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# Pressure-induced transition in the multiferroic $CoCr_2O_4$ spinel

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## SUPPLEMENTARY INFORMATION

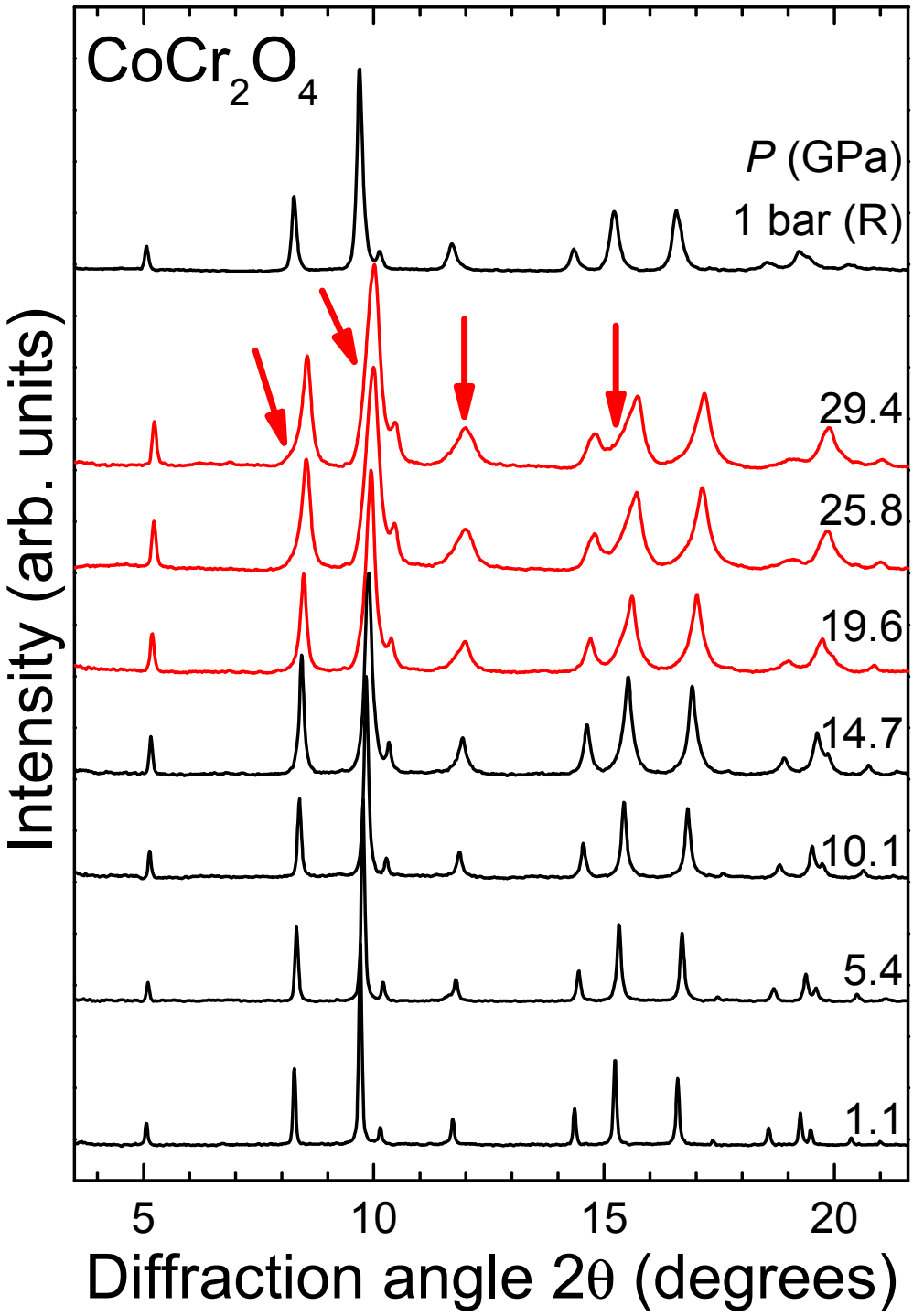


**FIG. S1:** Normalized XRD patterns of $CoCr_2O_4$ at selected pressures ($T$=300 K, $\lambda$=0.4246 Å). The black and red patterns correspond to the *Fd*-3*m* and the tetragonal phases, respectively. Arrows mark the Bragg peak splittings. Background has been subtracted for clarity.

