Electronic Supplementary Information

High Pressure Induced Charge Transfer in 3d-4f Bimetallic Photomagnetic Materials

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Further information of structural data collection and refinement

Ambient pressure single crystal X-ray diffraction data on **1** was collected on a Bruker APEXII diffractometer with a completeness of 99.9 % to $\theta = 25.242°$. The intensities were integrated with the program SAINT+.[1] Empirical absorption correction was done in SADABS,[2] and structure determination was carried out with the OLEX2 program.[3] **1** crystallizes in the monoclinic system with space group $P2_1/n$.[4] For **2** and **3,** ambient pressure data were measured on an OXFORD SuperNOVA diffractometer equipped with micro-focus Mo X-ray source and Atlas CCD detector. Data integration and reduction was performed by the CrysAlisPro system software.[5] The completeness of both data sets was 100 % with θ up to 27.4°. Both crystals crystallized in the monoclinic system with space groups $P2_1/c$ and $P2_1/n$, respectively. Further crystallographic and refinement details are given in the ESI.

High pressure X-ray Diffraction data were collected on an OXFORD SuperNOVA diffractometer. A Boehler-Almax plate DAC equipped with a pair of Type Ia Boehler Almax Design 600-μm-culet diamonds was used. Data collection, integration and reduction were performed using CrysAlisPro system software.[5] Structure determination was carried out by using the OLEX2 program.[3] The structures were refined using SHELXL and keywords DELU, SIMU, RIGU and SADI were used. However, for **1**, only the structures at 0.13(2), 0.70(5) and 1.30(3) GPa can obtained reliable structure. The completeness of those three data sets is 57.9%, 37.9% and 39%. For the others, the reliable structural refinement were obtained at 0.22(7), 1.01(6) and 2.40(4) GPa for **2** and 0.34(6) GPa for **3**.

Table S1. Crystal data and structure refinement for **1**

Identification code	P0-1a	P1-1a	P2-1b	P3-1b
Pressure (GPa)	ambient	0.70(5)	0.13(2)	1.30(3)
PTM*	paratone-N	paratone-N	iso-n-pentane	iso-n-pentane
Empirical formula	C18 H36 Fe N10 O8 Y	C18 H36 Fe N10 O8 Y	C18 H36 Fe N10 O8 Y	C18 H36 Fe N10 O8 Y
Formula weight (g/mol)	665.33	665.33	665.33	665.33
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/n	P 2_1/n	P 2_1/c	P 2_1/c
a (Å)	17.6022(11)	17.4248(10)	13.8745(3)	13.5987(3)
b (Å)	8.8842(7)	8.8021(8)	8.8220(11)	8.6050(12)
c (Å)	19.8991(12)	19.4853(7)	24.6765(7)	23.6701(11)
β (deg.)	95.832(3)	96.288(4)	96.215(2)	94.941(3)
Volume (Å^3)	3095.7(4)	2970.6(3)	3002.7(4)	2759.5(4)
Z	4	4	4	4
Absorption coefficient (mm^{-1})	2.387	2.488	2.461	2.678
F(000)	1372	1372	1372	1372
Crystal size (mm^3)	0.141x0.113x0.09	0.141x0.113x0.09	0.143x0.107x0.061	0.143x0.107x0.061
Theta range for data collection (°)	1.472 to 27.482	2.103 to 26.025	1.476 to 23.252	1.503 to 23.249
Index ranges	-21<=h<=22, -11<=k<=11, -25<=l<=25	-20<=h<=18, -7<=k<=7, -23<=l<=23	-15<=h<=15, -5<=k<=5, -27<=l<=27	-15<=h<=15, -5<=k<=5, -25<=l<=25
Reflections collected	26989	13709	16108	15666
Independent reflections	7101 [R(int)=0.0711]	3159 [R(int)=0.0796]	2235 [R(int)=0.0471]	2115 [R(int)=0.0620]
Completeness (%)	99.9	57.9	37.9	39.0
Absorption correction	Gaussian			
Refinement method	Full-matrix least-squares on F^2			
Data / restraints / parameters	7101 / 558 / 347	3159 / 589 / 349	2235 / 318 / 357	2115 / 318 / 357
Goodness-of-fit on F^2	1.238	1.618	1.158	1.035
Final R indices [I>2σ(I)]	R1=0.0995, wR2=0.2873	R1=0.1532, wR2=0.3647	R1=0.0396, wR2=0.0880	R1=0.0835, wR2=0.2204
R indices (all data)	R1=0.1366, wR2=0.3296	R1=0.1993, wR2=0.4100	R1=0.0556, wR2=0.0969	R1=0.1166, wR2=0.2534
Largest diff. peak and hole (e.Å^{-3})	4.548 and -2.368	2.333 and -2.447	0.356 and -0.361	0.867 and -0.844

