

**Supplementary Information to  
“Unraveling the role of Sm 4*f* electrons in the magnetism of SmFeO<sub>3</sub>”**

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Atomic pairs	<i>Pbnm</i> w/ Sm- <i>f</i> (Å)	Exp.[1] (Å)	<i>Pbnm</i> w/o Sm- <i>f</i> (Å)	RE w/ Sm- <i>f</i>	RE w/o Sm- <i>f</i>
Sm <sub>1</sub> -Sm <sub>2(2')</sub>	3.7975	3.7909	3.7604	0.17%	-0.81%
Sm <sub>1</sub> -Sm <sub>3</sub> (×2)	3.9011	3.9087	3.9139	-0.20%	0.13%
Sm <sub>1'</sub> -Sm <sub>2(2')</sub>	3.9882	3.9910	4.0091	-0.07%	-0.17%
Fe <sub>1</sub> -Fe <sub>3</sub> (×2)	3.8498	3.8530	3.8451	-0.08%	-0.21%
Fe <sub>1</sub> -Fe <sub>2</sub> (×4)	3.8916	3.8896	3.8826	0.05%	-0.18%
Fe <sub>1(1'')</sub> -Sm <sub>1(3)</sub>	3.1486	3.1406	3.1199	0.25%	-0.66%
Fe <sub>1(1')</sub> -Sm <sub>2(4)</sub>	3.2782	3.2740	3.2446	0.13%	-0.90%
Fe <sub>1'(1)</sub> -Sm <sub>2(4)</sub>	3.3895	3.3908	3.3902	-0.04%	-0.02%
Fe <sub>1''(1)</sub> -Sm <sub>1(3)</sub>	3.6549	3.6682	3.7030	-0.36%	0.95%
Fe <sub>3</sub> -O <sub>1(2)</sub>	2.0303	2.0276	2.0320	0.14%	0.21%
Fe <sub>3</sub> -O <sub>3(4)</sub>	2.0100	2.0008	2.0079	0.46%	0.36%
Fe <sub>3</sub> -O <sub>9(10)</sub>	1.9984	2.0120	2.0025	-0.68%	-0.47%
Sm <sub>2</sub> -O <sub>3(8)</sub>	2.3356	2.3370	2.3378	-0.06%	-0.18%
Sm <sub>2</sub> -O <sub>4(7)</sub>	2.7014	2.7026	2.7085	-0.04%	0.22%
Sm <sub>2</sub> -O <sub>9'</sub>	2.3084	2.3090	2.2987	-0.03%	-0.45%
Sm <sub>2</sub> -O <sub>12'</sub>	2.4017	2.3880	2.3653	0.57%	-0.95%
Sm <sub>2</sub> -O <sub>2(5)</sub>	2.5840	2.5730	2.5291	0.43%	-1.71%
Sm <sub>2</sub> -O <sub>1(6)</sub>	3.4804	3.4930	3.5273	-0.36%	0.98%
Sm <sub>2</sub> -O <sub>9</sub>	3.1827	3.1800	3.1663	0.09%	-0.43%
Sm <sub>2</sub> -O <sub>12</sub>	3.3178	3.3370	3.3948	-0.57%	1.73%
Sm <sub>1(1')</sub> -Sm <sub>4</sub> (×2)	5.1865	—	5.1364	—	—
Sm <sub>1</sub> -Sm <sub>1'</sub> (×2)	5.4086	5.3995	5.3594	0.17%	-0.74%
Sm <sub>2</sub> -Sm <sub>2'</sub> (×2)	5.5969	5.6001	5.6191	-0.06%	0.34%
Sm <sub>1(1')</sub> -Sm <sub>4'</sub> (×2)	5.8127	—	5.8599	—	—
Fe <sub>1</sub> -Fe <sub>1'</sub> (×2)	5.4086	5.3995	5.3594	0.17%	-0.74%
Fe <sub>1</sub> -Fe <sub>4</sub> (×8)	5.4740	—	5.4643	—	—
Fe <sub>1</sub> -Fe <sub>1''</sub> (×2)	5.5969	5.6001	5.6191	-0.06%	0.34%
Fe <sub>1'</sub> -Fe <sub>1'</sub>	7.6995	7.7060	7.6902	-0.08%	-0.21%
<b>Interatomic angles</b>					
∠ Fe <sub>1</sub> -O <sub>6</sub> -Fe <sub>2</sub>	148.81°	148.64°	147.51°	0.12%	-0.76%
∠ Fe <sub>1</sub> -O <sub>9</sub> -Fe <sub>3</sub>	148.83°	148.67°	147.91°	0.10%	-0.51%
∠ O <sub>10</sub> -Fe <sub>3</sub> -O <sub>2</sub>	88.72°	88.74°	88.73°	-0.03%	-0.01%
∠ O <sub>10</sub> -Fe <sub>3</sub> -O <sub>4</sub>	88.86°	88.75°	88.46°	0.13%	-0.32%
∠ O <sub>10</sub> -Fe <sub>3</sub> -O <sub>9</sub>	180.00°	180.00°	180.00°		

