MnCoO

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1 Co_3O_4 and Mn_3O_4

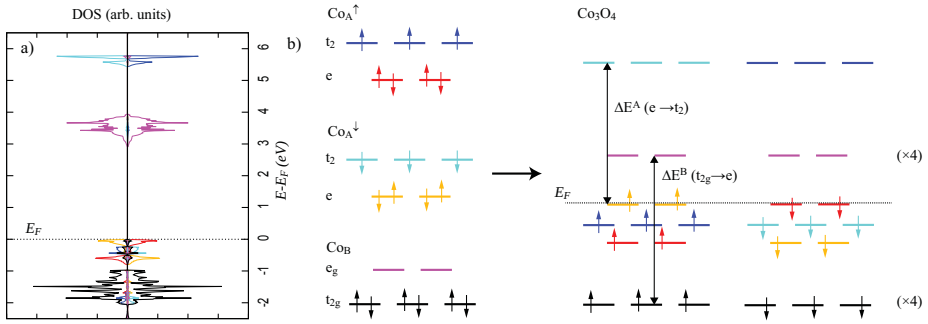

Figure 1S: a) Spin-resolved Co-d contribution to the DOS of Co_3O_4, b) schematic representation of the electron distribution in the d orbitals.

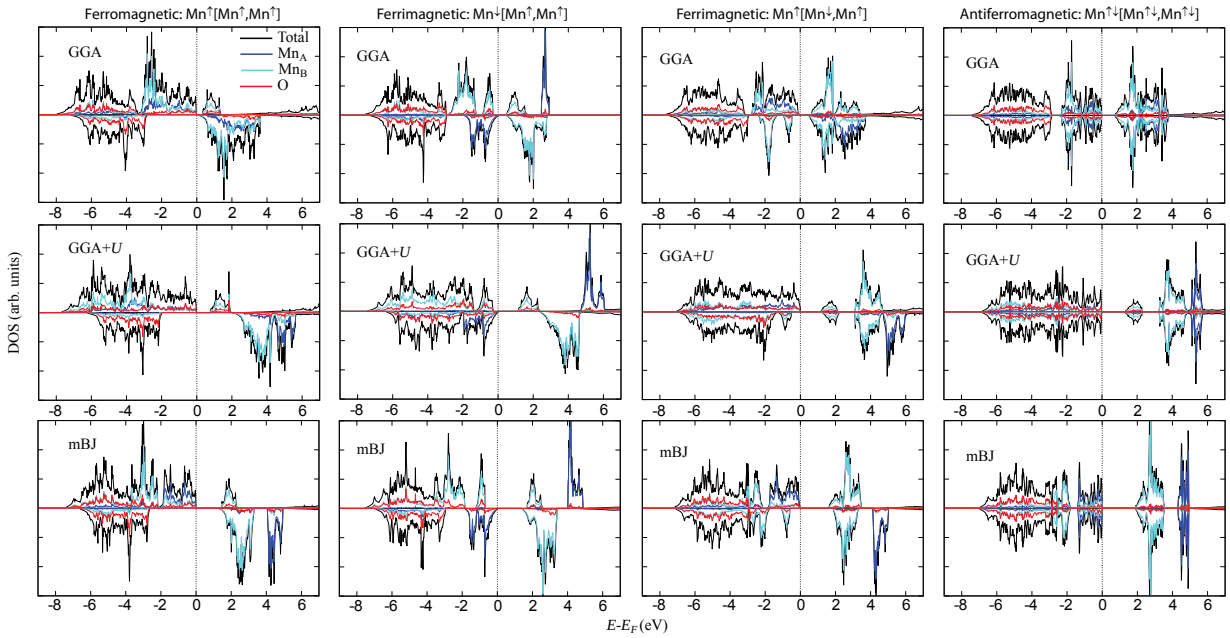

Figure 2S: Spin-resolved DOS for Mn_3O_4 calculated with the 3 approximations and for 3 different magnetic ordering.