*PTM: pressure transmitting medium

Table S2. Crystal data and structure refinement for **2**

Identification code	P0-2	P1-2	P2-2	P3-2
Pressure (GPa)	ambient	0.22(7)	1.01(6)	2.40(4)
PTM*	paratone-N	paratone-N	paratone-N	paratone-N
Empirical formula	C18 H36 Co N10 O8 Y	C18 H36 Co N10 O8 Y	C18 H36 Co N10 O8 Y	C18 H36 Co N10 O8 Y
Formula weight (g/mol)	668.41	668.41	668.41	668.41
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/c	P 2_1/c	P 2_1/c	P 2_1/c
a (Å)	13.90785(15)	13.8516(5)	13.6290(5)	13.358(2)
b (Å)	8.85452(10)	8.807(2)	8.649(2)	8.473(15)
c (Å)	24.7756(3)	24.6282(7)	23.9065(8)	23.152(7)
β (deg.)	96.3669(10)	96.348(3)	95.542(3)	94.748(18)
Volume (Å^3)	3032.23(6)	2985.9(7)	2804.8(8)	2611(5)
Z	4	4	4	4
Absorption coefficient (mm^{-1})	2.506	2.545	2.709	2.910
F(000)	1376	1376	1376	1376
Crystal size (mm^3)	0.163x0.142x0.07	0.163x0.142x0.07	0.163x0.142x0.07	0.163x0.142x0.07
Theta range for data collection (°)	1.473 to 27.482	1.664 to 24.656	1.712 to 24.691	1.765 to 24.691
Index ranges	-18<=h<=18, -11<=k<=11, -32<=l<=32	-16<=h<=16, -4<=k<=4, -28<=l<=27	-15<=h<=15, -4<=k<=4, -26<=l<=27	-15<=h<=15, -3<=k<=3, -27<=l<=26
Reflections collected	36743	9636	8753	7012
Independent reflections	6952 [R(int)=0.0327]	2092 [R(int)=0.0481]	1943 [R(int)=0.0476]	1748 [R(int)=0.1015]
Completeness (%)	100.0	38.6	38.1	37.1
Absorption correction	Gaussian			
Refinement method	Full-matrix least-squares on F^2			
Data / restraints / parameters	6952 / 276 / 362	2092 / 237 / 165	1943 / 231 / 165	1748 / 281 / 175
Goodness-of-fit on F^2	1.050	1.413	1.117	1.557
Final R indices [I>2σ(I)]	R1=0.0369, wR2=0.0887	R1=0.0943, wR2=0.2659	R1=0.0822, wR2=0.2238	R1=0.1625, wR2=0.4301
R indices (all data)	R1=0.0459, wR2=0.0936	R1=0.1216, wR2=0.3299	R1=0.1077, wR2=0.2697	R1=0.2332, wR2=0.4745
Largest diff. peak and hole (e.Å^{-3})	1.306 and -0.606	1.199 and -1.026	0.727 and -1.097	0.540 and -0.710

*PTM: pressure transmitting medium

Table S3. Crystal data and structure refinement for **3**

Identification code	P0-3	P1-3
Pressure (GPa)	ambient	0.34(6)
PTM*	paratone-N	paratone-N
Empirical formula	C18 H36 Fe N10 Nd O8	C18 H36 Fe N10 Nd O8
Formula weight (g/mol)	720.66	720.66
Crystal system	Monoclinic	Monoclinic
Space group	P 2_1/n	P 2_1/n
a (Å)	17.63656(14)	17.4888(3)
b (Å)	8.90528(7)	8.8242(6)
c (Å)	19.92280(18)	19.7041(6)
β (deg.)	95.8710(8)	96.039(2)
Volume (Å^3)	3112.63(5)	3024.0(2)
Z	4	4
Absorption coefficient (mm^{-1})	2.169	2.232
F(000)	1456	1456
Crystal size (mm^3)	0.17x0.158x0.074	0.17x0.158x0.074
Theta range for data collection (°)	1.469 to 27.484	1.482 to 23.246
Index ranges	-22<=h<=22, -11<=k<=11, -25<=l<=25	-19<=h<=19, -7<=k<=7, -20<=l<=21
Reflections collected	30365	12308
Independent reflections	7155 [R(int)=0.0265]	2765 [R(int)=0.0379]
Completeness (%)	100.0	50.5
Absorption correction	Gaussian	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7155 / 638 / 298	2765 / 558 / 300
Goodness-of-fit on F^2	1.049	1.092
Final R indices [I>2σ(I)]	R1=0.0401, wR2=0.1058	R1=0.0556, wR2=0.1652
R indices (all data)	R1=0.0475, wR2=0.1122	R1=0.0687, wR2=0.1912
Largest diff. peak and hole (e.Å^{-3})	1.995 and -2.355	1.013 and -1.300