**Table S1**: Experimentally determined structural data (lattice parameters, volume $V$, oxygen positional coordinate $u$, cation-anion bond lengths, and the Cr-O-Cr bond angle) for the $Fd$-3$m$ ($Z$=8) and the $I4_1/amd$ ($Z$=4) phases of $CoCr_2O_4$.

| ***Fd*-3*m*** | ***P* (GPa)** | ***a* (Å)** | ***V* (Å$^3$)** | **O-u** | **Co-O (Å)** | **Cr-O (Å)** | **Cr-O-Cr (degrees)** |
|---|---|---|---|---|---|---|---|
| | 0.0001 | 8.3341(1) | 578.86(2) | 0.2653(5) | 2.026(2) | 1.964(1) | 97.2(1) |
| | 1.1 | 8.3203(1) | 575.99(2) | 0.2655(5) | 2.025(2) | 1.960(1) | 97.3(1) |
| | 2.1 | 8.3069(1) | 573.21(2) | 0.2657(5) | 2.024(2) | 1.955(1) | 97.4(1) |
| | 3.1 | 8.2964(1) | 571.04(2) | 0.2650(5) | 2.012(2) | 1.957(1) | 97.1(1) |
| | 4.1 | 8.2845(1) | 568.58(2) | 0.2646(5) | 2.003(2) | 1.958(1) | 96.8(1) |
| | 5.4 | 8.2711(1) | 565.84(2) | 0.2651(5) | 2.007(2) | 1.951(1) | 97.1(1) |
| | 6.6 | 8.2541(1) | 562.35(2) | 0.2644(5) | 1.993(2) | 1.952(1) | 96.8(1) |
| | 8.1 | 8.2354(1) | 558.54(2) | 0.2637(5) | 1.979(2) | 1.952(1) | 96.4(1) |
| | 10.1 | 8.2126(1) | 553.91(2) | 0.2637(5) | 1.972(2) | 1.948(1) | 96.4(1) |
| | 11.8 | 8.1989(1) | 551.14(2) | 0.2629(5) | 1.958(2) | 1.950(1) | 96.0(1) |
| | 13.2 | 8.1829(1) | 547.93(2) | 0.2630(5) | 1.956(2) | 1.945(1) | 96.1(1) |
| | 14.7 | 8.1693(1) | 545.19(2) | 0.2624(5) | 1.944(2) | 1.946(1) | 95.8(1) |
| | 16.3 | 8.1579(1) | 542.93(2) | 0.2620(8) | 1.936(5) | 1.947(4) | 95.6(3) |
| ***I*4$_1$/*amd*** | ***P* (GPa)** | ***a* (Å)** | ***c*(Å)** | ***c*/*a*** | ***V* (Å$^3$)** | | |
| | 17.8 | 5.7649(1) | 8.142(1) | 0.9987(2) | 270.60(4) | | |
| | 19.6 | 5.7591(1) | 8.115(1) | 0.9963(2) | 269.14(4) | | |
| | 21.4 | 5.7572(1) | 8.084(1) | 0.9928(2) | 267.93(4) | | |
| | 23.6 | 5.7509(1) | 8.031(1) | 0.9875(2) | 265.61(4) | | |
| | 25.8 | 5.7451(2) | 7.997(1) | 0.9842(2) | 263.94(5) | | |
| | 27.4 | 5.7408(2) | 7.965(3) | 0.9811(5) | 262.6(1) | | |
| | 29.4 | 5.7312(2) | 7.925(3) | 0.9778(5) | 260.3(1) | | |

**Table S2**: Theoretically calculated (with DFT) structural parameters (lattice constants and volumes) for the paramagnetic cubic and the ferrimagnetic tetragonal phases of $CoCr_2O_4$ at various pressures. The energy $E$ of each configuration is also provided.