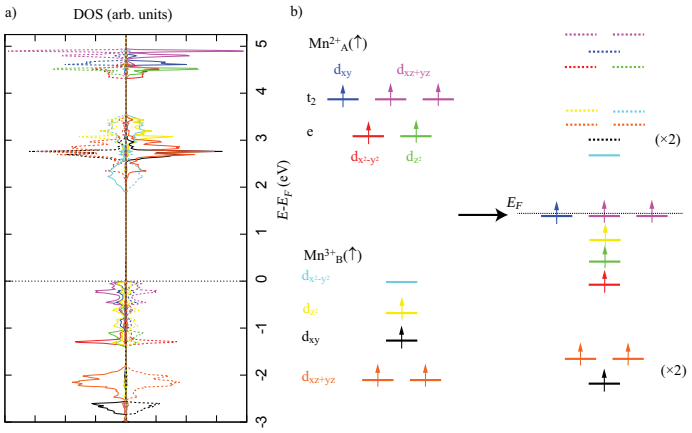

Figure 3S: a) Spin-resolved Mn-d contribution to the DOS of Mn_3O_4, b) schematic representation of the electron distribution in the d orbitals for one spin direction.

2 $Mn_xCo_{3-x}O_4$

2.1 Atomic structure

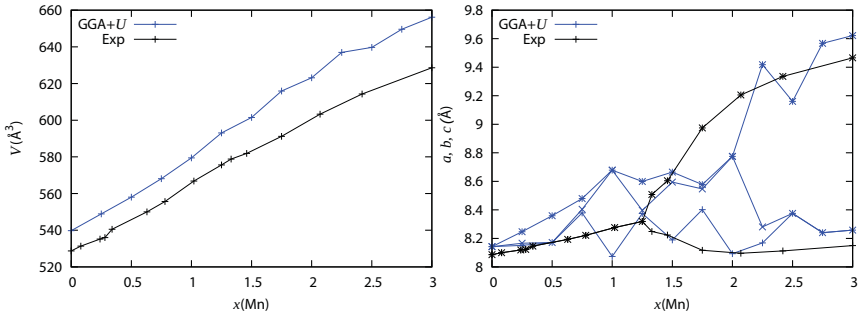

Figure 4S: Comparison of the volume and lattice parameters of $Mn_xCo_{3-x}O_4$ calculated with the GGA+U method with the experimental measurements.

The GGA calculations may be inadequate to describe correctly the atomic structure of these compounds. It seemed however to be the most reliable solution owing to the problem of computational times and the difficulty to choose a good U_{eff} parameter. We indeed performed a calculations with the GGA+U method, and found a more complex phase diagram than in GGA, with 3 different orthorhombic structures:

- with $a \sim b < c$ for $0 < x \leq 0.75$,
- with $a < b \sim c$ for $0.75 < x \leq 2.0$,
- with $a \sim b < c$ for $0 < x \leq 0.75$.

The small difference between a, b, and c can be due to the cation distribution, as we suggested it for the GGA calculations. In that case, the effect is much more noticeable. The lattice parameters are in general more sensitive to the cation distribution than with the GGA approximation. Moreover, instead of an underestimation of the volume, the GGA+U method overestimates it.

However, it is difficult to distinguish, with this method, if the difference found with the measurements are only artefactual, due to a spurious cationic ordering coming from the

supercell description of the lattice, or if the lattice really adopt an orthorhombic shape (more probable here), with $a \neq b \neq c$. Also not discussed, but the angles can also slightly vary from the ideal 90Âř value (less than 1Âř). The GGA+U calculations is not supported by our experimental measurements, but it can be consistent with the orthorhombic phase reported in some studies[1,2] and calculations performed by other authors on manganites.[3]