*PTM: pressure transmitting medium

Figure S1. Pressure dependent crystal color of compound **1**. The crystal is pressurized in a DAC with paratone-N as PTM from 0.14 GPa (P1) up to 10.22 GPa (P12), then depressurized to 2.98 GPa (P16). Then the whole DAC was put into an oven at 80°C for 10 min (P17) and cooling down to room temperature (P18). All pictures were taken at the same condition, such as same light source and exposure time.

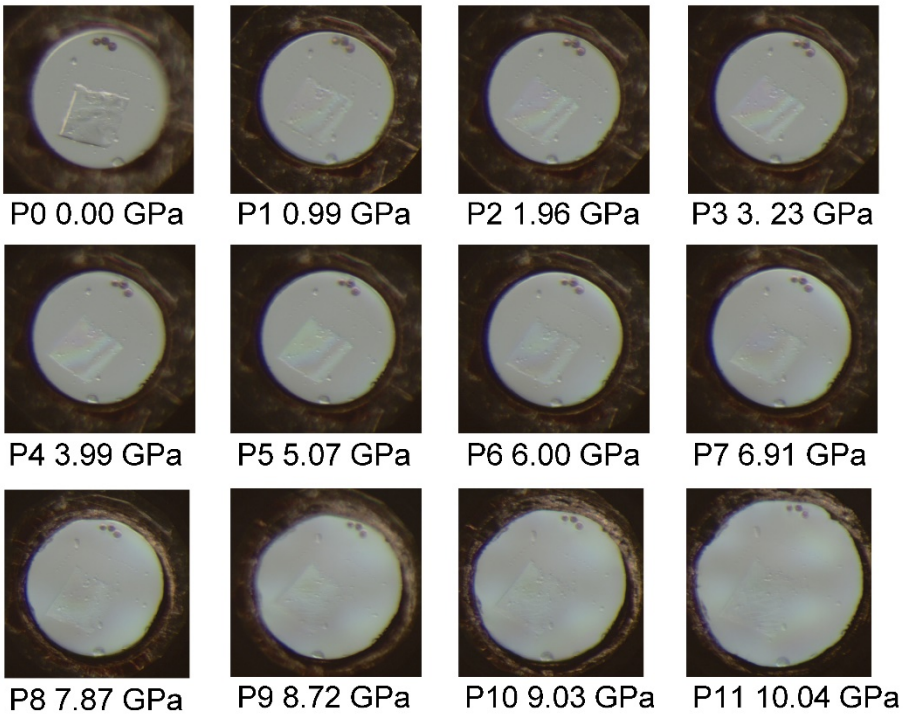


Figure S2. Pressure dependent crystal color of compound **2**. The crystal is pressurized in a DAC with paratone-N as PTM from ambient (P0) up to 10.07 GPa (P11). The crystal becomes invisible may cause by similar refractive index between crystal and PTM.

