

Supporting Information

Prediction of a Model Crystal Structure for Ni_2F_5 by First-Principles Calculations

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The crystallographic data for the most stable magnetic phases of all the investigated structures are presented in this supporting information. For all the structures there are two sets of data, the one with the average U value of Ni^{2+} and Ni^{3+} which is denoted in tables as $U(\text{av.})$ and the other with the specific U value given on the appropriate Ni atoms (see computational details for detailed explanation), denoted by U . The investigated structures are numbered depending on their parent crystal structures by Roman numerals: I (Cr_2F_5), II (FeAlF_5), III (MnAlF_5), IV (V_2O_5). Structures II, III and IV are described briefly in terms of their crystal structure and magnetic ordering. For discussion of the most stable structure I the reader is directed to the main text. The energies of all the structures are given relative to the most stable structure I (in the tables they are denoted as ΔE) and are shown in Figure S1.

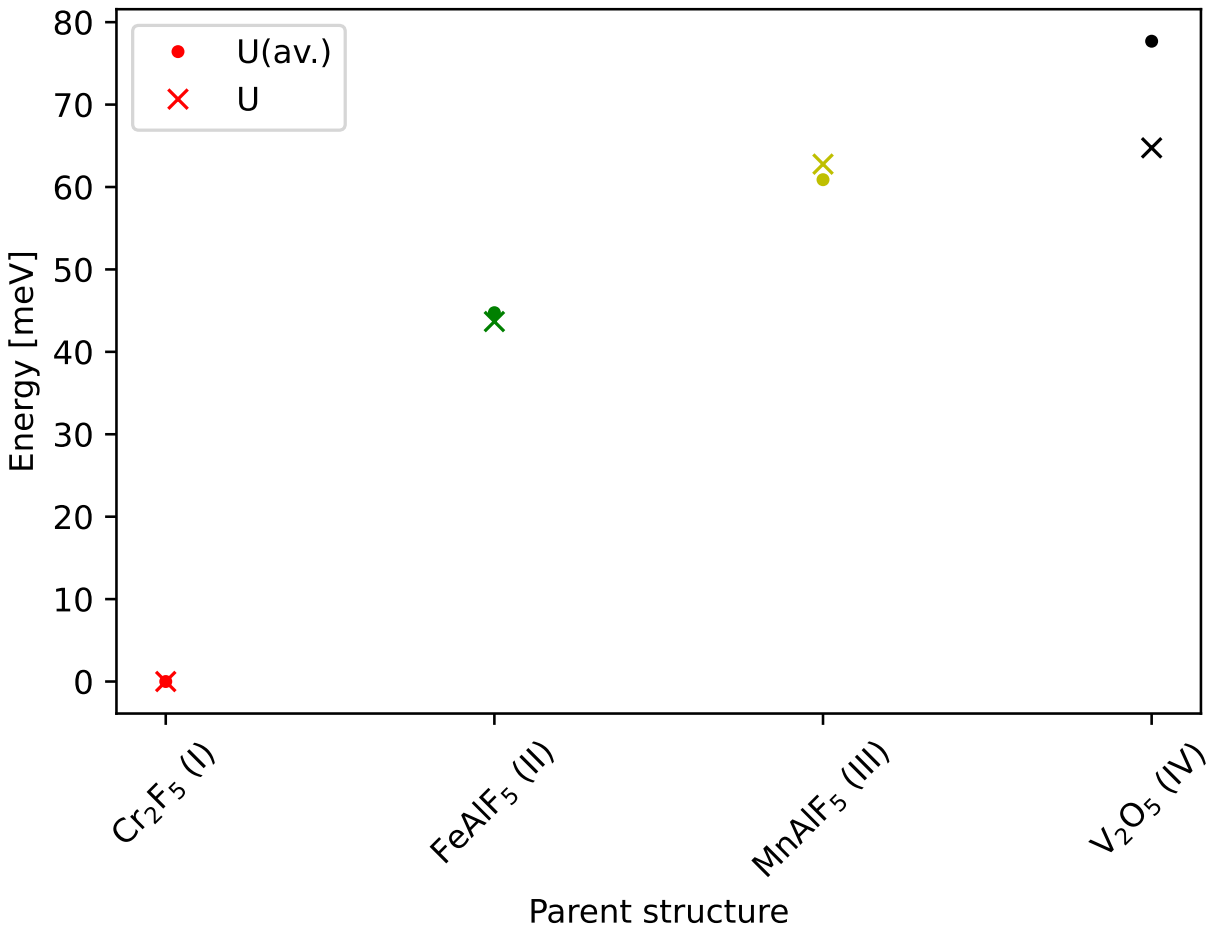


Figure S1: Stability of investigated structures relative to the most stable structure I.

1. Structure I - Cr_2F_5 -type

Table S1: ΔE (in meV), space group and optimised cell parameters, lengths in Å, volume in Å³, angles in °, total magnetic moment μ (in μ_B) for optimised structure I.

Case	ΔE	SG	V	a	b	c	β	μ
U(av.)	0	$C2/c$	331.86	7.24	7.40	7.08	118.9	0.00
U	0	$C2/c$	331.86	7.24	7.40	7.08	118.9	0.00

Table S2: Bond distances (in Å) between both Ni centres and surrounding F atoms. Atom numbering is the same as in Figure 1.

