AB INITIO DENSITY FUNCITONAL CALCULATIONS OF MAGNETIC SUPERSTRUCTURES

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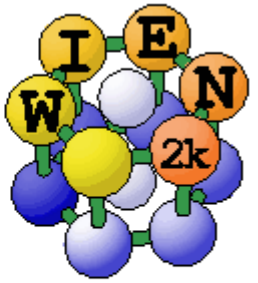
WIEN2k



P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka and J. Luitz

Inst. f. Materials Chemistry, TU Vienna

The program package WIEN2k allows to perform electronic structure calculations of solids using density functional theory (DFT). It is based on the full-potential (linearized) augmented plane-wave ((L)APW) + local orbitals (lo) method, one among the most accurate schemes for band structure calculations. In DFT the local (spin) density approximation (LDA) or the improved version of the generalized gradient approximation (GGA) can be used. WIEN2k is an all-electron scheme including relativistic effects and has many features.

www.wien2k.at

The basic concepts of the density functional theory

LSDA – local spin density approximation is an efficient and accurate scheme for solving the many-electron problem of a crystal within density functional theory.

Kohn W. and Sham L.J. 1965 Phys. Rev. 140, A1133

$$H\Psi = E\Psi$$

1. **Non-interacting electrons are in an "external" potential** V_{xc}^{σ}
2. **Nuclei at fixed positions**
3. $\rho_\sigma(r)$ **- the spin densities are the key quantities**

$$E_{tot}(\rho_\uparrow, \rho_\downarrow) = T_s(\rho_\uparrow, \rho_\downarrow) + E_{ee}(\rho_\uparrow, \rho_\downarrow) + E_{Ne}(\rho_\uparrow, \rho_\downarrow) + E_{xc}(\rho_\uparrow, \rho_\downarrow) + E_{NN} \quad (1)$$

The exact many-particle hamiltonian for this system is:

$$\hat{H} = -\frac{\hbar^2}{2}\sum_i \frac{\nabla^2_{\vec{R}_i}}{M_i} - \frac{\hbar^2}{2}\sum_i \frac{\nabla^2_{\vec{r}_i}}{m_e} - \frac{1}{4\pi\epsilon_0}\sum_{i,j}\frac{e^2 Z_i}{|\vec{R}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0}\sum_{i\neq j}\frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} \quad (1.1)$$

$$\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3\ldots\vec{r}_N)\rightarrow\rho(\vec{r})\qquad \rho=\frac{\#electrons}{V}\qquad \rho(\vec{r})=N\int\ldots\int\Psi^*(\vec{r},\vec{r}_2,\vec{r}_3\ldots\vec{r}_N)\Psi(\vec{r},\vec{r}_2,\vec{r}_3\ldots\vec{r}_N)d\vec{r}_2\ldots d\vec{r}_N.$$

To minimize E_{tot} in accordance with variational principle it is necessary introduce orbitals χ^{σ}_{ik} constrained to construct the spin densities as

$$\rho_\sigma(r)=\sum_{i,k}\rho^{\sigma}_{ik}|\chi^{\sigma}_{ik}(r)|^2 \qquad (2)$$

ρ^{σ}_{ik} are occupation numbers such that $0\le\rho^{\sigma}_{ik}\le 1/w_k$

w_k is the symmetry-required weight of point *k*

Two approximations comprise the LSDA:

i) the assumption that E_{xc} can be written in terms of a local exchange-correlation energy density μ_{xc} times the total (spin-up plus spin-down) electron density

$$E_{xc}=\int\mu_{xc}(\rho_\uparrow,\rho_\downarrow)*[\rho_\uparrow+\rho\downarrow]dr \qquad (3)$$

ii) the particular form chosen for that μ_{xc}.