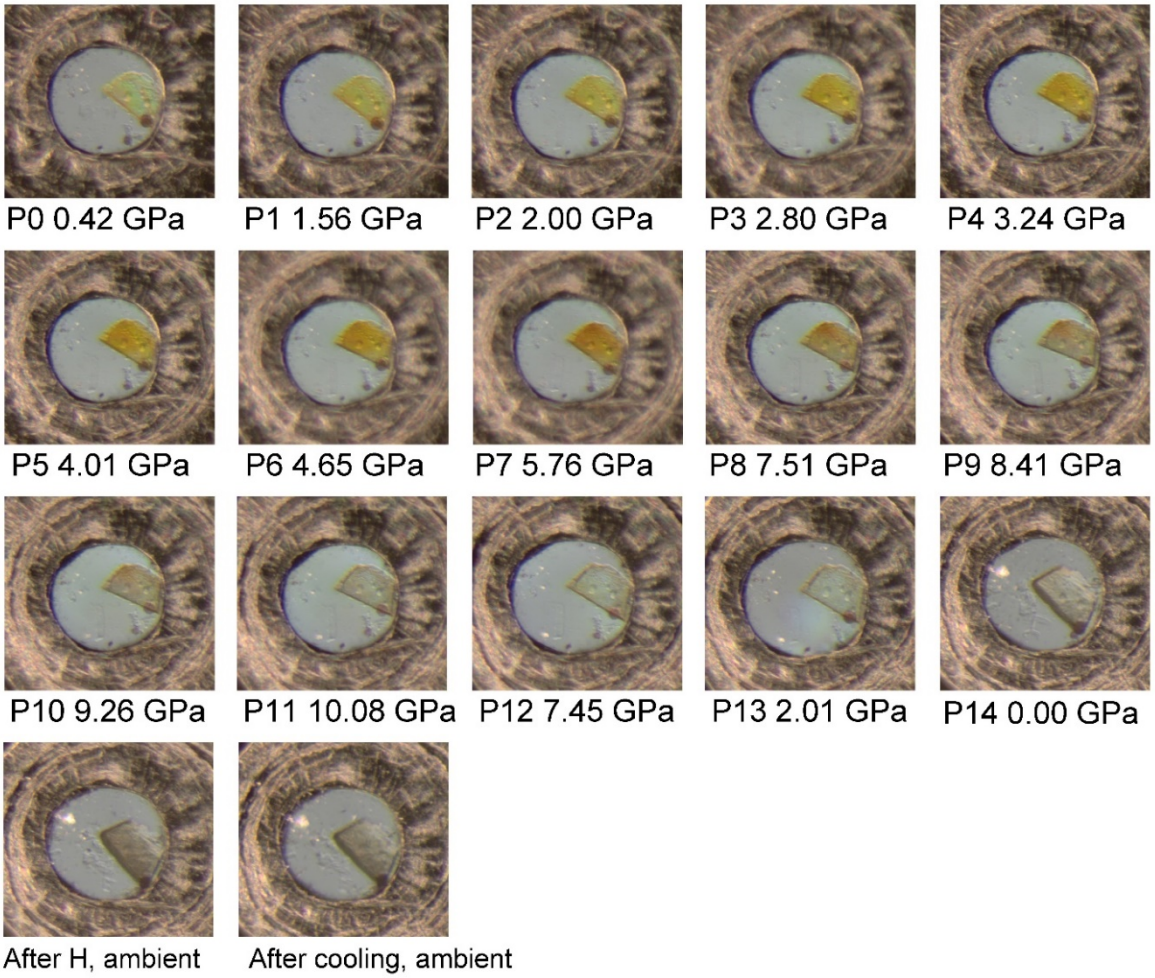
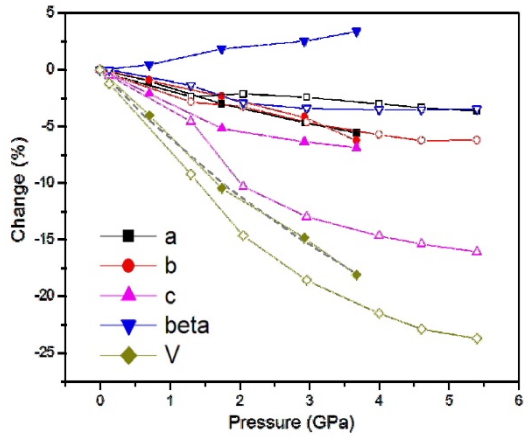
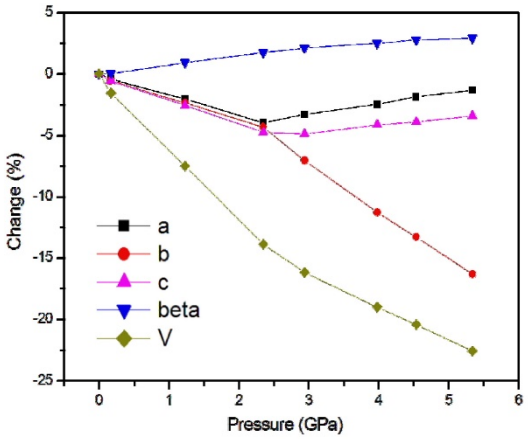