Table SI. Interatomic distances and angles properties calculated for the orthorhombic *Pbnm* SmFeO<sub>3</sub> either excluding (w/o) or including (w/) Sm-*f* electrons as valence states. Room temperature experimental data from Ref. [1] and relative errors (RE) are also reported. Atomic labels refer to labeling in Fig. 1(b) in the main-text.

[1] E. N. Maslen, V. A. Streltsov, and N. Ishizawa, *Acta Crystallographica Section B* **52**, 406 (1996).

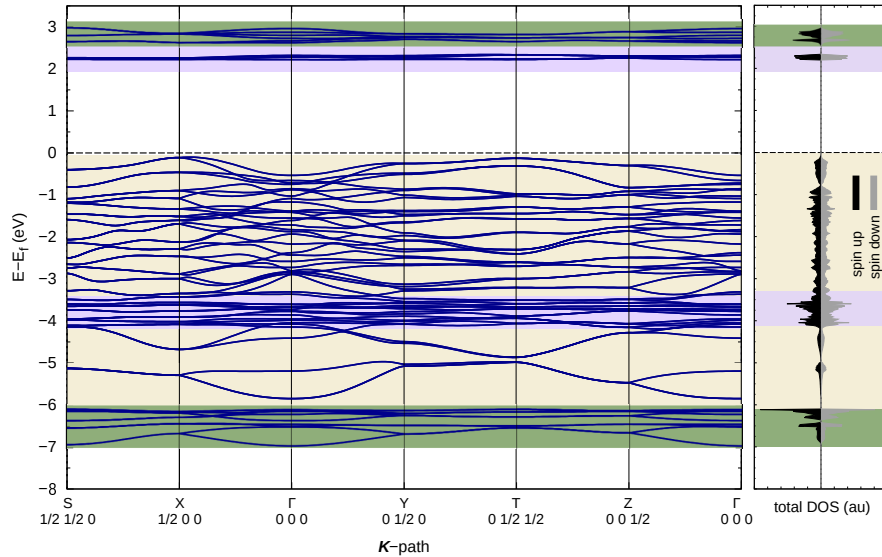


Figure S1. Electronic bands structure of collinear antiferromagnetic  $\text{SmFeO}_3$ , with  $\mathbf{G}$ -type spin order for both Sm and Fe sub-structures. Total density of states (DOS) for spin-up and spin-down channel is also shown. Colored area identify different atomic bands character: green mainly Fe- $d$  contribution, violet mainly Sm- $f$  contribution, yellow mainly O-Fe contribution. Orbital-resolved DOS are shown in Fig. 2 of the main-text.

