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The ferromagnetic and anti-ferromagnetic phases (cubic, tetragonal, orthorhombic) of $KMnF_3$. A quantum mechanical investigation.

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In this section, complementary material for the discussion in the main text is provided:

1. Figure S1 and S2 show the DOS for B3LYP and HF, AFM and FM, of the valence and lowest conduction bands, from which it turns out that the lowest transitions are in both cases of d →d type.

2. Figure S3 shows the spin density profile through the F and Mn atoms. It should be compared with Figure 1 of the main text, where, however, the spin density is truncated. The very narrow *spikes* at the nuclei document the polarization of the inner electrons (also see Table 2 of the main text), with the opposite sign with respect to the valence polarization.

3. Figure S4 provides the IR spectrum of the three phases, cubic (C), tetragonal (T) and orthorhombic (O), FM (left) and AFM (right). FM and AFM spectra display only minor differences. Indeed, the observed shifts are within 3 cm^{-1} even in the low wavenumbers region, which is normally the more sensitive to small geometry changes. This is not obvious *a priori*, as the total energy and volume FM-AFM difference is comparable, or even slightly larger, than the difference between the C and T FM phases, or T and O FM phases, that, however, are accompanied by larger differences in the low wavenumber region of the spectrum.

4. Figure S5 compares the HF FM IR spectra of two competitive T (left) and O (right) structures of $KMnF_3$. The high wavenumber peaks are essentially the same. In the low wavenumber region the difference between the 127 and 140 groups can be as large as 23 cm^{-1} (82 vs 105 cm^{-1}); for the O cases, the largest difference is 19 cm^{-1} (90 vs 109 cm^{-1}).

5. In Table S1 the equilibrium total energy and volume for the three FM phases (C, T, O) for HF and B3LYP are reported, with related quantities, such as the negative eigenvalues of the Hessian matrix, suggesting the way for reducing the symmetry and/or increasing the unit cell.
In Table S2 the corresponding AFM quantities are shown, with differences with respect to the FM solutions.

6. In Table S3, S4 and S5 the wavenumbers of the C, T and O structures are reported, with the IR and Raman intensities and the isotopic shift obtained when the K mass is increased by 25 %.

7. Table S6 shows the effect of pressure on the vibrational eigenvalues of the C phase, at Γ and at two other points of the first Brillouin zone.

8. Table S7 shows the effect of pressure P on the volume and enthalpy H of the C, T and O phases.

All figures and tables are referred to and commented in the main text.

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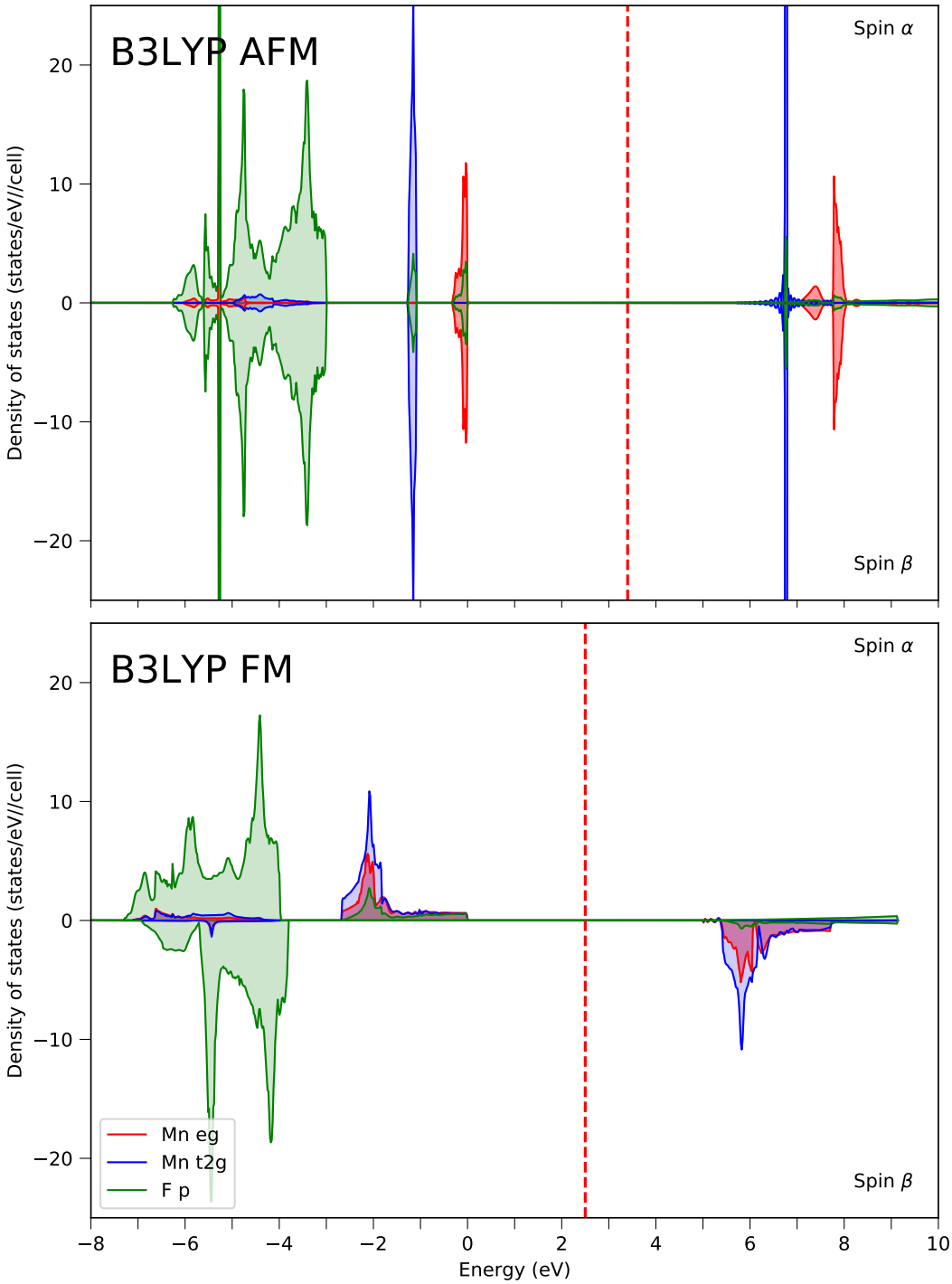