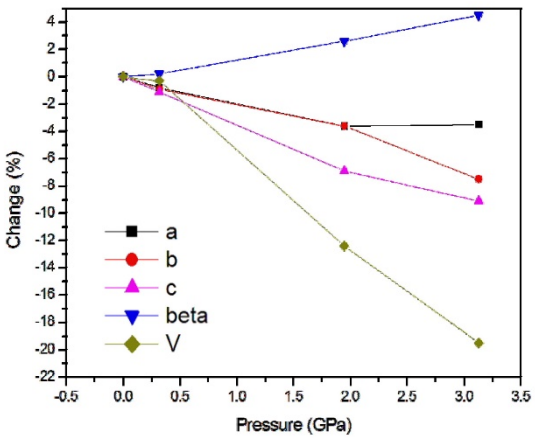
Figure S3. Pressure dependent crystal color of compound **3**. The crystal is pressurized in a DAC with paratone-N as PTM from ambient (P0) up to 10.08 GPa (P11), then depressurized to ambient (P14). Then the whole DAC was put into an oven at 80°C for 10 min (after H) and cooling down to room temperature (after cooling). All pictures were taken at the same condition, such as same light source and exposure time.



(a)



(b)



(c)

Figure S4. Pressure dependent changes of unit cell parameters of compound **1** (a), **2** (b) and **3** (c). Filled symbols show data collected in paratone-N oil, empty symbols show data collected in iso-n-pentane.

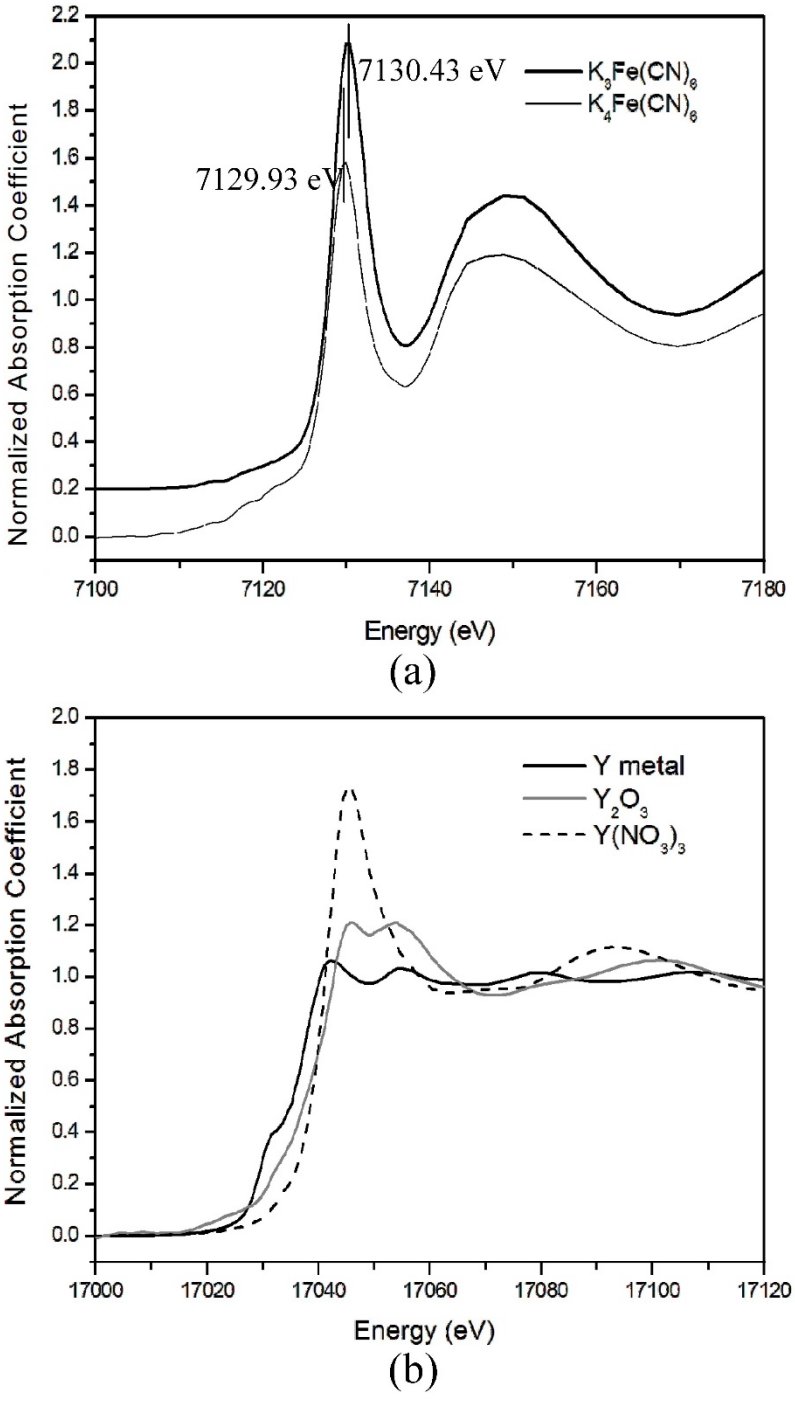


Figure S5. X-ray absorption K-edge of Fe and Y standard compounds.