2.2 Electronic structure

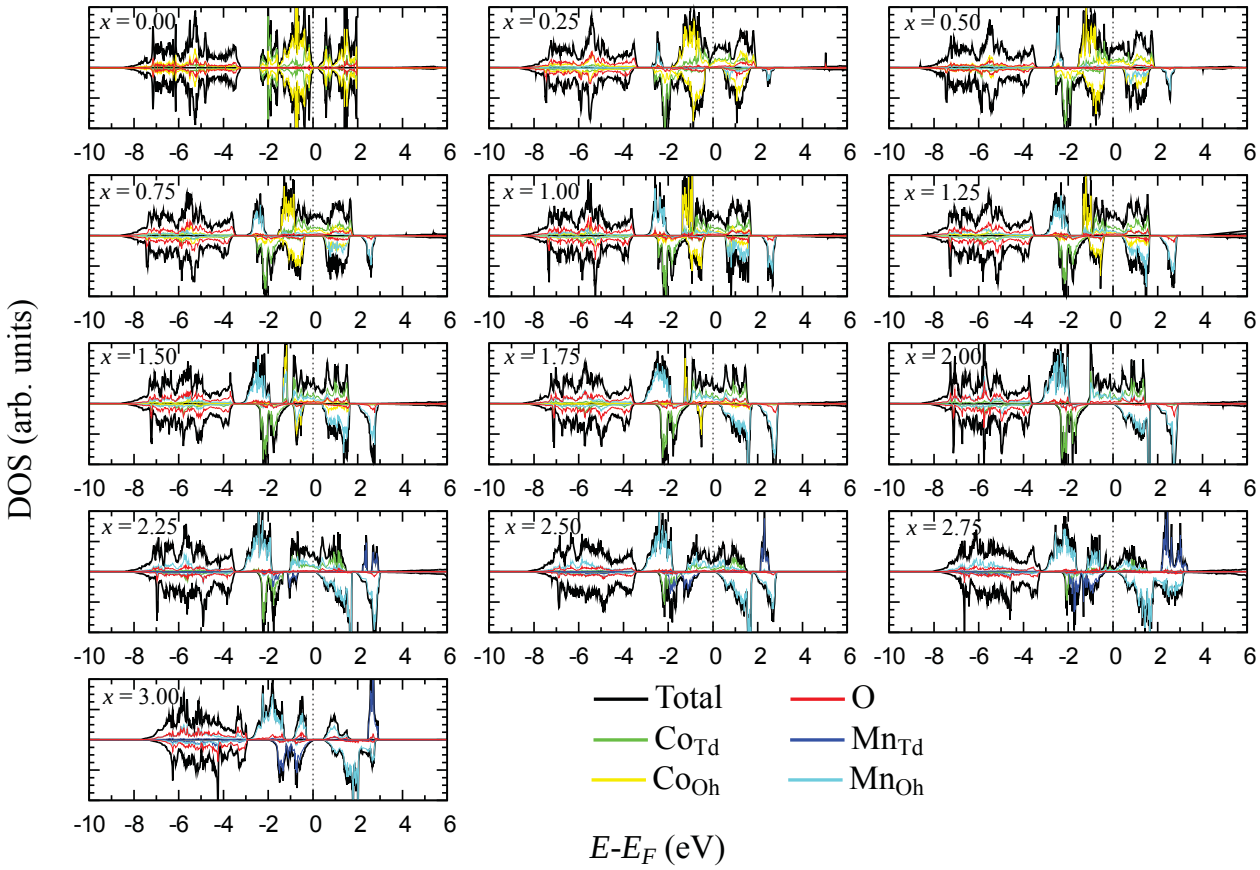

Figure 5S: Spin-resolved DOS for $Mn_xCo_{3-x}O_4$ ($0 \leq x \leq 3$) calculated with the GGA approximation.