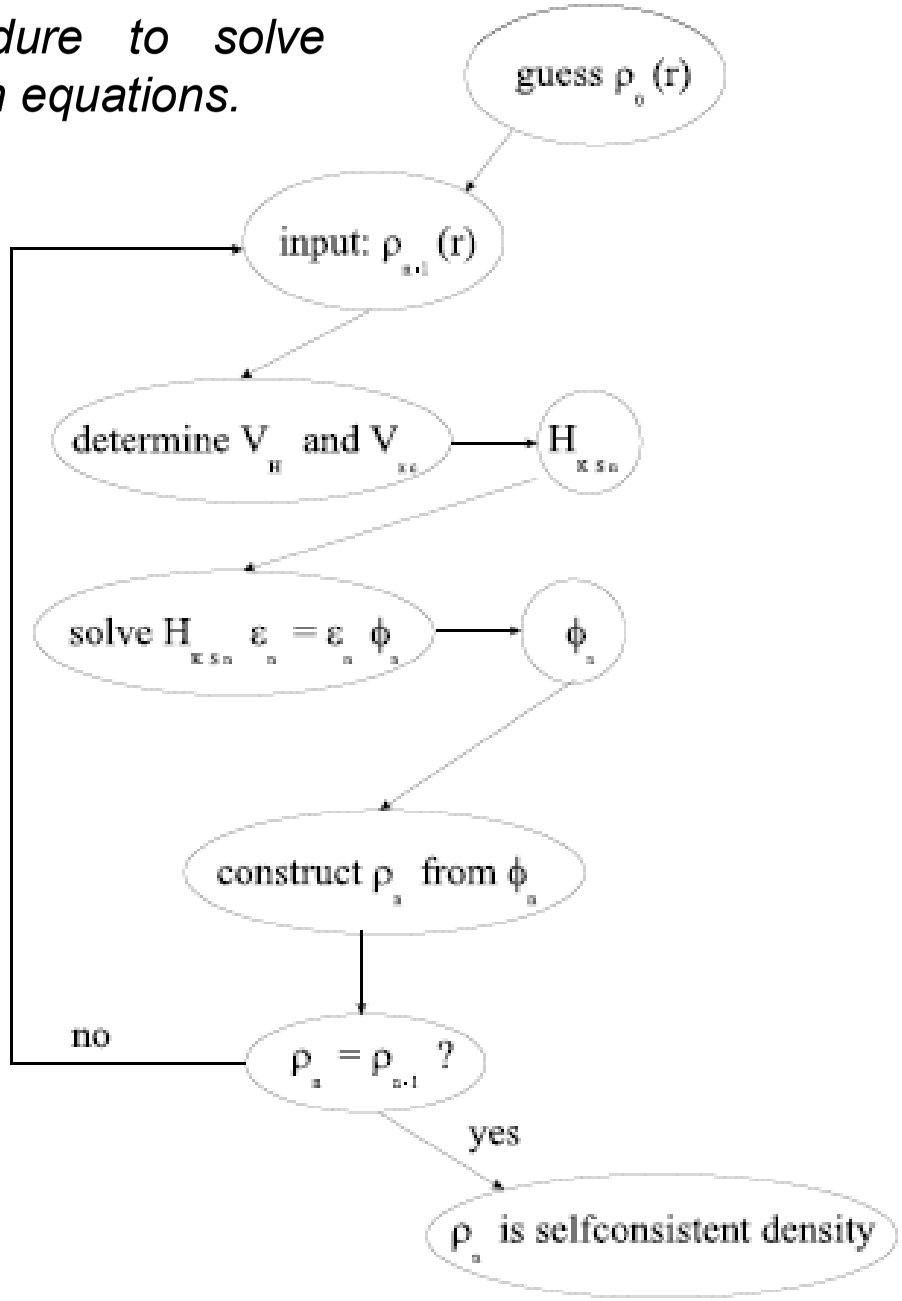
The accurate fit to the Monte-Carlo simulations has used in WIEN2k package. Perdew J.P, at. al. 1992 Phys.Rev.B46, 6671

The variation of E_{tot} gives the Kohn-Sham (KS) equations

$$[-\nabla^2 + V_{Ne} + V_{ee} + V_{xc}^{\sigma}]\chi_{ik}^{\sigma}(r) = \epsilon_{ik}^{\sigma}\chi_{ik}^{\sigma}(r) \quad (4)$$

This Kohn-Sham equations must be solved self-consistently in an iterative process, since finding the Kohn-Sham orbitals requires the knowledge of the potentials which themselves depend on the (spin-) density and thus on the orbitals again.

The selfconsistent procedure to solve Hartree-Fock or Kohn-Sham equations.

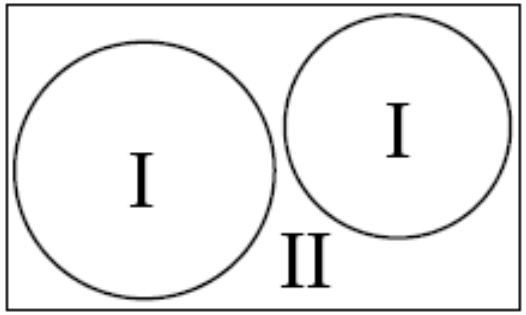


The LAPW method

The linearized augmented plane wave (LAPW from Slater's APW) is based on the DFT for the treatment of exchange and correlation. The LAPW method is a procedure for solving the KS equations for many-electron system (crystal)

- **Local spin density approximation (LSDA)**
- **Generalized gradient approximation (GGA)**
- **Relativistic effects (scalar relativistic treatment)**
- **Spin-orbit coupling**
- **Core states are treated fully relativistically**
- **Electron density in the ground state**
- **Total energy**
- **KS-eigenvalues (energy bands)**
- **Basis set**

The basis set is especially adapted to the problem.



This adaptation is achieved by dividing the unit cell into

(I) non-overlapping atomic spheres (centered at the atomic sites)

(II) an interstitial region.

In the two types of regions different basis sets are used:

(I) inside atomic sphere

(II) in the interstitial region

(I) inside atomic sphere

a linear combination of radial functions times spherical harmonics $Y_{lm}(r)$ is used

$$\phi_{\mathbf{k}_n} = \sum_{lm} [A_{lm,\mathbf{k}_n} u_l(r, E_l) + B_{lm,\mathbf{k}_n} \dot{u}_l(r, E_l)] Y_{lm}(\hat{\mathbf{r}}) \quad (5)$$

$u_l(r, E_l)$ is the regular solution of the radial Schrodinger equation E_l and the spherical part of the potential inside sphere

$\dot{u}_l(r, E_l)$ is the energy derivative of u_l evaluated at the same energy E_l.

u_l and $\dot{u}_l$ are obtained by numerical integration of the radial Schrodinger equation on a radial mesh inside the sphere. A linear combination of these two functions constitute the linearization of the radial function

The coefficients A_{lm} and B_{lm} are functions of k_n determined by requiring that this basis function matches (in value and slope) each plane wave (PW) the corresponding basis function of the interstitial region.