| | ***P* (GPa)** | ***a* (Å)** | | | ***V* (Å$^3$)** | ***E* (eV)** |
|---|---|---|---|---|---|---|
| **Paramagnetic cubic** | -3.3 | 8.527 | | | 620.00 | -419.050 |
| | 0 | 8.472 | | | 608.00 | -419.165 |
| | 2.9 | 8.425 | | | 598.00 | -419.072 |
| | 10.4 | 8.320 | | | 576.00 | -418.159 |
| | 19.3 | 8.213 | | | 554.00 | -416.110 |
| | 30 | 8.103 | | | 532.00 | -412.705 |
| | ***P* (GPa)** | ***a* (Å)** | ***c* (Å)** | ***c*/*a**** | ***V* (Å$^3$)** | ***E* (eV)** |
| **Ferrimagnetic tetragonal** | -3.3 | 6.043 | 8.489 | 0.993 | 310.00 | -209.511 |
| | 0 | 6.004 | 8.433 | 0.993 | 304.00 | -209.572 |
| | 2.9 | 5.971 | 8.386 | 0.993 | 299.00 | -209.525 |
| | 10.4 | 5.909 | 8.248 | 0.986 | 288.00 | -209.083 |
| | 19.3 | 5.849 | 8.098 | 0.978 | 277.00 | -208.067 |
| | 30 | 5.805 | 7.894 | 0.959 | 266.00 | -206.387 |

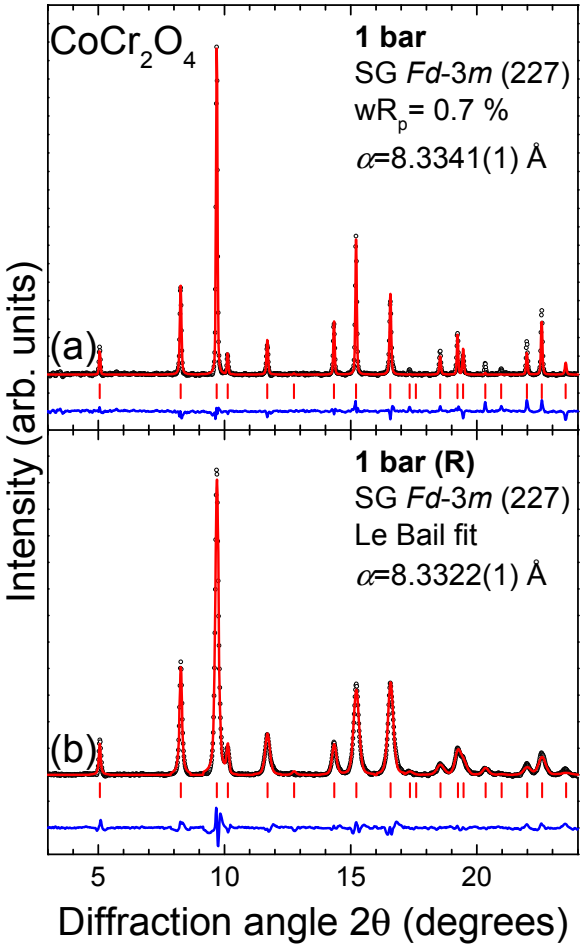


**FIG S2**: Refinements for the *Fd*-3*m* phase of $CoCr_2O_4$ at ambient pressure before [(a), Rietveld] and after [(b), Le Bal fit] after the experimental pressure run. Dots correspond to the measured spectrum, whereas the red and blue solid lines represent the best refinement and the difference between the experimental and refined pattern, respectively. Vertical ticks mark the Bragg peak positions.

**Table S3**: Elastic parameters, i.e. bulk modulus $B_0$ and its pressure derivative $B'_0$ for selected oxide spinels. The reported transition pressures $P_{Tr}$ and the respective high-pressure (HP) phases are also tabulated.

| Spinel | $B_0$ (GPa) | $B'_0$ | $P_{Tr}$ (GPa) | HP phase |
|---|---|---|---|---|
| $CoCr_2O_4$ | 209(±8) | 5(±1) | >16 | Tetragonal |
| | [a]170(±2) | [a]4.1(±2) | ~10 | Tetragonal |
| $FeCr_2O_4$[1] | 209 | 4 | 12 | $I4_1/amd$ |
| $MgCr_2O_4$[2] | 189 | 7.2 | 20 | $I4_1/amd$ |
| $ZnCr_2O_4$[3] | 183 | 7.9 | 23 | Orthorhombic |
| $MnCr_2O_4$[4] | 252 | 4.8 | 20-23 | Decomposition |
| $NiCr_2O_4$[5] | - | - | [a]16 | Decomposition |
| $CdCr_2O_4$[6] | - | - | 10 (+1100 °C) | $CaFe_2O_4$-type |
| $Co_3O_4$[7,8] | 190 | 6.2 | - | - |
| | 249 | 4 | 30 | $Ag_3O_4$-type |

[a]Our *ab initio* calculations.