#F	$\text{Ni}^{3+}(1)$		#F	$\text{Ni}^{2+}(2)$	
	U(av.)	U		U(av.)	U
1	1.847	1.847	6	1.930	1.930
2	1.834	1.834	7	2.154	2.154
3	1.941	1.941	8	2.171	2.171
4	1.834	1.834	9	2.154	2.154
5	1.941	1.941	10	2.171	2.171
6	1.847	1.847	11	1.930	1.930

Table S3: Bond angles in both Ni^{2+} and Ni^{3+} octahedra (in $^\circ$) in structure I. Atom numbering is the same as in Figure 1.

	U(av.)	U		U(av.)	U
F(1)–Ni(1)–F(2)	93.9	93.9	F(6)–Ni(2)–F(7)	92.9	92.9
F(2)–Ni(1)–F(3)	89.6	89.6	F(7)–Ni(2)–F(8)	69.5	69.5
F(3)–Ni(1)–F(4)	90.4	90.4	F(8)–Ni(2)–F(9)	110.5	110.5
F(4)–Ni(1)–F(5)	89.6	89.6	F(9)–Ni(2)–F(10)	69.5	69.5
F(5)–Ni(1)–F(2)	90.4	90.4	F(10)–Ni(2)–F(7)	110.5	110.5
F(1)–Ni(1)–F(6)	180.0	180.0	F(6)–Ni(2)–F(11)	180.0	180.0

Table S4: Absolute magnetic moments (in μ_B) and Bader charges (in e) for optimised structure I.

	μ		Bader charge	
	U(av.)	U	U(av.)	U
Ni^{2+}	2.28	2.32	1.74	1.74
Ni^{3+}	1.84	1.82	1.45	1.45
F	0.00-0.11	0.00-0.10	-(0.60-0.67)	-(0.61-0.67)

2. Structure II - FeAlF₅-type

Crystal structure II is derived from the crystal structure of FeAlF₅, space group *Immm* with 4 Ni₂F₅ formula units in the unit cell. Structurally it is very similar to the crystal structure of Cr₂F₅, consisting of rutile-like edge sharing octahedra formed by Ni²⁺ centres and rows of corner sharing octahedra formed by Ni³⁺ centres (see Figure S3). The main difference, compared to the structure I, is that the angles in the octahedron around the Ni³⁺ are 90° and the angles between the neighbouring octahedra of Ni atoms in different oxidation states (i.e. Ni(II)-F-Ni(III)) are 180°. The only angles which deviate from these are the ones shown in Table S6.