(II) in the interstitial region

a plane wave expansion is used

$$\phi_{\mathbf{k}_n} = \frac{1}{\sqrt{\omega}} e^{i\mathbf{k}_n \cdot \mathbf{r}} \qquad (6)$$

$$\mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$$

$\mathbf{K}_n$ are the reciprocal lattice vectors

$\mathbf{k}$ is the wave vector inside the first Brillouin zone.

Each plane wave is augmented by an atomic-like function in every atomic sphere.

The solutions to the Kohn-Sham equations are expanded in this combined basis set of LAPW's according to the linear variation method

$$\psi_{\mathbf{k}} = \sum_n c_n \phi_{\mathbf{k}_n} \tag{7}$$

c_n are the coefficients determined by the Rayleigh-Ritz variational principle.

Local Orbitals (LO)

additional k_n-independent basis functions can be added to improve the linearization (i.e. to increase the flexibility of the basis) and to make possible a consistent treatment of semicore and valence states in one energy window (to ensure orthogonality).

$$\phi_{lm}^{LO} = [A_{lm} u_l(r, E_{1,l}) + B_{lm} \dot{u}_l(r, E_{1,l}) + C_{lm} u_l(r, E_{2,l})] Y_{lm}(\hat{r}) \tag{8}$$

General considerations

The LAPW method expands the potential (and charge densities analogously) in the following form

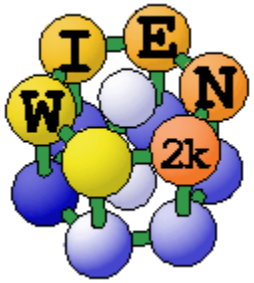
$$V(r) = \begin{cases} \sum_{lm} V_{lm}(r) Y_{lm}(\hat{r}) & \text{inside sphere} \\ \sum_{K} V_K e^{iKr} & \text{outside sphere} \end{cases} \qquad (9)$$

LAPW procedure frequently called the ``full-potential`` method because no shape approximations are made .

PROPERTIES:

- **The density of states (DOS) (modified tetrahedron method)**
- **X-ray absorption and emission spectra (Fermi's golden rule)**
- **X-ray structure factors (Fourier Transformation of the charge density)**
- **Optical properties (``Joint density of states'' modified with dipole matrix elements. A Kramers-Kronig transformation is also possible.**
- **An analysis of the electron density according to Bader's ``atoms in molecules'' theory can be made.**