Fig. S1 Density of states of the B3LYP AFM (top) and FM (bottom) solutions. The p states of F are green, the e_g and t_{2g} d states of Mn are red and blue, respectively. The red dashed line is the Fermi energy.

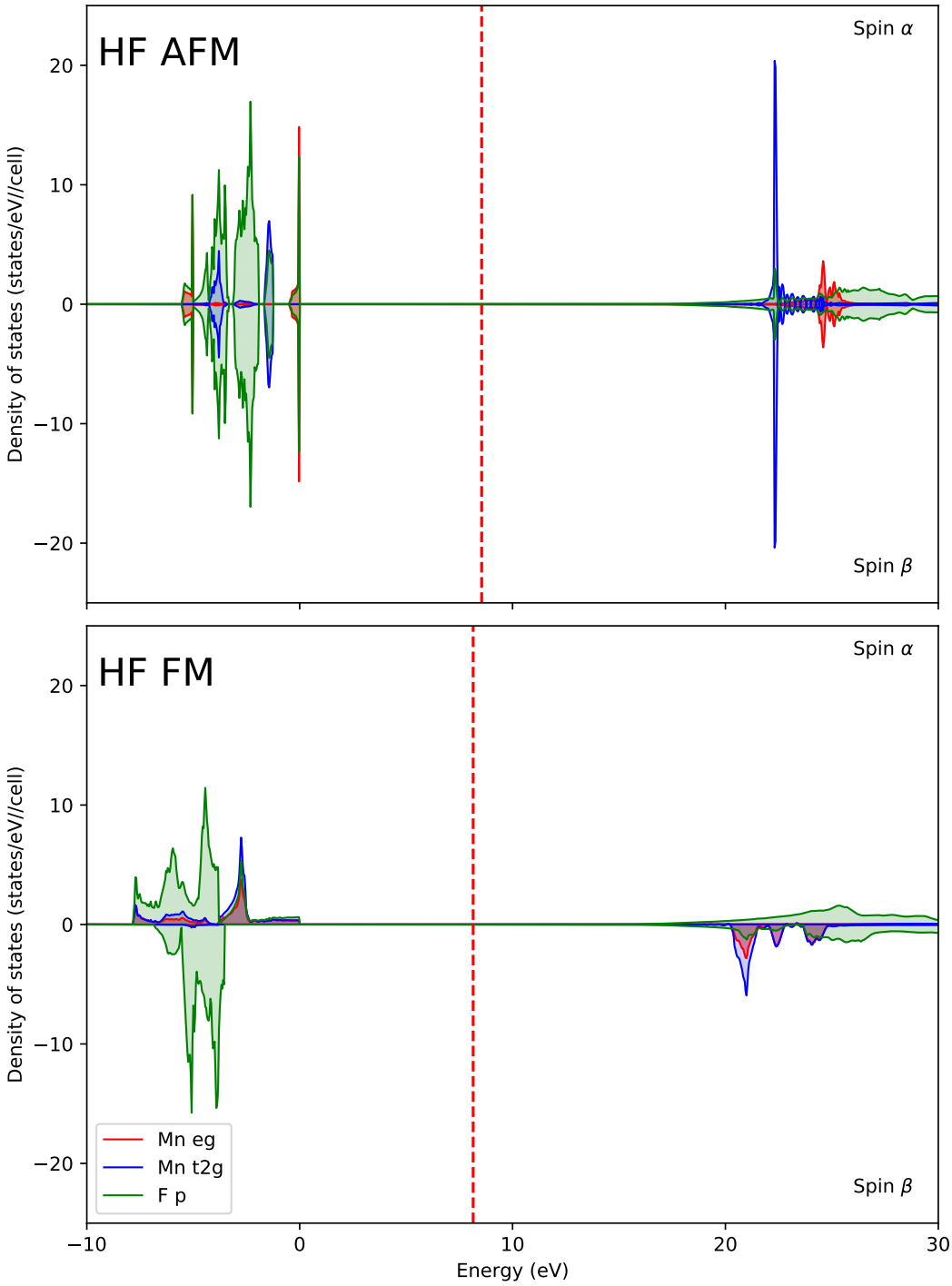