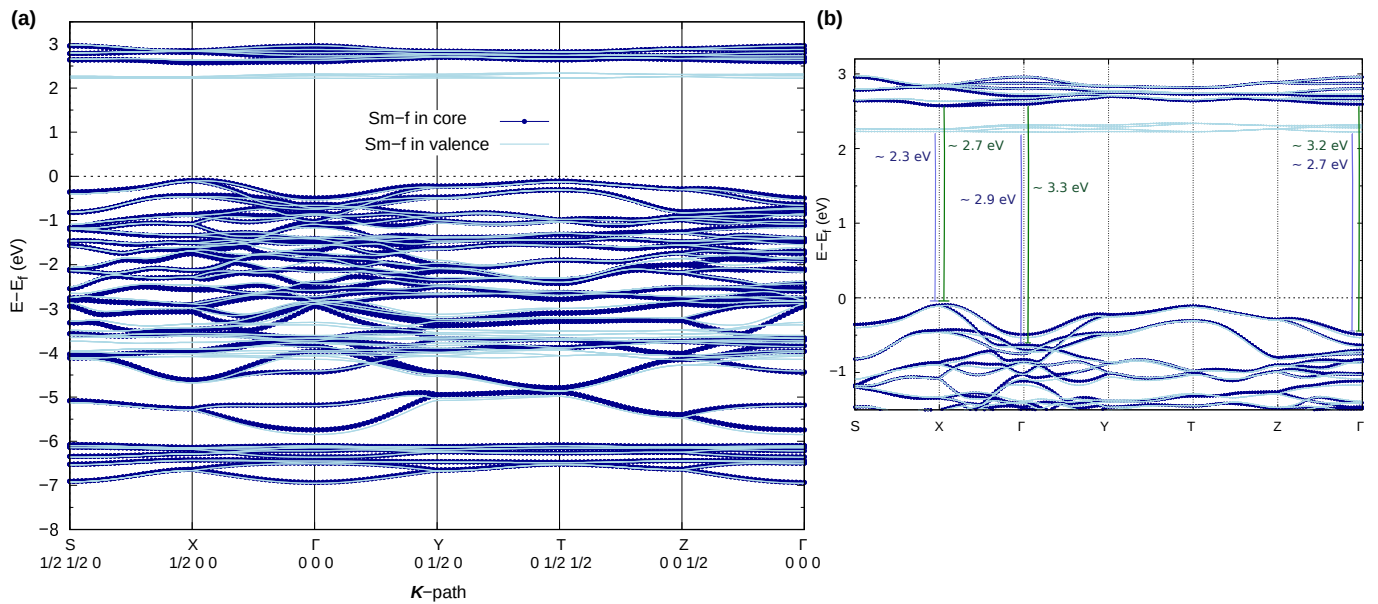


Figure S2. (a) Comparison of electronic bands obtained from including (light-blue line) and excluding (dark-blue line) Sm- $f$  electrons in the valence states; same Hubbard- $U$  value is added on Fe for the two cases, i.e. 4.5 eV. Underlying atomic structure has been relaxed within the two conditions. It is clear the Sm- $f$  states do not affect the overall electronic properties, but add the relative states. (b) Zoom highlighting different energy gap at  $\Gamma$  and out-of- $\Gamma$ , also considering the bottom either of the Sm- $f$  (violet line) or Fe- $d$  (green line) conduction bands.

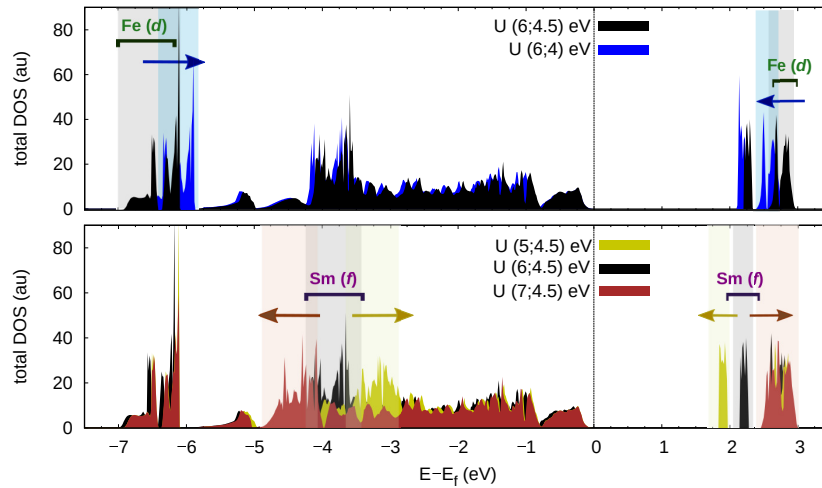


Figure S3. Effect of different Hubbard- $U$  values on the electronic properties of antiferromagnetic  $\text{SmFeO}_3$ , with G-type spin order for both Sm and Fe sub-structures. Only DOS from spin-up channel is shown. (top) Total DOS changing  $U$ -correction on Fe- $d$  states from 4.5 eV to 4 eV. (bottom) Total DOS changing  $U$ -correction on Sm- $f$  states from 6 eV to 5 eV and 7 eV. Energy shifts of the  $d$ - and  $f$ -states are highlighted. Underlying crystal structure is fixed to the one obtained relaxing with  $U(6;4.5)$  eV on Sm and Fe.