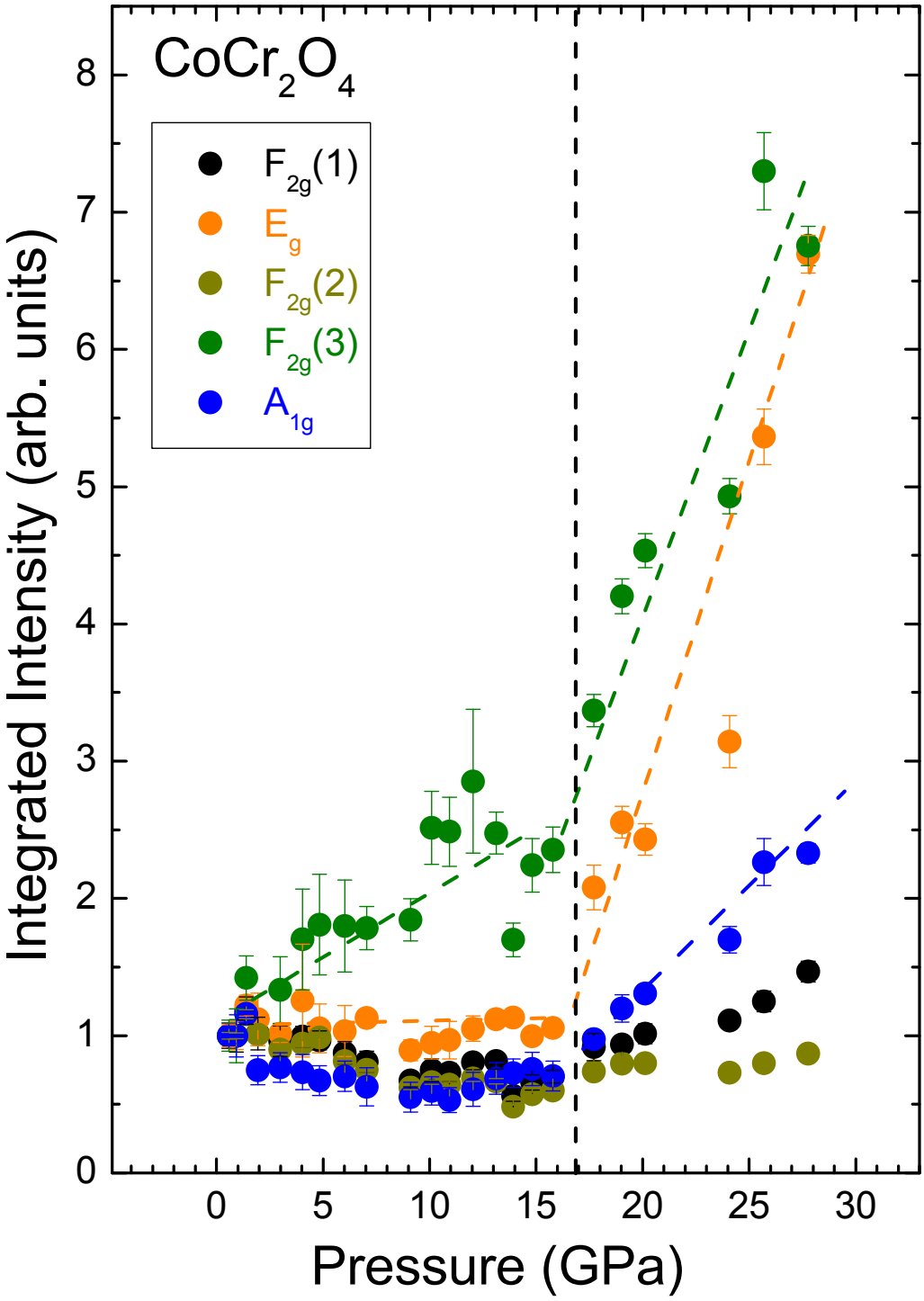


**FIG S3**: Integrated intensities for all of the observed Raman-active modes as a function of pressure. The vertical dashed line marks the onset of the cubic-tetragonal transition.