Fig. S2 Density of states of the HF AFM (top) and FM (bottom) solutions. The p states of F are green, the e_g and t_{2g} d states of Mn are red and blue, respectively.

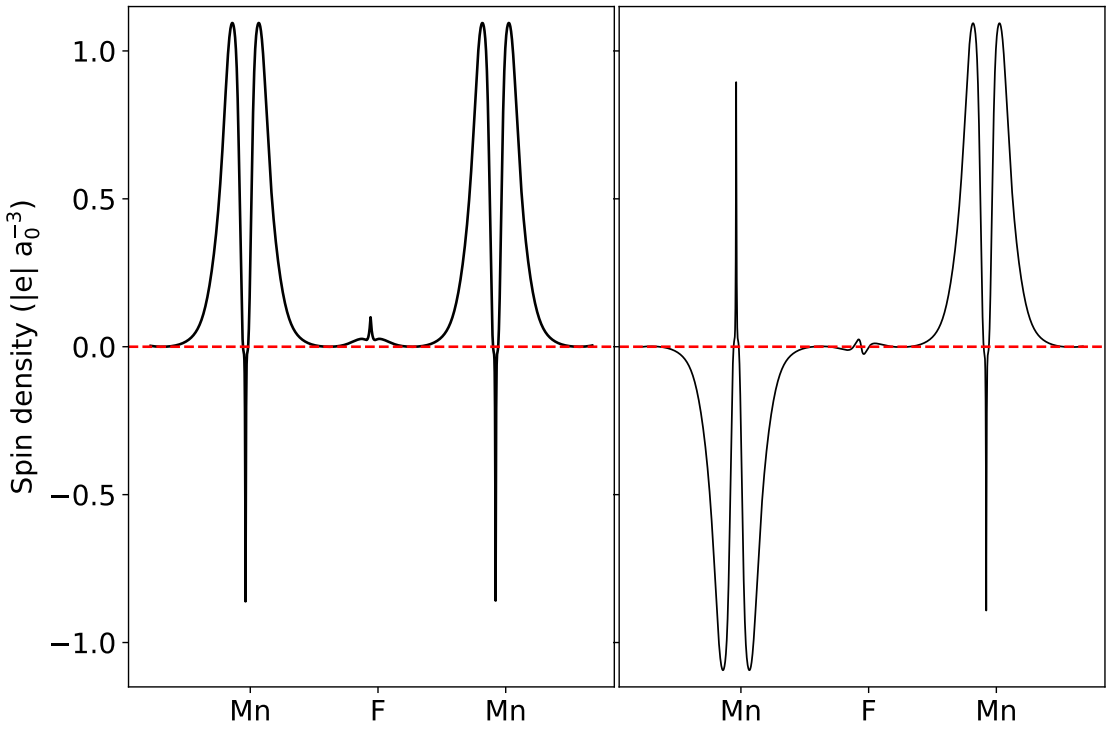

Fig. S3 FM (left) and AFM (right) spin density profiles through the Mn-F-Mn path.

