.4(4)	233333	2(2)	4(2)
111222	4(1)	-2(1)	122223	2(1)	5(1)			
111223	4(3)	7(3)	122233	-4(3)	-12(3)			

Table S6 Parameters of anharmonicity for yttrium atom.

3rd order (the parameters are multiplied by 105)

name	orbital	multipole	name	orbital	multipole	name	orbital	multipole
111	9(2)	10(2)	122	37(2)	37(2)	233	0.00	0.00
222	0.00	0.0	113	10(4)	9(4)	123	0.00	0.00
333	-7(2)	-4(2)	133	6(4)	6(4)			
112	0.00	0.0	223	18(2)	18(2)			

4th order (the parameters are multiplied by 10^5)

name	orbital	multipole	name	orbital	multipole	name	orbital	multipole
1111	21(1)	18(1)	1122	16(3)	20(3)	1233	0.00	0.0
2222	4.4(4)	8.6(4)	1123	0.00	0.0	1333	-4(3)	-2(3)
3333	25(2)	24(2)	1133	-9(5)	-29(5)	2223	0.00	0.0
1112	0.00	0.0	1222	0.00	0.0	2233	-4(3)	-4(3)
1113	-4(3)	1(3)	1223	-6(3)	-7(3)	2333	0.00	0.0

5th order (the parameters are multiplied by 10^5)

name	orbital	multipole	name	orbital	multipole	name	orbital	multipole
11111	1.1(5)	1.1(4)	11133	1(1)	1(1)	12233	3(1)	3(1)
22222	0.00	0.0	11222	0.00	0.0	12333	0.00	0.0
33333	-2.9(6)	-2.5(5)	11223	0(1)	0(1)	13333	1(1)	1(1)
11112	0.00	0.0	11233	0.00	0.0	22223	0.7(3)	0.8(3)
11113	4(1)	3(1)	11333	1(1)	1(1)	22233	0.00	0.0
11122	4.1(7)	4.0(7)	12222	3.1(3)	3.1(3)	22333	4.8(8)	5.1(7)
11123	0.00	0.0	12223	0.00	0.0	23333	0.00	0.0

6th order (the parameters are multiplied by 10^5)

name	orbital	multipole	name	orbital	multipole	name	orbital	multipole
111111	3.5(5)	3.1(5)	111233	0.00	0.0	122333	3(2)	2(1)

222222	0.4(1)	0.8(1)	111333	-4(2)	-3(2)	123333	0.00	0.0
333333	3.1(6)	3.3(5)	112222	3.8(5)	4.9(6)	133333	-1(1)	1(1)
111112	0.00	0.0	112223	0.00	0.0	222223	0.00	0.0
111113	0(1)	1(1)	112233	-17(2)	-19(2)	222233	-3.1(5)	-2.6(5)
111122	12.4(9)	12.7(9)	112333	0.00	0.0	222333	0.00	0.0
111123	0.00	0.0	113333	8(2)	3(1)	223333	5(1)	4.9(9)
111133	8(2)	3(2)	122222	0.00	0.0	233333	0.00	0.0
111222	0.00	0.0	122223	-0.8(6)	-1.1(6)			
111223	-4(2)	-4(2)	122233	0.00	0.0			

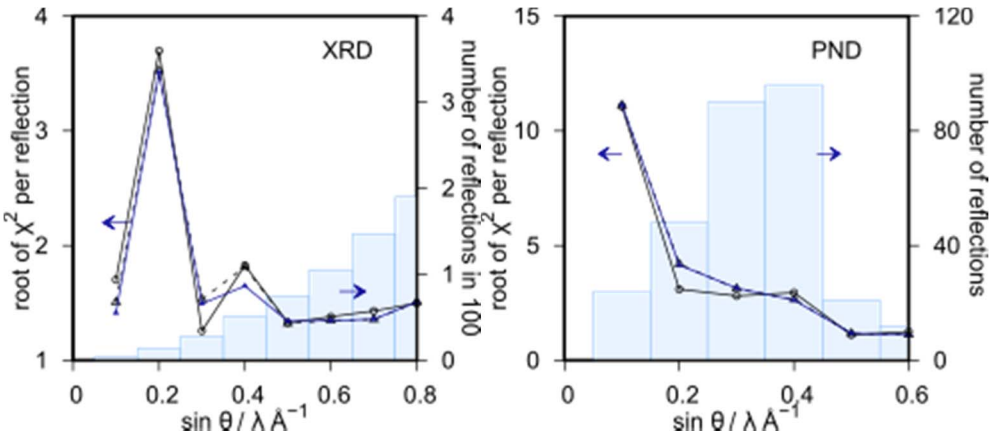

Figure S3 The goodness-of-fit of reflections grouped in 0.1 Å−1 ranges of sinθ/λ (XRD and PND data) for multipole (circles with solid line) and orbital model with and without out “interaction” term (black open and blue closed triangles).