**Table S4**: Construction parameters (lattice vectors and fractional coordinates) for the special quasi-random paramagnetic $CoCr_2O_4$ supercell. The first half of Co and Cr cations are set to spin-up, and the second half spin-down.

| Lattice vector (Å) | x | y | z |
|---|---|---|---|
| **a** | -6.0295128 | 0 | 8.5270194 |
| **b** | 6.0295128 | 0 | 8.5270194 |
| **c** | 0 | 6.0295128 | -8.5270194 |

| | Fractional coordinates | | | | Fractional coordinates | | |
|---|---|---|---|---|---|---|---|
| **Ion** | $\mathbf{u_1}$ | $\mathbf{u_2}$ | $\mathbf{u_3}$ | **Ion** | $\mathbf{u_1}$ | $\mathbf{u_2}$ | $\mathbf{u_3}$ |
| Co | 0.875554 | 0.875722 | 0.501083 | O | 0.330552 | 0.830808 | 0.27383 |
| Co | 0.125579 | 0.625537 | 0.001117 | O | 0.830985 | 0.330766 | 0.274063 |
| Co | 0.250916 | 0.750671 | 0.502005 | O | 0.306792 | 0.306417 | 0.227742 |
| Co | 0.000864 | 0.000857 | 0.001472 | O | 0.806197 | 0.806594 | 0.227529 |
| Co | 0.375384 | 0.375415 | 0.501102 | O | 0.942313 | 0.670085 | 0.498696 |
| Co | 0.625897 | 0.125731 | 0.001094 | O | 0.442466 | 0.169813 | 0.49861 |
| Co | 0.750643 | 0.250614 | 0.5012 | O | 0.919871 | 0.692478 | -0.001364 |
| Co | 0.500687 | 0.500985 | 0.002139 | O | 0.420125 | 0.192364 | -0.001275 |
| Cr | 0.31349 | 0.063618 | 0.501779 | O | 0.567988 | 0.56813 | 0.27411 |
| Cr | 0.812463 | 0.562347 | 0.500132 | O | 0.06842 | 0.068303 | 0.27397 |
| Cr | 0.935828 | 0.936853 | 0.248623 | O | 0.046348 | 0.546081 | 0.227744 |
| Cr | 0.436639 | 0.435499 | 0.248593 | O | 0.546007 | 0.046264 | 0.227705 |
| Cr | 0.937123 | 0.43704 | 0.248318 | O | 0.19223 | 0.419765 | -0.001621 |
| Cr | 0.437538 | 0.937725 | 0.248814 | O | 0.692693 | 0.920162 | -0.000976 |
| Cr | 0.562754 | 0.812829 | 0.500899 | O | 0.169711 | 0.442213 | 0.498351 |
| Cr | 0.063214 | 0.313128 | 0.500993 | O | 0.670114 | 0.942655 | 0.498986 |
| Cr | 0.18703 | 0.187148 | 0.748344 | O | 0.9315 | 0.203597 | -0.001691 |
| Cr | 0.687753 | 0.687577 | 0.748887 | O | 0.431013 | 0.703911 | -0.000951 |
| Cr | 0.813639 | 0.563484 | 0.001767 | O | 0.453916 | 0.681018 | 0.499065 |
| Cr | 0.312355 | 0.062511 | 0.000118 | O | 0.953577 | 0.181481 | 0.498305 |
| Cr | 0.68691 | 0.185819 | 0.748652 | O | 0.580789 | 0.580513 | 0.773826 |
| Cr | 0.185491 | 0.686694 | 0.748596 | O | 0.080733 | 0.080963 | 0.774066 |
| Cr | 0.063163 | 0.313226 | 0.000994 | O | 0.556627 | 0.056193 | 0.727512 |
| Cr | 0.562836 | 0.812727 | 0.000849 | O | 0.056434 | 0.556827 | 0.727744 |
| O | 0.181257 | 0.954006 | 0.499165 | O | 0.318123 | 0.818002 | 0.774076 |
| O | 0.681344 | 0.453403 | 0.498263 | O | 0.818315 | 0.3184 | 0.773981 |
| O | 0.703981 | 0.431256 | -0.000851 | O | 0.796312 | 0.796058 | 0.727788 |
| O | 0.203427 | 0.931366 | -0.001751 | O | 0.296091 | 0.296351 | 0.727784 |