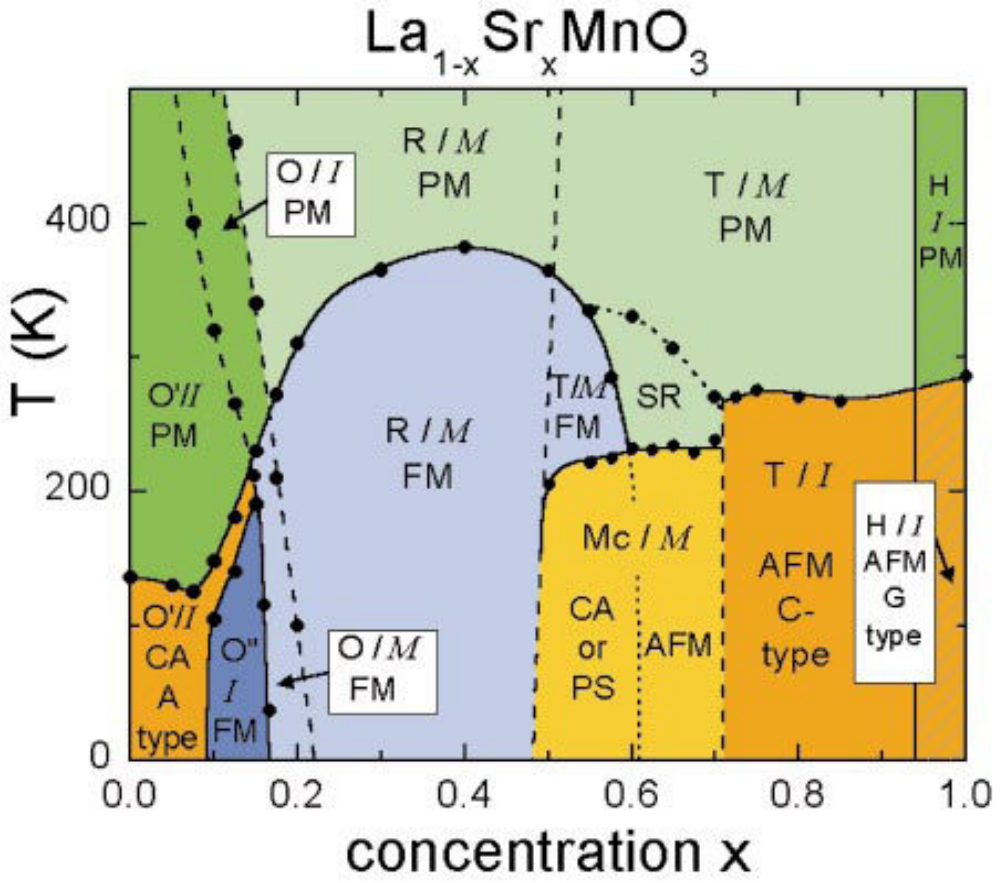
Calculated properties



- Energy bands and density of states,
- electron densities and spin densities, x-ray structure factors,
- Baders's "atoms-in-molecule" concept,
- total energy, forces, equilibrium geometries, structure optimization, molecular dynamics,
- Phonons, with an interface to K.Parlinski's PHONON program
- electric field gradients, isomer shifts, hyperfine fields,
- spin-polarization (ferro- or antiferromagnetic structures), spin-orbit coupling,
- x-ray emission and absorption spectra, electron energy loss spectra
- optical properties,
- fermi surfaces,
- LDA, GGA, meta-GGA, LDA+U, orbital polarization,
- centro- or non-centrosymmetric cells, all 230 spacegroups built in

Manganise oxides

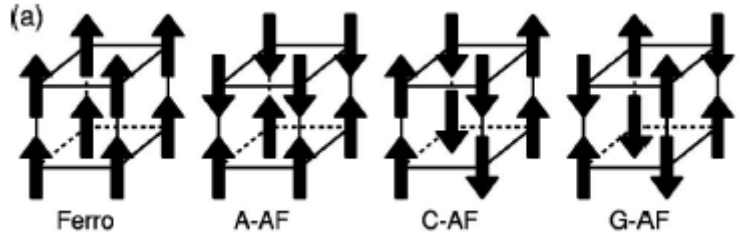
- **Manganise oxides $A_{1-x}B_x MnO_3$**
  (A rare-earth ions, B divalent ions) with perovskite structure
- **Very rich structure-property phase diagram**
  (a lot of phase transitions over x, field induced phase transitions)
- **Half-metallic behavior**
- **Magnetic semiconductors**
  (spintronics)