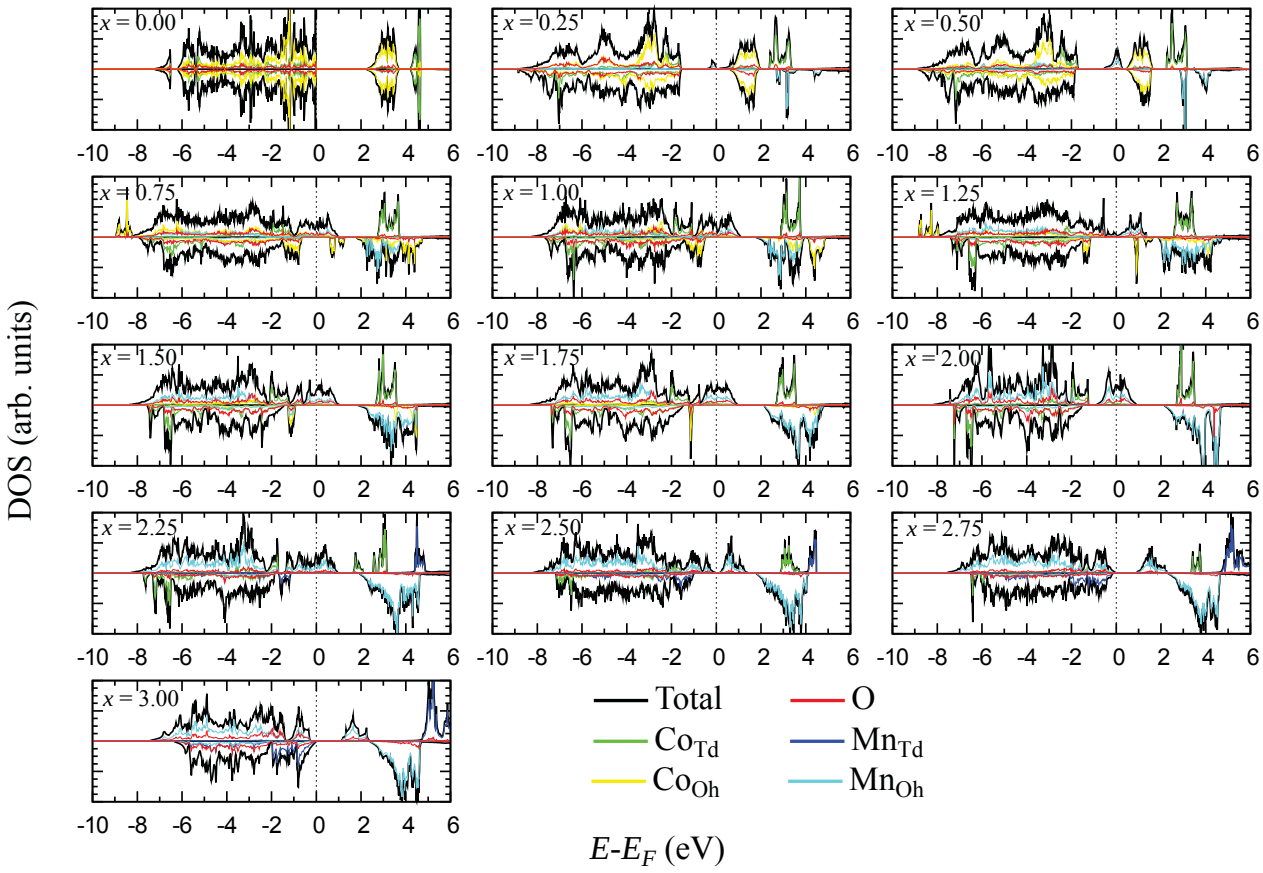

Figure 6S: Spin-resolved DOS for $Mn_xCo_{3-x}O_4$ ($0 \leq x \leq 3$) calculated with the GGA+U approximation.