Table S1 Energy (ΔE) and volume (ΔV) differences between the various ferromagnetic $KMnF_3$ phases discussed in the text, differences with respect to the previous line (in μE_h and Å^3 per 2 formula units (*fu*), respectively). The total energy of the cubic phase is -4095.29455543 and -4101.06310852 E_h (per 2 *fu*) for HF and B3LYP, respectively. The corresponding volume is 156.301 and 155.133 Å^3 (per 2 *fu*). nk is the number of $\vec{k}$ points with negatives frequencies; for nk positive, ν_{min} are the frequency minima for those $\vec{k}$ points shown as superscripts. For nk=0, the smallest wavenumber in Γ is reported. For the cubic case, k points (011), (101) and (110) are equivalents. For each phase, the imposed or found space group(SG) is indicated. Data relative to HF energies, volumes, and geometry are reported in Figure 3 of the text.
For a complete description of the relation between successive lines, see Table 3 in ref.[?]

		SG	ΔE	ΔV	nk	$\vec{k}$ points
HF	1	$Pm\bar{3}m$	0.00	0.00	4	$-43.1^{(111)}$,$-41.5^{(011)}$
	2	$P\frac{4}{m}bm$	-195.17	-0.538	1	$-17.0^{(001),(110)}$
	3	$Pnma$	-53.04	-0.111	0	$11.3^{(110)}$,$37.6^{(000)}$
B3LYP	1	$Pm\bar{3}m$	0.00	0.000	4	$-46.2^{(011)}$,$-48.0^{(111)}$
	2	$P\frac{4}{m}bm$	-208.09	-0.584	1	$-25.5^{(001)}$
	3	$Pnma$	-49.67	-0.113	0	$22.1^{(000)}$

Table S2 Energy (ΔE) and volume (ΔV) differences between the various anti-ferromagnetic $KMnF_3$ phases discussed in the text, differences with respect to the previous line (in μE_h and Å^3 per 2 *fu*, respectively). The total energy of the cubic phase is -4095.29497096 and -4101.06618272 E_h (per 2 *fu*) for HF and B3LYP, respectively. The corresponding volume is 156.143 and 154.377 Å^3 (per 2 *fu*). δE and δV are the energy and volume difference with respect to the FM solution (see Table S1). nk is the number of $\vec{k}$ points with negatives frequencies; for nk positive, ν_{min} are the frequency minima for those $\vec{k}$ points shown as superscripts. For nk=0, the smallest wavenumber in Γ is reported. For the cubic system, we report only the (110) k point that is equivalent to (101) and (011).
For the tetragonal system, we report only the (001) k point that is equivalent to (110).
Data relative to HF energies, volumes, and geometry are reported in Figure 3 of the text.
For a complete description of the relation between successive lines, see Table 3 in ref.[?]

	SG	ΔE	ΔV	δE	δV	nk	ν
HF	$Fm\bar{3}m$	0.00	0.000	-415.53	-0.158	4	$-42.15^{(000)}$, $-40.56^{(110)}$
	$I4/m$	-207.58	-0.549	-427.94	-0.169	2	$-16.80^{(001)}$
	$C2/c$	-7.66	-0.030	-382.56	-0.088	1	$-9.58^{(000)}$
	$P\bar{1}$	-12.75	-0.033	-395.31	-0.120	0	20.61
B3LYP	$Fm\bar{3}m$	0.00	0.00	-3074.2	-0.756	4	$-42.86^{(000)}$, $-40.95^{(110)}$
	$I4/m$	-148.03	-0.459	-3014.1	-0.631	2	$-11.2^{(001)}$,$-11.1^{(110)}$
	$C2/c$	-1.18	-0.476	-2965.65	-0.535	0	11.9