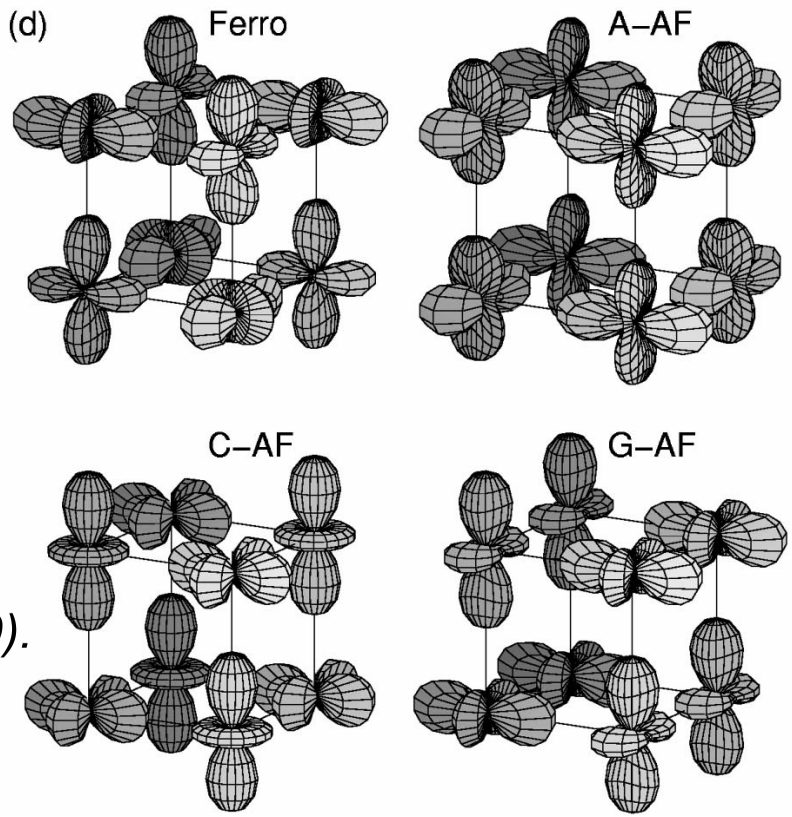


J. Hemberger, A. Krimmel et all, Phys. Rev. B ***66,*** *094410 (2002).*

Manganise oxides

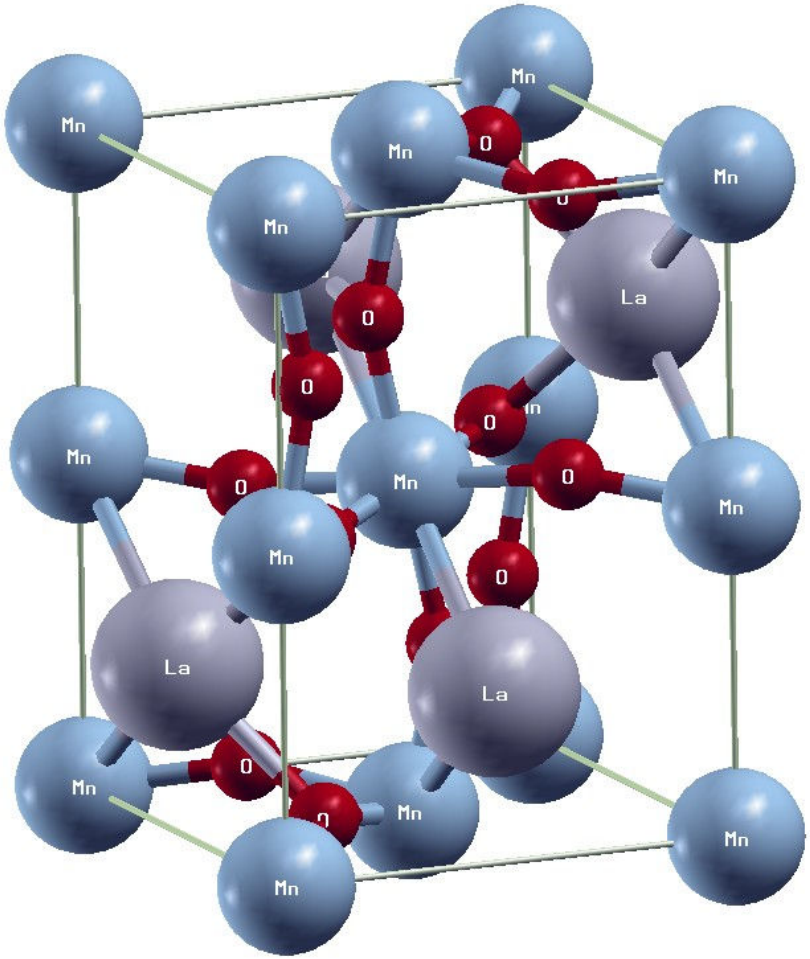
- **Giant magnetoresistance**
  (very large negative magnetoresistance – decreasing on some orders of value)
- **Giant volume magnetostriction effect**
- **Correlations between charge and magnetic ordering**
- **Magneto-optic Faraday effect**





T. Hotta et. al., Phys. Rev. B ***60,*** *15009 (1999).*

$LaMnO_3$ 62-Pnma orthorhombic structure



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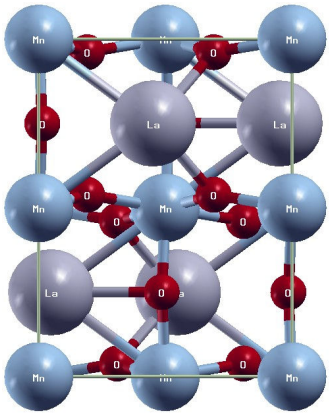

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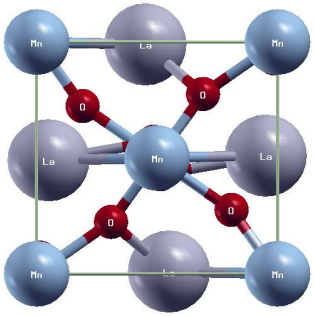

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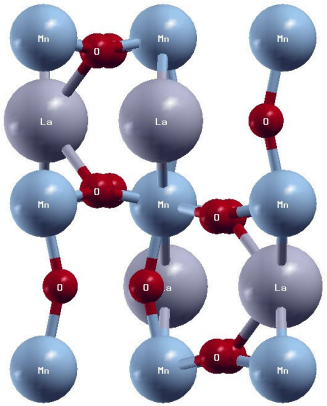


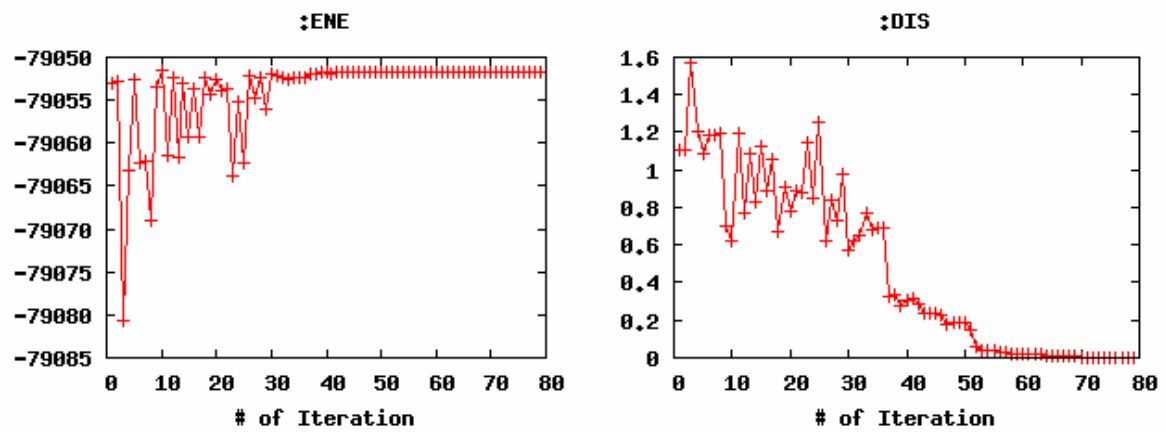
$_{57}$**La** $Xe5d6s^2$
$_{38}$**Sr** $Kr5s^2$
$_{25}$**Mn** $Ar3d^54s^2$
$_{8}$**O** $He2s^22p^4$

$LaMnO_3$

Nonequivalent atoms, $R_{mt}*K_{max}$=4, Max L=10, V_{nmt}=4, G_{max}=12
a=10.454, b=10.85, c=14.49 (bohr), Angles 90, Tot Number electrons per unit cell=262, Temp 0.005