Magnetic ordering in the structure is antiferromagnetic (for the magnitudes of magnetic moments and Bader charges see Table S7) with alternating spin up and spin down magnetic moments within the Ni²⁺ and Ni³⁺ rows and antiferromagnetic coupling between the neighbouring nickel centres of different oxidation states (see Figure S3). Similarly as in the case of the C2/c structure five superexchange couplings can be identified (see main text for detailed discussion), antiferromagnetic between the Ni centres in the like oxidation state (with the superexchange angle of 111.7° for Ni²⁺ and 180.0° for Ni³⁺), two ferrimagnetic (with the superexchange angles of 124.7° and 180°) and one ferromagnetic between the Ni centres of different oxidations states (superexchange angle of 123.6°) .

Table S5: ΔE (in meV), space group and optimised cell parameters, lengths in Å, volume in Å³, total magnetic moment μ (in μ_B) for optimised structure II.

Case	ΔE	SG	V	a	b	c	μ
U(av.)	44.8	<i>Immm</i>	342.84	7.53	6.34	7.18	0.00
U	43.7	<i>Immm</i>	342.84	7.53	6.34	7.18	0.00

Table S6: Bond distances (in Å) between both Ni centres and surrounding F atoms and some selected bond angles (in °). Atom numbering is the same as in Figure S2.

#F	Ni ²⁺ (1)		#F	Ni ³⁺ (2)		Angles	
	U(av.)	U(Ni ²⁺)		U(av.)	U(Ni ³⁺)		
1	2.188	2.188	6	1.953	1.953	U(av.)	
2	2.150	2.150	7	1.794	1.794	F(1)-Ni(1)-F(2)	111.7
3	1.920	1.920	8	1.845	1.845	F(1)-Ni(1)-F(4)	67.6
4	2.188	2.188	9	1.796	1.796	U(av.)	
5	1.920	1.920	10	1.845	1.845	F(1)-Ni(1)-F(2)	111.7
6	2.150	2.150	11	1.953	1.953	F(1)-Ni(1)-F(4)	67.6

Table S7: Absolute magnetic moments (in μ_B) and Bader charges (in e) for optimised structure II.

	μ		Bader charge	
	U(av.)	U	U(av.)	U
Ni ²⁺	1.83	1.81	1.48	1.48
Ni ³⁺	2.28	2.32	1.72	1.73
F	0.00-0.10	0.00-0.10	-(0.60-0.68)	-(0.60-0.68)

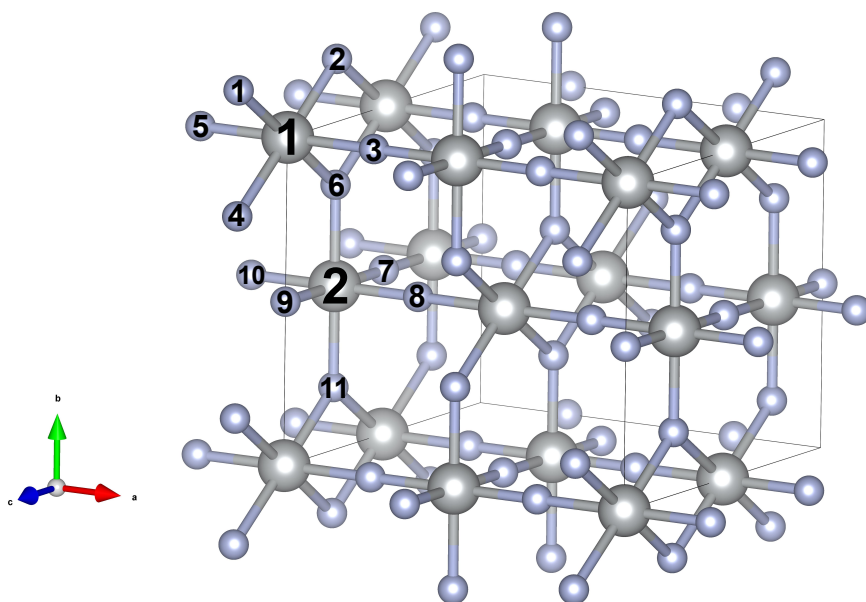


Figure S2: PBE+U optimised structure of Ni_2F_5 derived from the crystal structure of FeAlF_5 , Ni atoms are shown in grey and F atoms in blue.