A variation of  $U$  from 4.5 eV to 4 eV on Fe- $d$  states translates (by about 0.25 eV) the Fe- $d$  state peaks up at the VB top and the Sm- $f$  and Fe- $d$  states peaks down at the CB bottom; no substantial changes in the hybridization or spin-polarization are observed. A variation of  $U$  from 6 eV to 5 eV on Sm- $f$  states produces upward and downward shifts of the Sm- $f$  states in the VB and CB, respectively; *vice versa*, for  $U=7$  eV, with an overlap of the Fe- $d$  and Sm- $f$  higher energy states (CB).

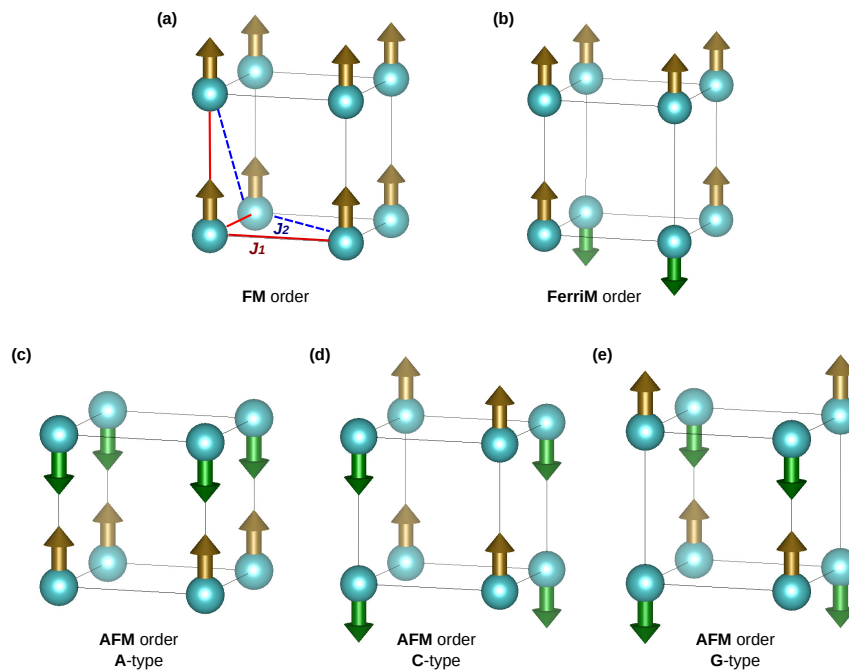


Figure S4. Schematic view of (a) ferromagnetic (FM), (b) ferrimagnetic (FerriM) and antiferromagnetic (AFM) (c) A-type, (d) C-type, (e) G-type collinear spin orders for the pseudo-cubic Sm- and Fe- atomic substructures in orthorhombic  $\text{SmFeO}_3$ . Sketch of first- ( $J_1$ ) and second- ( $J_2$ ) neighbour interactions is also shown in (a).