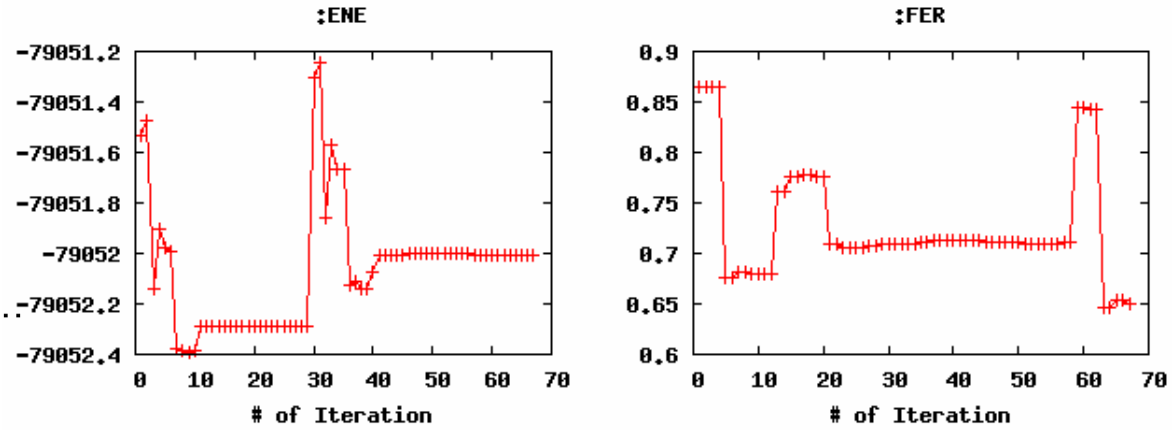
A-type antiferromagnet

Total Energy -79051.781922 Ry
Magnetic moment for Mn +(-)0.001
Interstitial magnetic moment 0.0000…
Total magnetic moment 0.00000…
Mn1 0, 0, 0 (up);
Mn2 0.5, 0.5, 0 (up);
Mn3 0, 0, 0.5 (dn);
Mn4 0.5, 0.5, 0.5 (dn).
AFM translation vector (0,0,0.5).



Ferromagnet

Total Energy -79052.003942 Ry
Total magnetic moment on
unit cell 15.93511
Interstitial magnetic moment 0.0000…
All atoms of Mn have spin up



Eigenvalues FM $LaMnO_3$

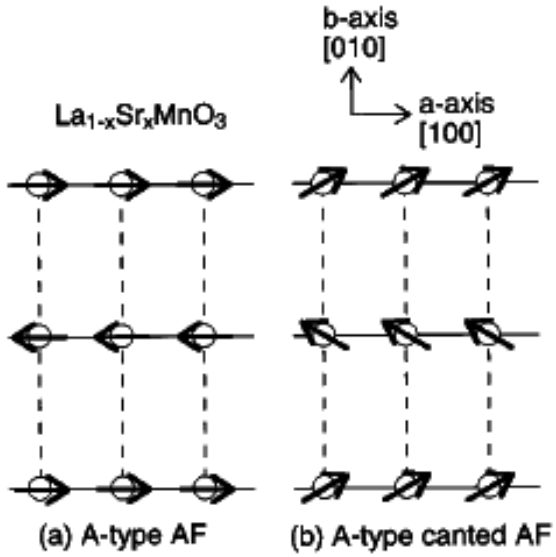
-5.4416173	-5.4414292	-5.4405377	-5.4391653	-3.1225084
-3.1206812	-3.1198857	-3.1171011	-3.1157927	-3.1144662
-3.1126133	-3.1087108	-3.1051687	-3.1012278	-3.1005985
-3.1004642	-1.7309450	-1.7253740	-1.7225515	-1.7185326
-0.8480429	-0.8185905	-0.8166376	-0.8036936	-0.8013134
-0.7761941	-0.7642879	-0.7608794	-0.7570046	-0.7551710
-0.7505847	-0.7436605	-0.5274214	-0.5239525	-0.5230813
-0.5190848	-0.5068669	-0.5023301	-0.4990767	-0.4947775
-0.4938860	-0.4600076	-0.4459121	-0.4435057	0.0737671
0.1122331	0.1261263	0.1684213	0.1781869	0.1906303
0.2036890	0.2231221	0.2270528	0.2472858	0.2529675
0.2548682	0.2593005	0.2641558	0.2683438	0.2721087
0.2874842	0.2976954	0.2984495	0.3028571	0.3218561
0.3474525	0.3726757	0.3851128	0.3912785	0.4011647
0.4166230	0.4259865	0.4303605	0.4345113	0.4419577
0.4426580	0.4498687	0.4712547	0.4777048	0.4867209
0.4896292	0.4979274	0.5188305	0.5199017	0.5423010
0.5505000	0.5539338	0.5777726	0.5780689	0.5947139
0.5963476	0.6216158	0.6366225	0.6510183	0.6586623
0.6953304	0.7116210	0.8360416	0.8852830	0.9059289