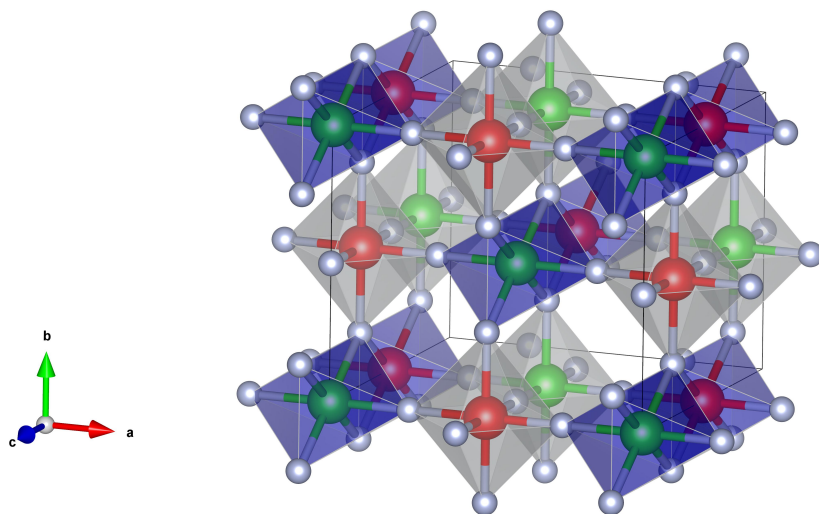


Figure S3: Crystal structure of Ni_2F_5 with blue and grey octahedra representing Ni^{2+} and Ni^{3+} environments, respectively. Red and green represent the opposite orientation of magnetic moments of Ni atoms.

3. Structure III - MnAlF_5 -type

Structure III is derived from the crystal structure of MnAlF_5 , space group $Cmcm$, with 8 formula units in the unit cell. It can be described as consisting of edge sharing octahedra of Ni^{2+} centres, similar as in the rutile, and corner sharing Ni^{3+} centre octahedra. These chains are connected to each other in two ways, each Ni^{3+} octahedron shares one corner with one free corner of the Ni^{2+} octahedron and another corner with the fluorine atom which is part of the rutile-like edge shared chain, making the fluorine connected to three Ni atoms (see Figure S5). Both types of octahedra have three pairs of equal bond lengths (see Table S9), but are highly distorted with respect to the bond angles (see Table S10).

Magnetic ordering in the structure is antiferromagnetic (for the magnitude of magnetic moments and Bader charges see Table S11). Similarly as in the structures I and II magnetic ordering within the rows of both Ni^{2+} and Ni^{3+} is antiferromagnetic (with the superexchange angles of 111.5° for the former and 164.5° for the latter). In contrast to the structures I and II there are two ferromagnetic couplings between the Ni^{2+} and Ni^{3+} octahedra (with a superexchange angles of 168.0° and 124.2°) and one ferrimagnetic coupling (with a superexchange angle of 123.3°).

Table S8: ΔE (in meV), space group and optimised cell parameters, lengths in Å, volume in Å³, total magnetic moment μ (in μ_B) for optimised structure III.

Case	ΔE	SG	V	a	b	c	μ
U(av.)	60.9	$Cmcm$	683.73	7.90	9.88	9.63	0.00
U	62.8	$Cmcm$	683.73	7.19	9.88	9.63	0.00

Table S9: Bond distances (in Å) between both Ni centres and surrounding F atoms. Atom numbering is the same as in Figure S4.

#F	Ni ²⁺ (1)		#F	Ni ³⁺ (2)	
	U(av.)	U		U(av.)	U
1	1.919	1.919	6	1.851	1.851
2	2.152	2.152	7	1.815	1.815
3	2.152	2.152	8	1.851	1.851
4	2.200	2.200	9	1.954	1.954
5	2.200	2.200	10	1.813	1.813
6	1.919	1.919	11	1.954	1.954

Table S10: Bond angles in both Ni²⁺ and Ni³⁺ octahedra (in °). Atom numbering is the same as in Figure S4.