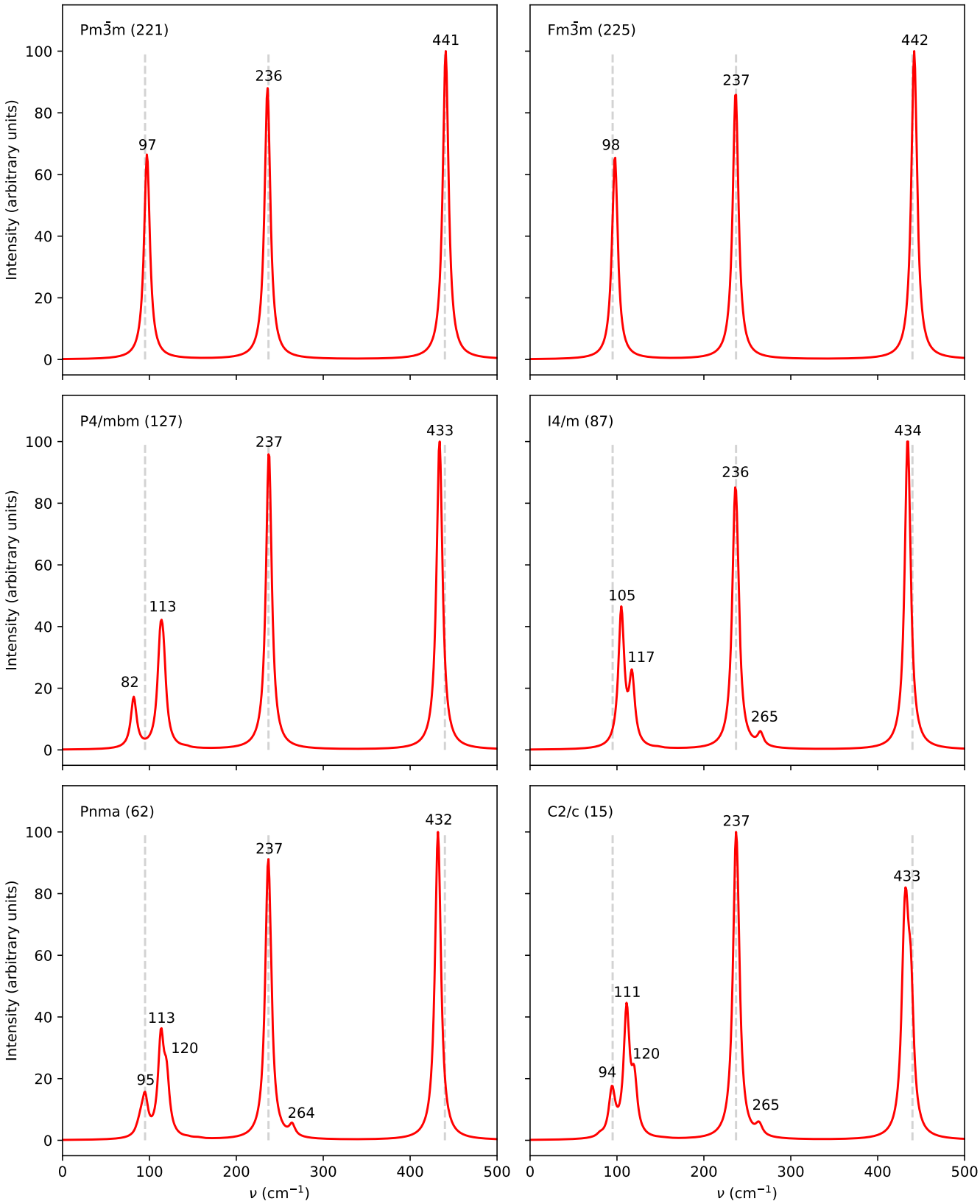

Fig. S4 The HF IR spectra of the FM (left) and AFM (right) solutions for $KMnF_3$. The three space groups for FM are Pm$\bar{3}$m (top), P $\frac{4}{m}$bm (center) and Pnma (bottom). The AFM space groups are $Fm\bar{3}m$ (top), $I\frac{4}{m}$ (center) and $C2/c$ (bottom). As discussed in the text, the most intense peaks of the tetragonal, orthorhombic and monoclinic phases are the superposition of 2 or 3 quasi degenerate peaks. Then, the peaks in the spectrum are the result of the convolution of these individual peaks and their intensity is the sum of the intensities of the corresponding modes. For a convenient identification of these modes in Tables S3, S4 and S5 of the Supplementary material, an indicative wavenumber is associated with each peak.