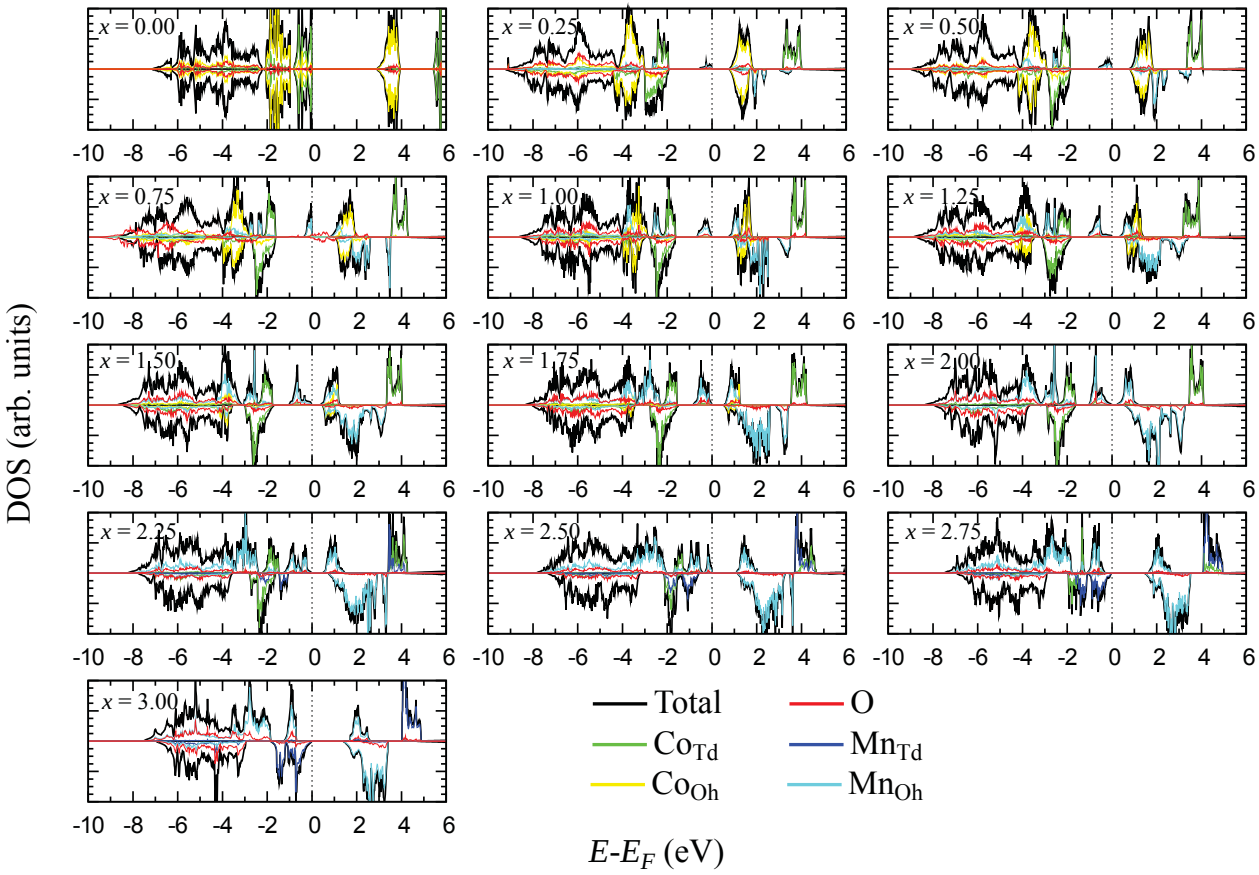

Figure 7S: Spin-resolved DOS for $Mn_xCo_{3-x}O_4$ ($0 \leq x \leq 3$) calculated with the mBJ approximation.