	U(av.)	U		U(av.)	U
F(1)–Ni(1)–F(2)	90.4	90.4	F(6)–Ni(2)–F(7)	91.2	91.2
F(2)–Ni(1)–F(3)	69.4	69.4	F(7)–Ni(2)–F(8)	95.4	95.4
F(3)–Ni(1)–F(4)	111.5	111.5	F(8)–Ni(2)–F(9)	84.6	84.6
F(4)–Ni(1)–F(5)	67.7	67.7	F(9)–Ni(2)–F(10)	84.7	84.7
F(5)–Ni(1)–F(2)	111.5	111.5	F(10)–Ni(2)–F(8)	95.4	95.4
F(1)–Ni(1)–F(6)	178.7	178.7	F(6)–Ni(2)–F(11)	179.9	179.9

Table S11: Absolute magnetic moments (in μ_B) and Bader charges (in e) for optimised structure III.

	μ		Bader charge	
	U(av.)	U	U(av.)	U
Ni ²⁺	1.83	1.82	1.46	1.46
Ni ³⁺	2.30	2.33	1.76	1.77
F	0.00-0.10	0.00-0.10	-(0.62-0.66)	-(0.60-0.68)

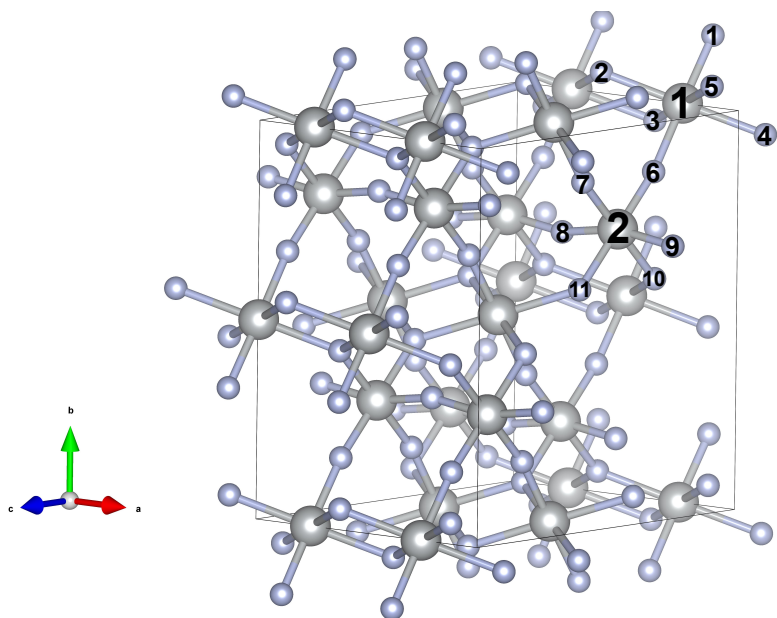


Figure S4: PBE+U optimised structure of Ni_2F_5 derived from the crystal structure of MnAlF_5 , Ni atoms are shown in grey and F atoms in blue.

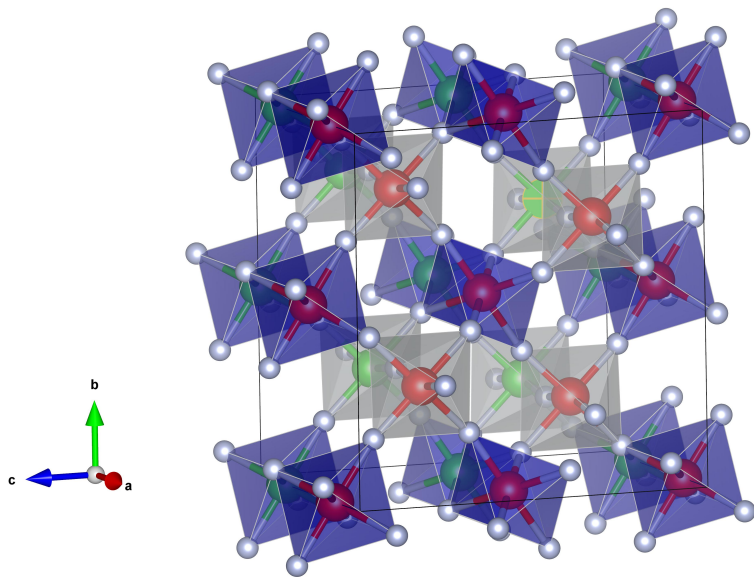


Figure S5: Crystal structure of Ni_2F_5 (III) with blue and grey octahedra representing Ni^{2+} and Ni^{3+} environments, respectively. Red and green represent the opposite orientation of magnetic moments of Ni atoms.