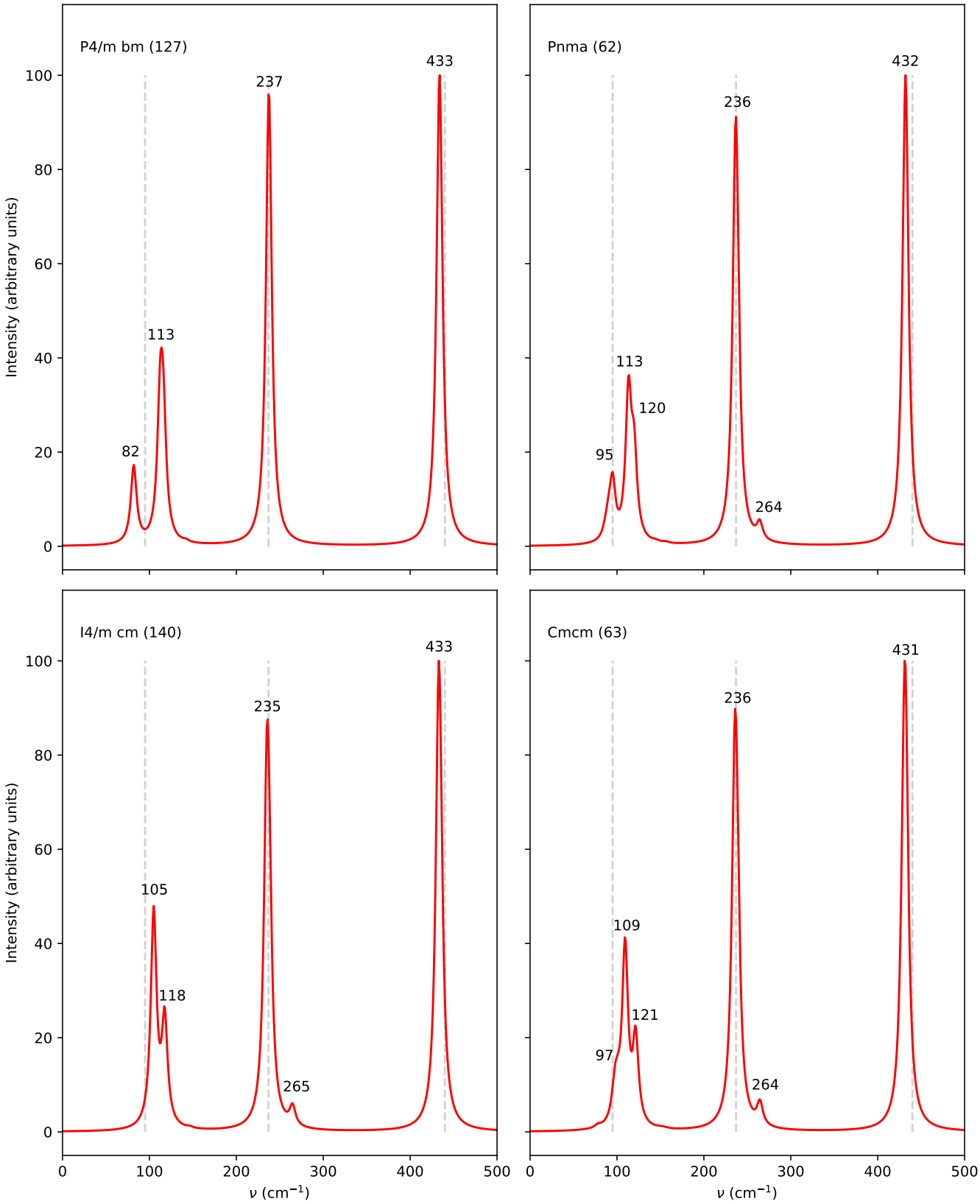

Fig. S5 HF FM IR spectra of $KMnF_3$ in two tetragonal (127, 140) and two orthorhombic (62, 63) space groups. For the intensity, see the caption of the previous Figure.

Table S3 Wavenumbers (in cm^{-1}) and intensities (in km/mol) of the IR spectrum of the cubic $KMnF_3$ compound at Hartree-Fock level. IRR, A and I stand for irreducible representation, active and inactive, respectively. Note that each reported intensity is the sum of the intensities of the three degenerate modes. So, for example, for the mode at 441 cm^{-1}, the intensity per mode is 321/3 = 107 km/mol. Modes 1-3 are translations, and have been omitted. For the definition of Δ^{calc} and Δ^{theor} see the text. Δ^{theor} is shown only for Δ^{calc} larger than 5 cm^{-1}.

cubic – $Pm\bar{3}m$ –								
				Infra Red		Raman		
N	ν	IRR		Intensity		Intensity	Δ^{calc}	Δ^{theor}
4-6	97	F_{1u}	A	214	I	-	-7.2	-10.3
7-9	139	F_{2u}	I	-	I	-	0.0	-
10-12	236	F_{1u}	A	283	I	-	-0.9	-
13-15	441	F_{1u}	A	321	I	-	0.0	-