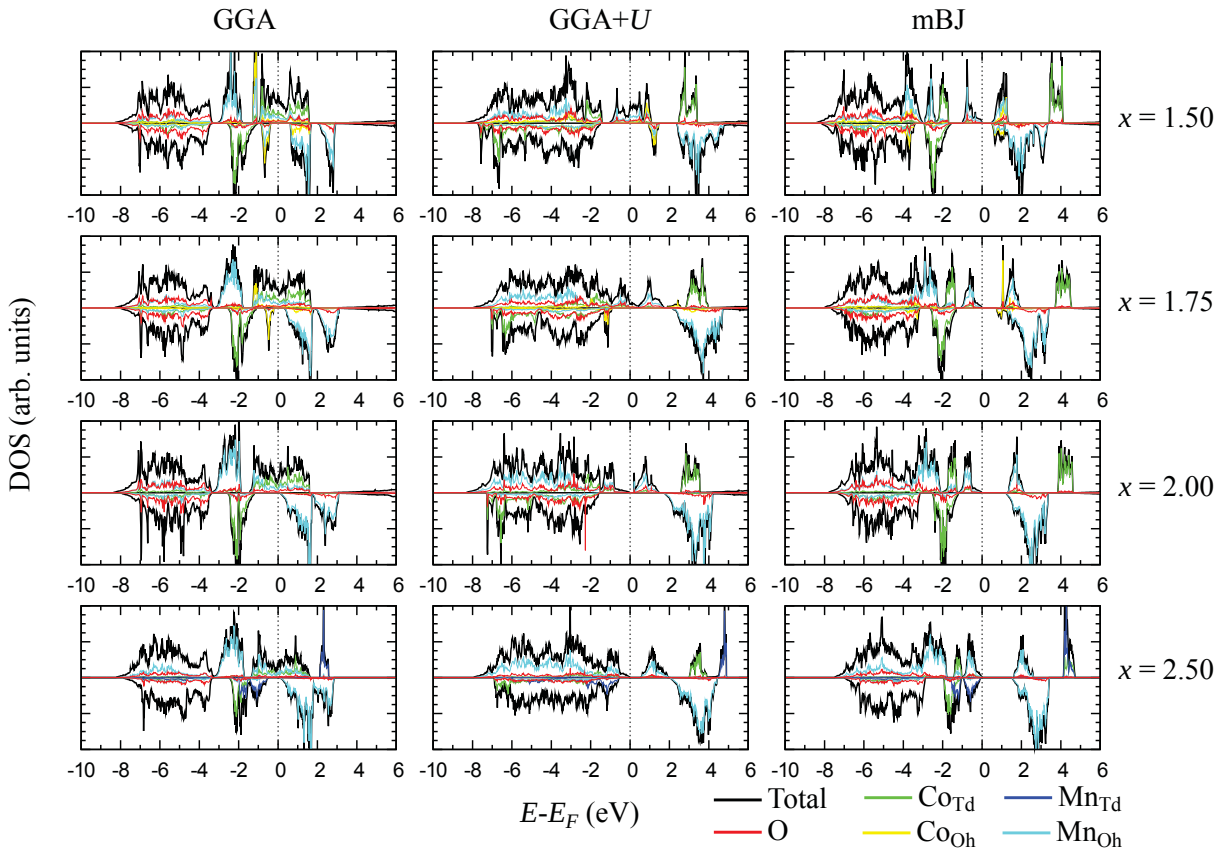

Figure 8S: Spin-resolved DOS for $Mn_xCo_{3-x}O_4$ ($1.5 \leq x \leq 2.5$) calculated with the experimental lattice parameters.

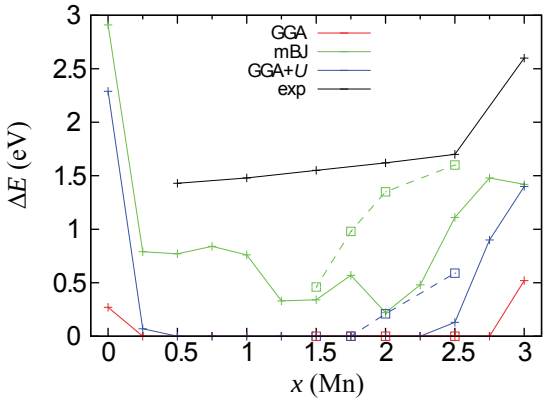

Figure 9S: Band gap energy as a function of x. Solide lines with + symbols corresponds to values obtained with the calculated lattice parameters, while dashed lines with □ symbols are the values calculated with the experimental lattice parameters.

Acknowledgement

This work was granted access to the HPC resources of CALMIP supercomputing center under the allocation p1313 (2014-2016).

References

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(2) Kemei, M. C.; Harada, J. K.; Seshadri, R.; Suchomel, M. R. *Phys. Rev. B* **2014**, *90*, 064418.

(3) Singh, G.; Gupta, S.; Prasad, R.; Auluck, S.; Gupta, R.; Sil, A. *Journal of Physics and Chemistry of Solids* **2009**, *70*, 1200.