4. Structure IV - V_2O_5 -type

Structure IV is derived from the crystal structure of V_2O_5 , space group $Pmn2_1$ with 8 Ni_2F_5 formula units in the investigated unit cell. V atoms in the parent crystal structure are symmetry related, hence to produce two distinct environments for Ni^{2+} and Ni^{3+} symmetry reduction was carried out by displacing some Ni atoms prior to the optimisation of internal coordinates.

The structure consists of chains of corner sharing octahedra of Ni^{2+} and Ni^{3+} , respectively. These chains are connected together by sharing an edge and a corner opposite to that edge (see Figure S7). The octahedra around both metal centres are highly distorted (see Tables S13 and S14).

Overall magnetic ordering in the structure is antiferromagnetic (for the magnitudes of magnetic moments and Bader charges see S15). As with the other structures the ordering within the chains of the atoms in the like oxidation states is antiferromagnetic (see Figure S7). The superexchange angles are 178.4° (b-axis direction) and 152.9° (c-axis direction) between the Ni^{2+} centres and 166.5° (b-axis direction) and 177.9° (c-axis direction) between the Ni^{3+} octahedra. Among the Ni centres in different oxidation states there are three different superexchange interactions: ferrimagnetic through the corner sharing fluorine atom (with the superexchange angle of 179.9°) and through the edge sharing fluorines (with the superexchange angles of 103.8° and 96.8°). The last magnetic coupling is ferromagnetic through the edge sharing fluorines (with the superexchange angles of 103.2° and 96.4°).

One of the possible reasons for this structure being the highest in energy can be found in its magnetic structure. It consist of magnetically frustrated platelets, where the Goodenough Kanamori rules are not satisfied and consequently the energy is raised.

Table S12: ΔE (in meV), space group and optimised cell parameters, lengths in Å, volume in Å³, angles in °, total magnetic moment μ (in μ_B) for optimised structure IV.

Case	ΔE	SG	V	a	b	c	μ
U(av.)	77.7	$Pmn2_1$	716.85	12.21	7.84	7.49	0.00
U	64.8	$Pmn2_1$	739.41	12.35	7.94	7.54	0.00

Table S13: Bond distances (in Å) between both Ni centres and surrounding F atoms. Atom numbering is the same as in Figure S6.

#F	Ni ²⁺ (1)		#F	Ni ³⁺ (2)	
	U(av.)	U		U(av.)	U
1	2.016	2.047	5	1.970	1.998
2	1.872	1.886	6	1.900	1.900
3	1.961	1.991	7	1.873	1.886
4	1.873	1.886	8	1.776	1.785
5	2.142	2.146	9	1.872	1.885
6	2.015	2.046	10	1.974	2.004

Table S14: Bond angles in both Ni²⁺ and Ni³⁺ octahedra (in °). Atom numbering is the same as in Figure S6.

	U(av.)	U		U(av.)	U
F(1)–Ni(1)–F(2)	90.2	90.1	F(6)–Ni(2)–F(7)	88.9	89.0
F(2)–Ni(1)–F(3)	89.3	89.3	F(7)–Ni(2)–F(8)	91.0	90.9
F(3)–Ni(1)–F(4)	89.1	89.1	F(8)–Ni(2)–F(9)	91.1	91.0
F(4)–Ni(1)–F(5)	90.9	90.8	F(9)–Ni(2)–F(6)	89.0	89.1
F(5)–Ni(1)–F(2)	90.8	90.7	F(6)–Ni(2)–F(5)	83.7	83.0
F(1)–Ni(1)–F(6)	152.9	151.8	F(5)–Ni(2)–F(10)	166.8	165.5