Table S4 IR/Raman data calculated for the tetragonal unit cell (HF results). As the volume of the unit cell is twice the one of the cubic cell, and the intensity is proportional to the volume, in order to compare the T intensities with the C ones, the former must be divided by 2. So for comparison with C, the intensity of the mode at 435 cm^{-1} becomes I= 210/2 = 105. Modes 1-3 are translations, and have been omitted. IRR, A and I, Δ^{calc} and Δ^{theor} as in previous table. Intensities are rounded to integer and the first decimal for IR and Raman, respectively

tetragonal – $P\frac{4}{m}bm$ –								
				Infra Red		Raman		
N	ν	IRR		Intensity		Intensity	Δ^{calc}	Δ^{theor}
4-4	63	A_{1g}	I	-	A	0.8	0.0	-
5-6	82	E_u	A	101	I	-	-7.2	-8.7
7-7	92	B_{1u}	I	-	I	-	-8.8	-9.7
8-9	113	E_u	A	171	I	-	-8.6	-11.9
10-10	116	A_{2u}	A	134	I	-	-8.6	-12.3
11-12	142	E_u	A	2	I	-	-0.4	-
13-13	149	A_{1u}	I	-	I	-	0.0	-
14-14	153	B_{1u}	I	-	I	-	-1.5	-
15-16	169	E_g	I	-	A	0.8	0.0	-
17-18	172	E_u	A	0.00	I	-	-0.8	-
19-20	237	E_u	A	396	I	-	-0.8	-
21-21	237	A_{2u}	A	200	I	-	-0.7	-
22-22	284	B_{2g}	I	-	A	0.8	0.0	-
23-24	308	E_u	A	0	I	-	-2.7	-
25-25	355	B_{1g}	I	-	A	0.0	0.0	-
26-26	430	A_{1u}	I	-	I	-	0.0	-
27-28	433	E_u	A	419	I	-	0.0	-
29-29	435	A_{2u}	A	210	I	-	0.0	-
30-30	486	A_{2g}	I	-	I	-	0.0	-

Table S5 IR/Raman data calculated for the orthorhombic unit cell (HF results). As the volume of the unit cell is four times the one of the cubic cell, and the intensity is proportional to the volume, in order to compare the O intensities with the C ones, the former must be divided by 4. So for comparison with C, the intensity of the mode at 433 cm^{-1}, becomes I= 417/4 = 104 km/mol. Modes 1-3 are translations, and have been omitted. IRR, A and I, Δ^{calc} and Δ^{theor} as in previous table. Intensities are rounded to integer and the first decimal for IR and Raman, respectively

orthorhombic – $Pnma$ –.								
				Infra Red		Raman		
N	ν	IRR		Intensity		Intensity	Δ^{calc}	Δ^{theor}
4	21	B_{3g}	I	-	A	0.2	0.0	-
5	31	A_g	I	-	A	0.8	0.0	-
6	43	B_{1g}	I	-	A	1.4	0.0	-
7	57	A_g	I	-	A	3.2	-1.7	-
8	81	A_u	I	-	I	-	-4.1	-
9	85	B_{3u}	A	14	I	-	0.0	-
10	90	B_{1u}	A	48	I	-	-8.3	-9.5
11	95	B_{2u}	A	146	I	-	-8.1	-10.0
12	96	B_{3g}	I	-	A	0.1	-9.9	-10.1
13	98	A_g	I	-	A	0.7	-7.6	-10.4
14	99	A_u	I	-	I	-	-5.2	-10.5
15	113	B_{3u}	A	254	I	-	-7.9	-11.9
16	114	B_{2u}	A	126	I	-	-9.0	-12.0
17	115	B_{2g}	I	-	A	0.2	-11.6	-12.1
18	118	B_{3g}	I	-	A	0.1	-12.0	-12.5
19	120	B_{1u}	A	208	I	-	-9.1	-12.6
20	124	A_g	I	-	A	0.6	-12.4	-13.1
21	144	B_{1g}	I	-	A	0.5	-12.5	-15.2
22	144	B_{2u}	A	4	I	-	0.0	-
23	148	A_u	I	-	I	-	0.0	-
24	150	B_{1u}	A	1	I	-	0.0	-
25	151	A_u	I	-	I	-	0.0	-
26	156	B_{1u}	A	3.25	I	-	0.0	-
27	166	A_g	I	-	A	0.1	0.0	-
28	169	B_{2g}	I	-	A	0.7	0.0	-
29	172	B_{2u}	A	0	I	-	0.0	-
30	176	B_{3g}	I	-	A	0.0	-3.0	-
31	177	B_{1g}	I	-	A	0.4	0.0	-
32	179	B_{1u}	A	0	I	-	0.0	-
33	185	B_{2u}	A	0	I	-	0.0	-
34	205	B_{3u}	A	0	I	-	0.0	-
35	208	A_u	I	-	I	-	0.0	-
36	236	B_{3u}	A	378	I	-	0.0	-
37	236	B_{2u}	A	393	I	-	0.0	-
38	238	B_{1u}	A	392	I	-	0.0	-
39	263	A_u	I	-	I	-	0.0	-
40	264	B_{1u}	A	24	I	-	0.0	-
41	264	B_{3u}	A	22	I	-	0.0	-
42	267	B_{3g}	I	-	A	0.5	-1.3	-
43	269	B_{2g}	I	-	A	1.2	-1.1	-
44	269	A_g	I	-	A	2.7	-1.0	-
45	283	B_{3g}	I	-	A	1.5	0.0	-
46	308	B_{1u}	A	0	I	-	-2.7	-
47	309	B_{2u}	A	0	I	-	-2.6	-
48	353	B_{1g}	I	-	A	0.0	0.0	-
49	353	B_{2g}	I	-	A	0.0	0.0	-
50	354	A_g	I	-	A	0.0	0.0	-
51	371	B_{2u}	A	0	I	-	0.0	-
52	428	A_u	I	-	I	-	0.0	-
53	429	B_{3u}	A	1	I	-	0.0	-
54	430	A_u	I	-	I	-	0.0	-
55	431	B_{2u}	A	422	I	-	0.0	-
56	432	B_{3u}	A	419	I	-	0.0	-
57	433	B_{1u}	A	417	I	-	0.0	-
58	453	B_{1g}	I	-	A	0.0	0.0	-
59	486	B_{3g}	I	-	A	0.0	0.0	-
60	515	B_{2g}	I	-	A	0.0	0.0	-