Spin up eigenvalues
96 levels till Fermi_En

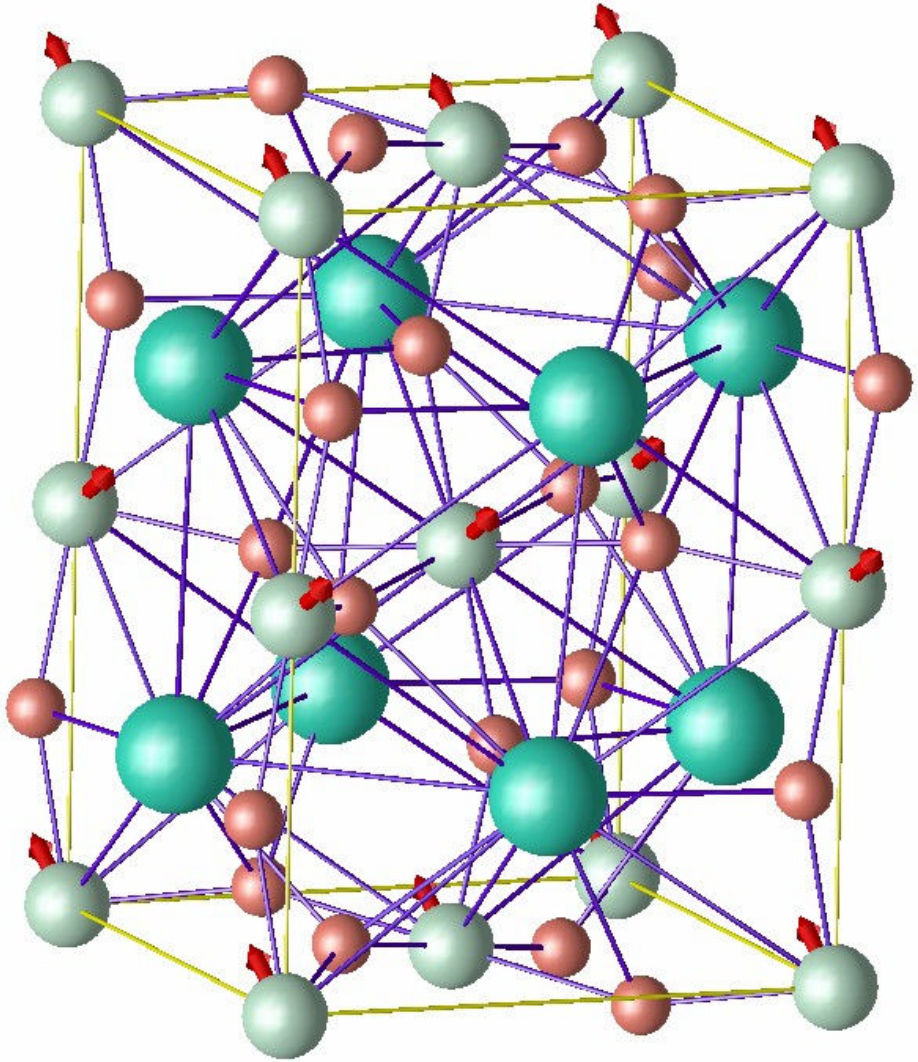
-5.1471806	-5.1468945	-5.1460184	-5.1447119	-2.8530340
-2.8520102	-2.8499407	-2.8472225	-2.8398241	-2.8324627
-2.8314742	-2.8265639	-2.7957210	-2.7904425	-2.7897570
-2.7894719	-1.7295814	-1.7240796	-1.7213022	-1.7173063
-0.8354591	-0.8053001	-0.8041667	-0.7926085	-0.7901285
-0.7648742	-0.7526091	-0.7484022	-0.7439943	-0.7428883
-0.7380413	-0.7301787	-0.5236563	-0.5212239	-0.5202364
-0.5166909	-0.5043266	-0.5005257	-0.4965775	-0.4915095
-0.4905313	-0.4561729	-0.4417674	-0.4390665	0.1088354
0.1620069	0.1674153	0.2193394	0.2339339	0.2432990
0.2466562	0.2622541	0.2646841	0.2750207	0.2764147
0.2897645	0.3019328	0.3032957	0.3125719	0.3164985
0.3293745	0.3340113	0.3403835	0.3506205	0.3559188
0.3726179	0.3898546	0.4068933	0.4159481	0.4398185
0.4437244	0.4507547	0.4526375	0.4532665	0.4554251
0.4709108	0.4749137	0.4957298	0.4974291	0.5071695
0.7121077	0.7317433	0.7361979	0.7451132	0.7757815
0.7822771	0.7962134	0.8030715	0.8125679	0.8212903
0.8251314	0.8548808	0.8700094	0.8742290	0.8852254

Spin down eigenvalues
80 levels till Fermi_En

Canted A-type antiferromagnetic $LaMnO_3$

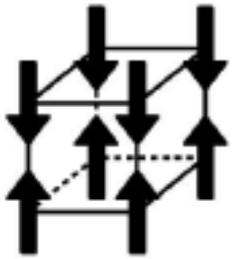


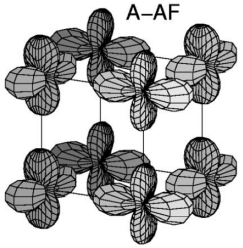
Schematic illustration of a layer-type antiferromagnetic structure. This structure is labeled as *A*-type after E.O. Wollan and W.C. Koehler, Phys. Rev. **100**, 545 (1955)