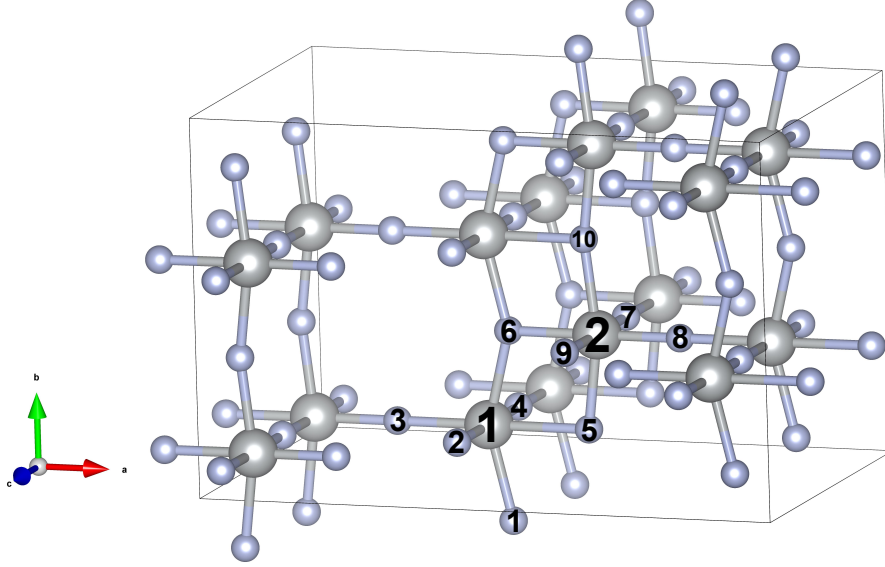


Figure S6: PBE+U optimised structure of Ni_2F_5 derived from the crystal structure of V_2O_5 , Ni atoms are shown in grey and F atoms in blue.

Table S15: Absolute magnetic moments (in μ_B) and Bader charges (in e) for optimised structure III.

	μ		Bader charge	
	U(av.)	U	U(av.)	U
Ni^{2+}	1.82	1.780	1.44	1.45
Ni^{3+}	2.24	2.27	1.74	1.74
F	0.00-0.20	0.00-0.15	-(0.58-0.69)	-(0.60-0.67)

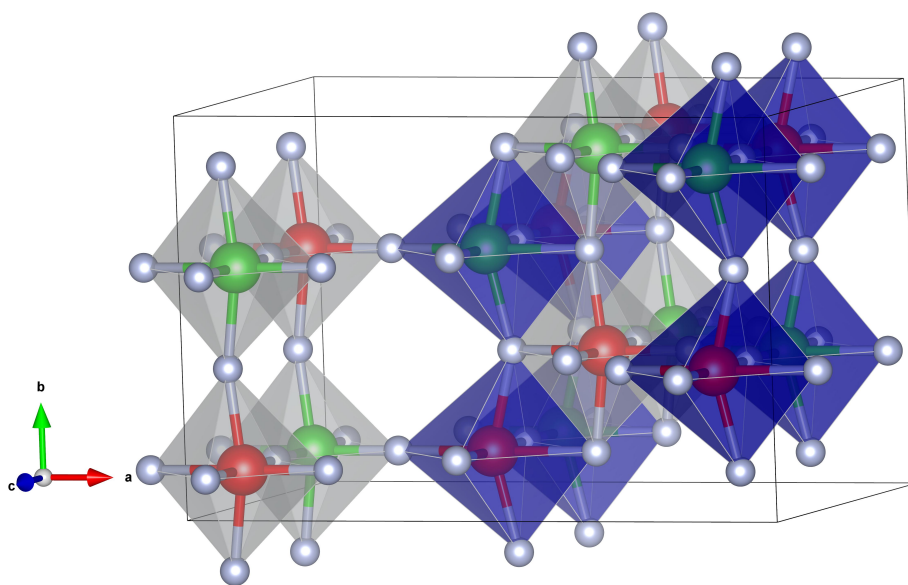


Figure S7: Crystal structure of Ni_2F_5 (IV) with blue and grey octahedra representing Ni^{2+} and Ni^{3+} environments, respectively. Red and green represent the opposite orientation of magnetic moments of Ni atoms.