spin configuration		U(6;4.5) eV	U(5;4.5) eV	U(7;4.5) eV	U(6;4) eV	w/o Sm- <i>f</i>	U(0;4.5) eV
Sm-order	Fe-order	$\Delta E$ (meV/f.u.)	$\Delta E$ (meV/f.u.)	$\Delta E$ (meV/f.u.)	$\Delta E$ (meV/f.u.)	Fe-order	$\Delta E$ (meV/f.u.)
<b>G</b>	<b>G</b>	0.00	0.00	0.00	0.00	<b>G</b>	0.00
<b>C</b>	<b>G</b>	-0.40	-0.49	-0.35	-0.40		
<b>FerriM</b>	<b>G</b>	-0.19	–	–	-0.18		
<b>FM</b>	<b>G</b>	-0.02	-0.23	+0.10	-0.01		
<b>C</b>	<b>C</b>	+60.58	+59.65	+61.24	+64.41	<b>C</b>	+61.59
<b>FM</b>	<b>C</b>	+63.59	+63.20	+63.47	+67.29		
<b>G</b>	<b>FerriM</b>	+103.26	–	–	+110.16	<b>FerriM</b>	+102.55
<b>FM</b>	<b>FerriM</b>	+105.04	–	–	+111.87		
<b>A</b>	<b>A</b>	+136.05	+135.62	+136.34	+145.03	<b>A</b>	+137.00
<b>FM</b>	<b>A</b>	+136.40	+135.87	+136.73	+145.38		
<b>FM</b>	<b>FM</b>	+219.86	+220.06	+219.43	+234.85	<b>FM</b>	+214.72

Table SII. Energy differences between various collinear spin orders as a function of different Hubbard- $U$  corrections [ $U(\text{Sm};\text{Fe})$  eV]. Underlying crystal structure is fixed to the one obtained relaxing within **G-G** spin order for the Sm- and Fe- spin substructures and  $U$ -correction of (6;4.5) eV on Sm- $f$  and Fe- $d$  electronic states, respectively. At variance, the energy differences in the last column have been calculated by freezing the Sm- $4f$  electrons in the core and we used the related optimized **G**-type structure. Schematic visualization of the different magnetic sub-substructures is shown in Fig. S4.

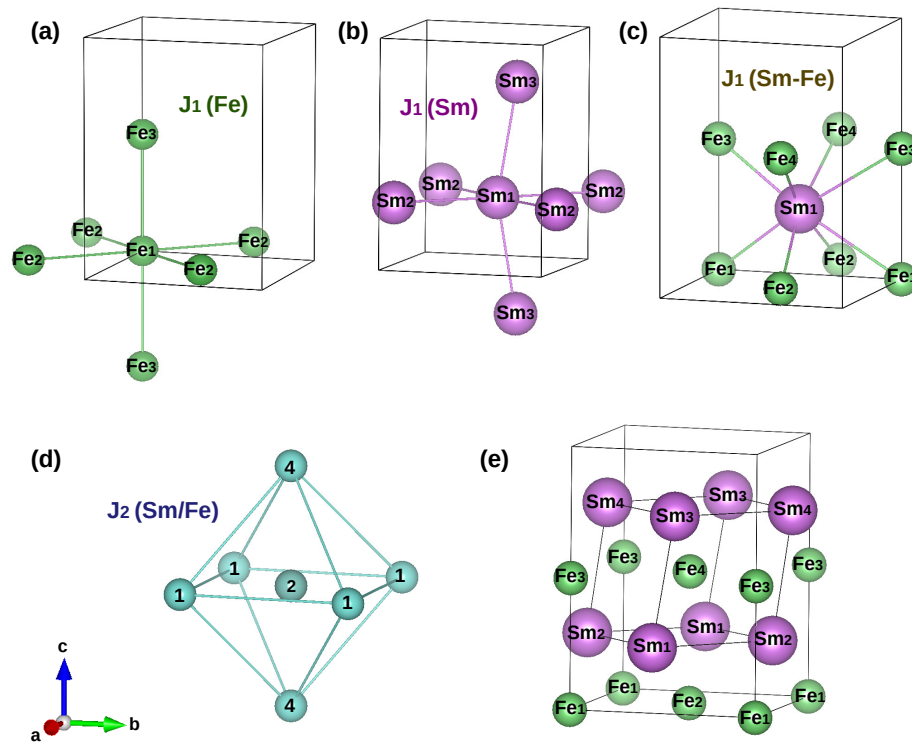


Figure S5. Examples of coordination for the considered nearest neighbour atomic pairs, defining effective, average first- ( $J_1$ ) and second- ( $J_2$ ) neighbour magnetic interactions; as an approximation, all atoms of the same species are treated as structurally equivalent (equidistant). (a) Six Fe-Fe  $J_1$ . (b) Six Sm-Sm  $J_1$ . (c) Eight Sm-Fe  $J_1$ . (d) Schematic second-neighbors coordination including twelve  $J_2$ -interactions for either Sm-Sm and Fe-Fe pairs; numbers refer to numbering of atoms in (e). The latter shows Sm and Fe sub-structures in the orthorhombic unit cell as a reference.