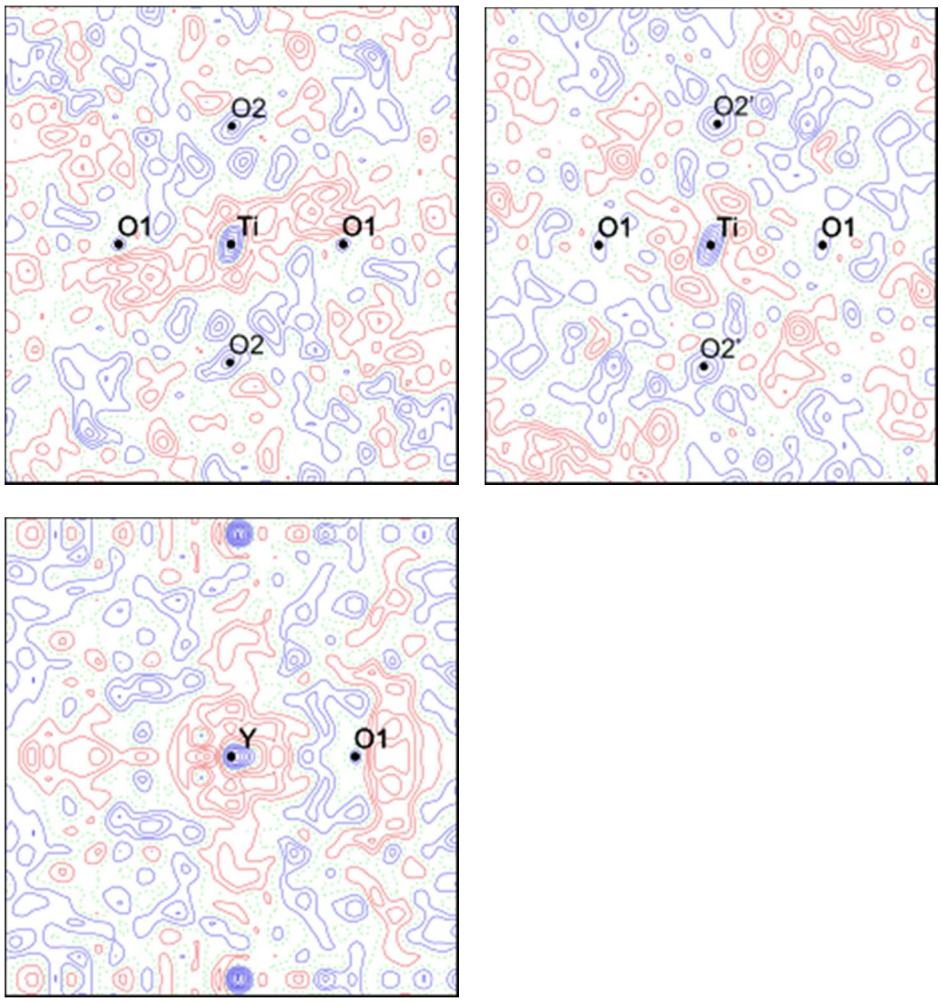

Figure S4 Low-order residual densities around titanium and yttrium atoms Ti-O_1-O_2, Ti-O_1-O_2', Y-O_1-axis "b". Contours are 0.10 el./Å^3. $sin(\theta)/\lambda < 1.2$Å^{-1}.

S3. Orientation and population of "valence" atomic orbitals located on Y, O_1, O_2

Table S7 "Valence" atomic orbitals located on yttrium.