**Table S5**: Summations of the Heisenberg model[9] employed for the determination of the magnetic exchange parameters $J_{AA}$, $J_{AB}$, and $J_{BB}$ in $CoCr_2O_4$.

| | Co-Co | Co-Cr | Cr-Cr |
|---|---|---|---|
| Ferromagnetic | 8 | 24 | 24 |
| Néel-type ferrimagnetic | 8 | -24 | 24 |
| Ferrimagnetic in Cr | 8 | 0 | -8 |
| Ferrimagnetic in Co | -8 | 0 | 24 |

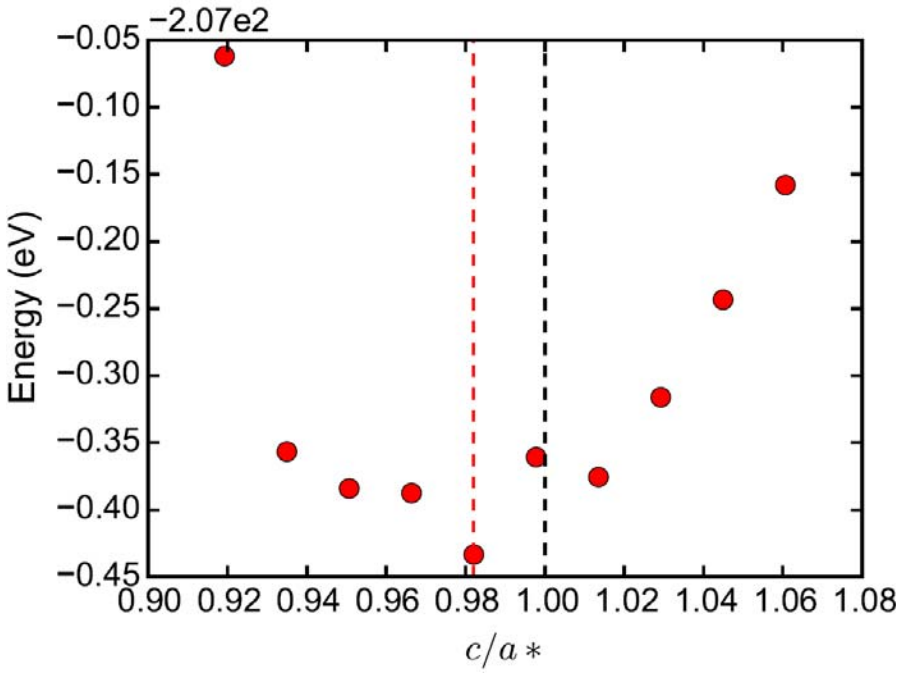


**FIG S4**: The ferrimagnetic energy surface against the axial ratio $c/a^*$ at 26 GPa. The energy surface minimum is achieved at $c/a^*$=0.98.

**Table S6**: Extracted ionic charge transfer from the Bader charge analysis of the paramagnetic cubic and ferrimagnetic tetragonal phases of $CoCr_2O_4$ at various pressures. Notice that the pressure-induced changes of the ionic charge is not much different between the two phases.

| | **Atomic Species** | $q_{trans}$ (C) | | |
|---|---|---|---|---|
| | | 0 GPa | 10 GPa | 30 GPa |
| **Paramagnetic cubic** | Co | -1.277 | -1.271 | -1.255 |
| | Cr | -1.777 | -1.768 | -1.751 |
| | O | 1.208 | 1.202 | 1.190 |
| **Ferrimagnetic tetragonal** | Co | -1.284 | -1.275 | -1.262 |
| | Cr | -1.775 | -1.770 | -1.754 |
| | O | 1.209 | 1.204 | 1.192 |

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