HSE (meV)	U(6;4.5) eV	U(5;4.5) eV	U(7;4.5) eV	U(6;4) eV
$J_1$ (Fe-Fe)	$\simeq 5.85$	$\simeq 5.82$	$\simeq 5.86$	$\simeq 6.25$
$J_1$ (Sm-Sm)	$\simeq 0.00$	$\simeq -0.01$	$\simeq 0.00$	$\simeq 0.00$
$J_2$ (Fe-Fe)	$\simeq 0.19$	$\simeq 0.19$	$\simeq 0.20$	$\simeq 0.22$
$J_2$ (Sm-Sm)	$\simeq 0.01$	$\simeq 0.01$	$\simeq 0.01$	$\simeq 0.01$
$J_1$ (Sm-Fe)	$\simeq 0.01$	$\simeq 0.04$	$\simeq -0.01$	$\simeq 0.01$

Table SIII. Heisenberg spin exchange (HSE) for first ( $J_1$ ) and second ( $J_2$ ) Fe-Fe and Sm-Sm neighbor interactions and Sm-Fe first-neighbor interaction estimated with different Hubbard- $U$  corrections [ $U(\text{Sm};\text{Fe})$  eV], considering **FM-FM**, **A-A**, **FM-C**, **FM-G**, **C-G** and **G-G** Sm- and Fe- spins configurations among those listed in Table SII. Underlying crystal structure is fixed to the one obtained relaxing within the **G-G** spin order and  $U$ -correction of (6;4.5) eV on Sm- $f$  and Fe- $d$  states, respectively.

Symmetry	w/o Sm- $f$ structure				w/ Sm- $f$ structure				
	Sm- $f$ core			Sm- $f$ valence	Sm- $f$ core	Sm- $f$ valence			
	w/o SOC	w/ SOC		w/o SOC	w/o SOC	w/o SOC	w/ SOC		w/ SOC
	<b>G</b>	<b>G<sub>x</sub></b>	<b>G<sub>z</sub></b>	<b>G-G</b>	<b>G</b>	<b>G-G</b>	<b>FM-G</b>	<b>C-G</b>	<b>FM<sub>x</sub>C<sub>y</sub>-FM<sub>x</sub>C<sub>y</sub>G<sub>z</sub></b>
$A_g$ (1)	110	107	110	112	104	107	107	107	107
$B_{1g}$ (1)	110	110	110	114	106	110	110	110	108
$B_{2g}$ (1)	134	134	134	131	127	125	125	125	128
$A_g$ (2)	139	138	139	145	127	134	134	135	134
$B_{3g}$ (1)	150	153	154	150	152	151	151	150	152
$B_{1g}$ (2)	160	160	160	162	149	152	152	152	152
$B_{3g}$ (2)	236	234	235	244	210	218	218	218	215
$A_g$ (3)	247	245	246	245	232	229	229	229	224
$B_{1g}$ (3)	281	281	281	277	255	252	253	252	253
$B_{2g}$ (2)	313	313	313	314	306	306	306	306	304
$A_g$ (4)	319	320	320	322	306	310	310	310	309
$B_{1g}$ (4)	345	345	345	345	344	342	342	343	341
$B_{3g}$ (3)	354	355	354	353	356	353	354	353	352
$A_g$ (5)	386	386	386	389	374	377	376	377	375
$A_g$ (6)	417	417	416	415	420	419	419	419	418
$B_{3g}$ (4)	426	427	426	424	427	426	426	425	425
$B_{2g}$ (3)	425	428	427	421	433	429	428	428	429
$B_{2g}$ (4)	449	448	448	445	446	443	443	444	443
$B_{1g}$ (5)	460	460	461	460	446	446	446	446	445
$A_g$ (7)	468	468	468	466	459	457	457	457	457
$B_{1g}$ (6)	512	513	513	516	503	505	505	505	505
$B_{3g}$ (5)	597	597	598	593	604	600	600	600	600
$B_{1g}$ (7)	619	618	618	616	620	617	617	617	617
$B_{2g}$ (5)	648	646	646	645	652	650	650	650	650