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
$\|5s\rangle$	0	0	0	0	0	1
$\|4d_{z^2}\rangle$	0	-0.51(3)	0.17(43)	0	0.84(54)	0
$\|4d_{zx}\rangle$	-0.97(10)	0	0	-0.26(4)	0	0
$\|4d_{yz}\rangle$	-0.26(13)	0	0	0.97(2)	0	0
$\|4d_{x^2y^2}\rangle$	0	-0.75(3)	0.39(28)	0	-0.54(74)	0
$\|4d_{xy}\rangle$	0	-0.42(3)	-0.90(13)	0	-0.07(132)	0
$n_i^{\uparrow}$	0.07(2)	0.01(2)	0.04(1)	0.21(2)	0.02(1)	0.40(33)
$n_i^{\downarrow}$	0.07(2)	0.15(2)	0.02(2)	0.10(2)	0.01(2)	0.35(33)
charge	0.14(2)	0.16(3)	0.05(2)	0.32(2)	0.03(2)	0.75(47)
spin	0.00(2)	-0.15(3)	0.02(2)	0.11(2)	0.00(2)	0.05(48)

Table S8 "Valence" atomic orbitals located on oxygen 1.

	ϕ_1	ϕ_2	ϕ_3	ϕ_4
$\|2s\rangle$	1	0	0	0
$\|2p_x\rangle$	0	0.988(5)	-0.15(25)	0
$\|2p_y\rangle$	0	-0.155(25)	-0.988(5)	0
$\|2p_z\rangle$	0	0	0	1.00
$n_i^{\uparrow}$	0.72(5)	0.93(2)	0.92(2)	0.90(2)
$n_i^{\downarrow}$	0.69(5)	0.95(2)	0.89(2)	0.95(2)
charge	1.41(7)	1.88(3)	1.81(3)	1.84(3)
spin	0.04(7)	-0.02(3)	0.04(3)	-0.05(3)

Table S9 "Valence" atomic orbitals located on oxygen 2.

	ϕ_1	ϕ_2	ϕ_3	ϕ_4
$\|2s\rangle$	1	0	0	0
$\|2p_x\rangle$	0	0.95(1)	-0.08(10)	0.31(2)
$\|2p_y\rangle$	0	0.06(9)	1.00(1)	0.07(4)
$\|2p_z\rangle$	0	-0.31(2)	-0.05(4)	0.95(1)
$n_i^{\uparrow}$	0.79(4)	0.93(2)	0.89(2)	0.91(2)
$n_i^{\downarrow}$	0.50(4)	1.07(2)	1.01(2)	0.99(2)
charge	1.29(6)	1.99(2)	1.90(2)	1.90(2)
spin	0.30(6)	-0.14(2)	-0.12(2)	-0.08(2)

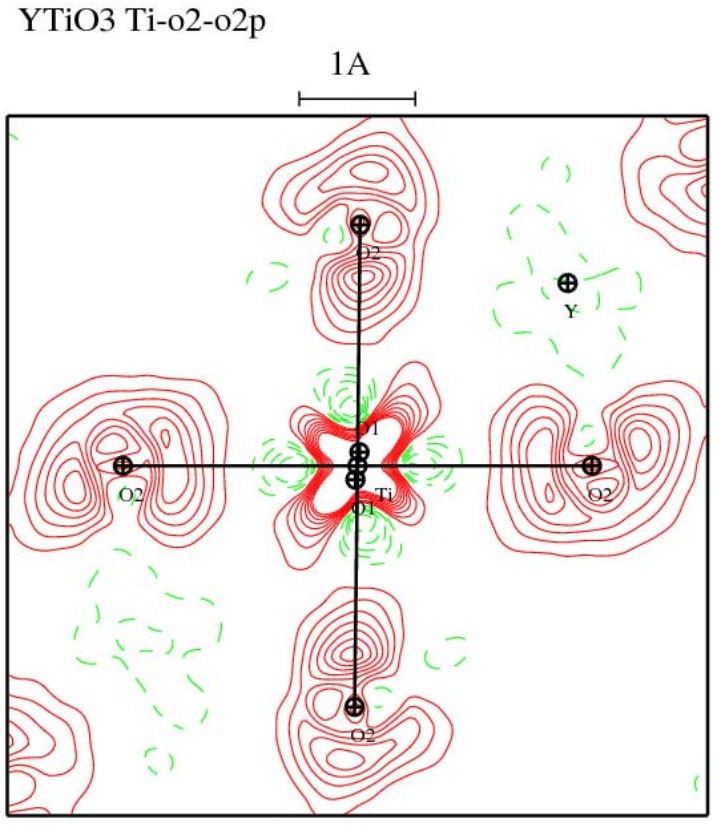

Figure S5 Dynamic deformation densities around titanium Ti-O_1-O_2'. Contours are 0.05 el./Å^3, with all data ($0 < sin(\theta)/\lambda < 1.67$Å^{-1}.