**Supporting information**

Table I. The unit cell dimensions of $VF_3$-type $FeF_3$ at various pressure by the X-ray powder diffraction experiment.

| Pressure(GPa) | *a*(Å) | *c*(Å) | volume(Å$^3$) |
|---|---|---|---|
| 0.0001 | 5.202(1) | 13.319(3) | 312.14(3) |
| 2.6 | 4.924(2) | 13.425(7) | 281.84(9) |
| 3.5 | 4.888(1) | 13.448(7) | 278.22(9) |
| 4.7 | 4.838(1) | 13.451(7) | 272.65(8) |
| 5.6 | 4.807(2) | 13.442(8) | 268.98(10) |
| 6.6 | 4.775(2) | 13.439(8) | 265.38(9) |
| 7.7 | 4.741(2) | 13.421(9) | 261.21(11) |
| 8.9 | 4.711(2) | 13.442(8) | 258.39(9) |
| 10.1 | 4.680(2) | 13.446(10) | 255.08(11) |
| 11.3 | 4.653(2) | 13.419(10) | 251.59(11) |
| 12.6 | 4.642(3) | 13.372(11) | 249.53(14) |
| 14.2 | 4.612(2) | 13.379(11) | 246.49(13) |
| 15.4 | 4.599(2) | 13.358(11) | 244.70(13) |
| 16.5 | 4.585(2) | 13.331(11) | 242.71(12) |
| 17.7 | 4.568(2) | 13.295(10) | 240.27(11) |
| 19.0 | 4.555(2) | 13.266(11) | 238.34(12) |
| 20.4 | 4.542(2) | 13.246(11) | 236.68(12) |
| 22.0 | 4.530(2) | 13.226(11) | 235.04(12) |
| 23.4 | 4.513(3) | 13.216(12) | 233.12(13) |
| 24.9 | 4.500(2) | 13.190(10) | 231.28(11) |
| 27.4 | 4.469(2) | 13.163(10) | 227.72(12) |
| 28.7 | 4.460(2) | 13.095(10) | 225.59(11) |
| 30.2 | 4.449(2) | 13.061(11) | 223.92(12) |

Table II. The unit cell dimensions of $VF_3$-type $FeF_3$ at various pressure by the DFT calculation.

| Pressure(GPa) | *a*(Å) | *c*(Å) | volume(Å$^3$) |
|---|---|---|---|
| 0.02 | 5.406 | 13.496 | 341.52 |
| 0.4 | 5.327 | 13.495 | 331.68 |
| 0.9 | 5.250 | 13.489 | 322.02 |
| 1.6 | 5.172 | 13.490 | 312.54 |
| 2.4 | 5.088 | 13.527 | 303.27 |
| 3.5 | 5.009 | 13.537 | 294.15 |
| 4.9 | 4.930 | 13.550 | 285.24 |
| 6.6 | 4.855 | 13.548 | 276.51 |
| 8.7 | 4.784 | 13.523 | 267.96 |
| 11.2 | 4.717 | 13.474 | 259.59 |
| 14.3 | 4.655 | 13.395 | 251.40 |
| 18.0 | 4.599 | 13.286 | 243.36 |
| 22.5 | 4.547 | 13.152 | 235.53 |

| | | | |
|---|---|---|---|
| 27.9 | 4.500 | 12.991 | 227.85 |
| 34.3 | 4.458 | 12.802 | 220.32 |
| 42.0 | 4.420 | 12.589 | 213.00 |
| 51.1 | 4.386 | 12.354 | 205.80 |
| 62.0 | 4.356 | 12.098 | 198.78 |