Table SIV. Phonon frequencies (in  $\text{cm}^{-1}$ ) of the Raman active modes in the  $Pbnm$  crystal structure excluding (w/o) and including (w/) either Sm- $f$  electrons and SOC contributions. Main AFM **G**-type spin order is considered for Fe-substructure (**G<sub>x</sub>** and **G<sub>z</sub>** indicate **G**-type spin order along  $x$  and  $z$  spatial directions, respectively). **G**-, **FM**-, **C**-type collinear spin orders are considered for the Sm-substructure. The non-collinear **FM<sub>x</sub>C<sub>y</sub>-FM<sub>x</sub>C<sub>y</sub>G<sub>z</sub>** Sm-Fe spin configuration is also considered. Underlying atomic structure is fixed: to the one optimized excluding both Sm- $f$  electrons and SOC contributions (w/o Sm- $f$  structure), considering collinear **G**-type Fe-spins order and Hubbard- $U$  correction of 4.5 eV on Fe- $d$  states; to the one optimized including Sm- $f$  electrons contribution (w/ Sm- $f$  structure), collinear **G**-type spin order for both Sm and Fe substructures and  $U$  of 6 eV and 4.5 eV on the Sm- $f$  and Fe- $d$  states.

Symmetry Silent and IR modes	w/o Sm- <i>f</i> structure		w/ Sm- <i>f</i> structure		1 GPa structure
	Sm- <i>f</i> core	Sm- <i>f</i> valence	Sm- <i>f</i> core	Sm- <i>f</i> valence	Sm- <i>f</i> valence
A <sub>u</sub> (1)	86	74	86	79	79
B <sub>2u</sub> (1)	104	102	100	103	104
B <sub>3u</sub> (1)	113	114	102	106	107
B <sub>1u</sub> (1)	159	156	148	140	144
A <sub>u</sub> (2)	161	152	152	156	156
B <sub>3u</sub> (2)	175	182	161	172	174
B <sub>1u</sub> (2)	171	182	156	181	180
B <sub>2u</sub> (2)	191	189	181	184	185
A <sub>u</sub> (3)	208	184	188	187	183
B <sub>2u</sub> (3)	245	241	226	233	233
A <sub>u</sub> (4)	248	246	235	236	238
B <sub>1u</sub> (3)	273		262	243	266
B <sub>3u</sub> (3)	256	249/274	245	249	250
B <sub>3u</sub> (4)	281	317	271	271	272
B <sub>2u</sub> (4)	289	288	276	279	280
A <sub>u</sub> (5)	300	294	293	290	291
B <sub>2u</sub> (5)	308	302	299	300	302
B <sub>3u</sub> (5)	320	317	308	309	309
B <sub>2u</sub> (6)	331	328	320	321	323
B <sub>1u</sub> (4)	302	333	296	330	339
B <sub>3u</sub> (6)	349	339	341	338	340
A <sub>u</sub> (6)	354	349	351	347	350
B <sub>3u</sub> (7)	386	379	376	371	374
B <sub>1u</sub> (5)	354	386	347	378	350
B <sub>2u</sub> (7)	417	417	409	409	412
B <sub>3u</sub> (8)	474	477	459	461	464
B <sub>2u</sub> (8)	512	510	507	506	509
A <sub>u</sub> (7)	504	499	511	506	513
B <sub>1u</sub> (6)	501	509	502	513	505
B <sub>2u</sub> (9)	524	521	522	520	525
A <sub>u</sub> (8)	523	519	530	526	532
B <sub>3u</sub> (9)	545	543	547	540	550
B <sub>1u</sub> (7)	536	536	545	544	546

Table SV. Phonon frequencies (in  $\text{cm}^{-1}$ ) of the silent and infrared (IR) active modes in the  $Pbnm$  crystal structure, considering collinear G-type AFM magnetic ordering for Fe atoms when freezing Sm-*f* electrons in the core states, and for both Sm and Fe sub-structures when including those in VB.