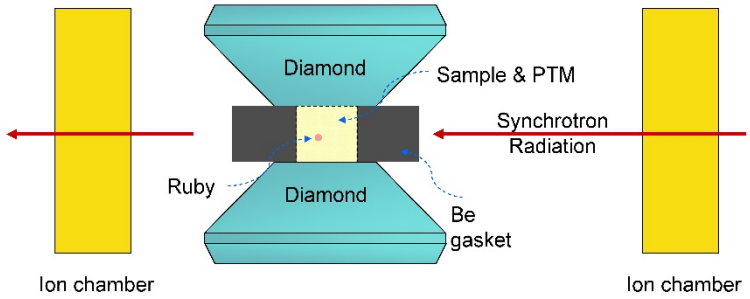


Figure S6. Experimental setup of high-pressure XANES.

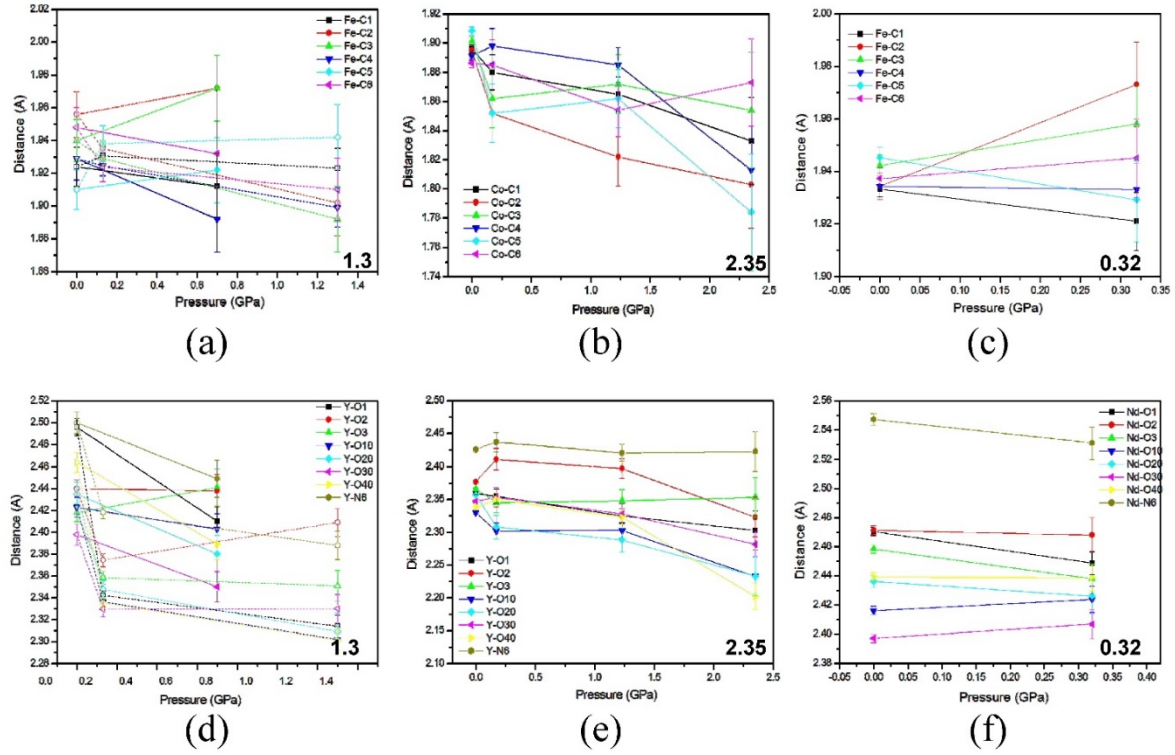


Figure S7. Pressure dependent Fe/Co-C (a-c) and Y/Nd-O/N (d-f) bond distances of compound **1** (a,d), **2** (b,e), and **3** (c,f). The highest pressure of the determined structures are 1.3, 2.35 and 0.32 GPa for **1**, **2** and **3** respectively.

Reference

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