Table S6 Variation of the wavenumbers (cm^{-1}) as a function of the volume V of the cubic structure for the $KMnF_3$ HF FM system. The four triply degenerate eigenvalues in Γ (3 of F_{1g} symmetry, and 1 of F_{2g} symmetry) and the two negative eigenvalues in the (110) and (111) $\vec{k}$ points are shown. The eigenvalues in (001) and (101) are degenerate with (110), and are not reported. The translations are omitted

Volume	(110)	(111)	(000)	(000)	(000)	(000)
156.3	-42	-43	97	139	236	441
153.2	-50	-52	104.5	139	235	462
150.0	-58	-60	112	138	233	483
146.9	-66	-67	119	137	231	505
143.8	-73	-74	127	136	228	528
140.7	-80	-81	135	136	225	552

Table S7 Variation of the enthalpy H (in E_h for 2 *fu*) as a function of volume (Å^3) using the Birch-Murnaghan equation of state (1947) for the three $KMnF_3$ phases obtained from HF energy.
P is the pressure in GPa

	Cubic		Tetra		Ortho	
P	V	H	V	H	V	H
0.0	156.3	-4095.294407	155.8	-4095.294637	155.7	-4095.294737
1.0	153.9	-4095.257914	153.3	-4095.258285	153.2	-4095.258409
2.0	151.8	-4095.221958	151.0	-4095.222501	150.9	-4095.222647
3.1	149.7	-4095.186498	148.8	-4095.187244	148.7	-4095.187409
4.1	147.8	-4095.151500	146.8	-4095.152475	146.7	-4095.152656
5.1	146.1	-4095.116934	144.9	-4095.118163	144.9	-4095.118358
6.2	144.4	-4095.082769	143.2	-4095.084280	143.1	-4095.084486
7.2	142.8	-4095.048988	141.5	-4095.050801	141.5	-4095.051014
8.2	141.3	-4095.015564	139.9	-4095.017701	139.9	-4095.017921
9.2	139.9	-4094.982484	138.4	-4094.984962	138.4	-4094.985187
9.7	139.2	-4094.966065	137.7	-4094.968723	137.7	-4094.968948
10.8	137.9	-4094.933463	136.3	-4094.936490	136.3	-4094.936717
11.8	136.7	-4094.901163	135.0	-4094.904577	135.0	-4094.904803
12.8	135.5	-4094.869147	133.7	-4094.872968	133.8	-4094.873191
13.8	134.3	-4094.837410	132.5	-4094.841648	132.6	-4094.841868
14.9	133.3	-4094.805933	131.4	-4094.810607	131.4	-4094.810820
15.9	132.2	-4094.774711	130.3	-4094.779832	130.3	-4094.780039
16.9	131.2	-4094.743732	129.2	-4094.749313	129.2	-4094.749511
17.9	130.2	-4094.712984	128.2	-4094.719042	128.2	-4094.719230
19.0	129.3	-4094.682465	127.2	-4094.689008	127.2	-4094.689185
20.0	128.4	-4094.652164	126.2	-4094.659203	126.3	-4094.659368