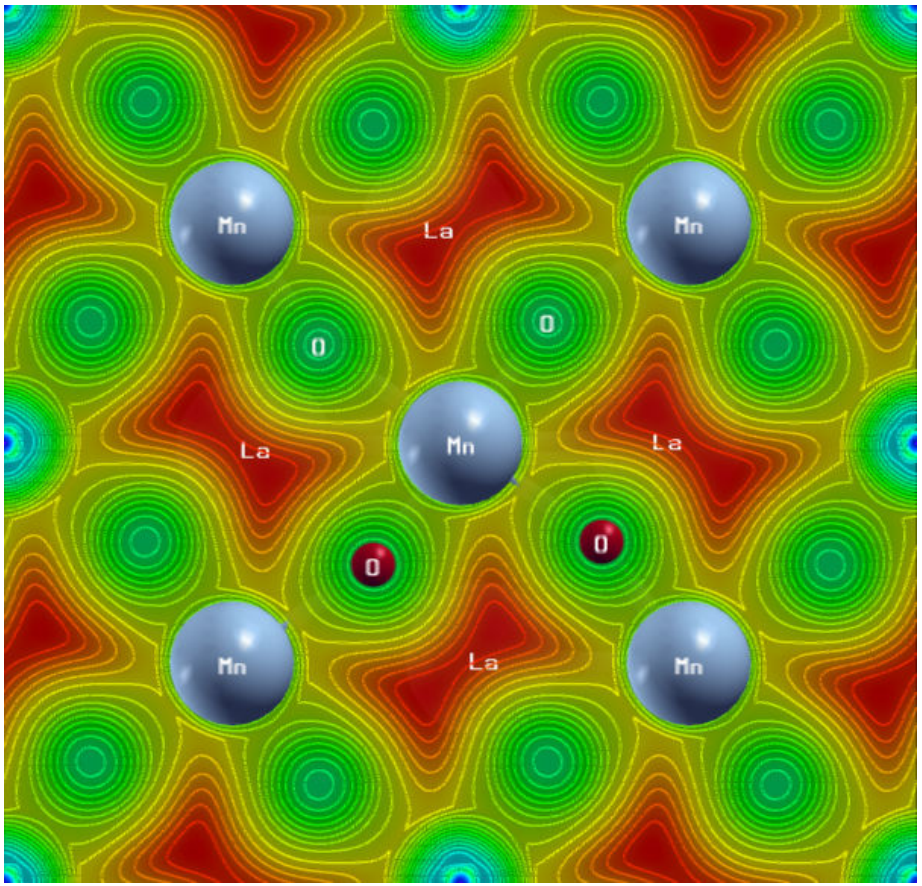
Electron density plots A-AFM $LaMnO_3$

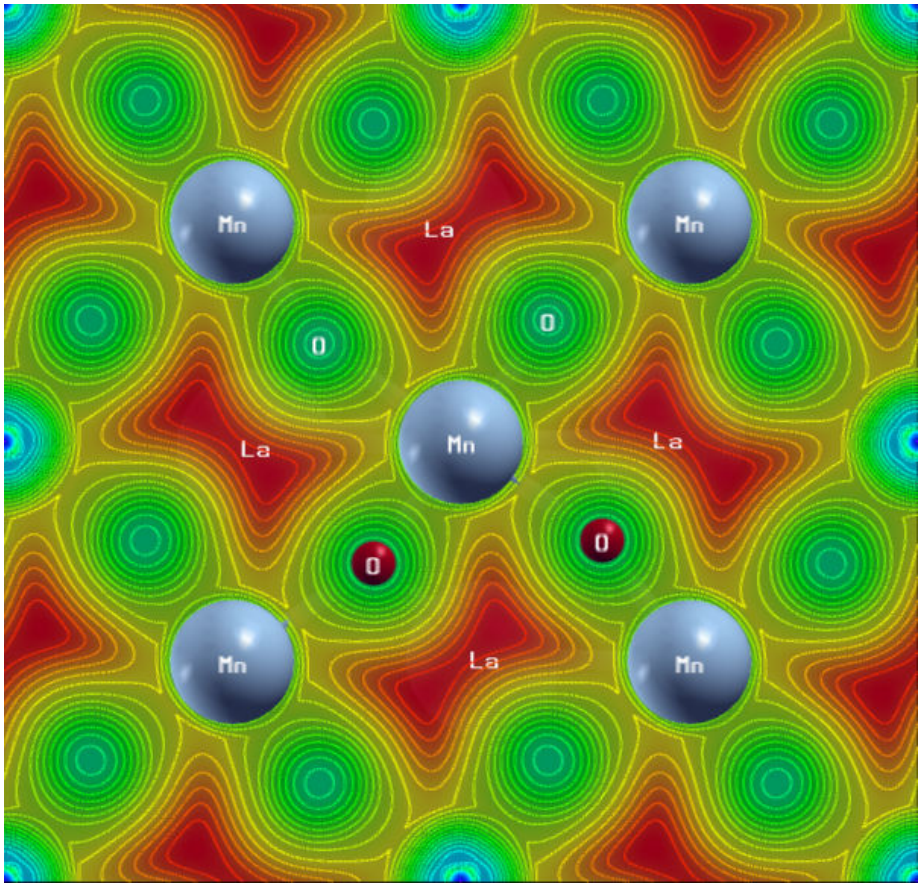
(001), spin up



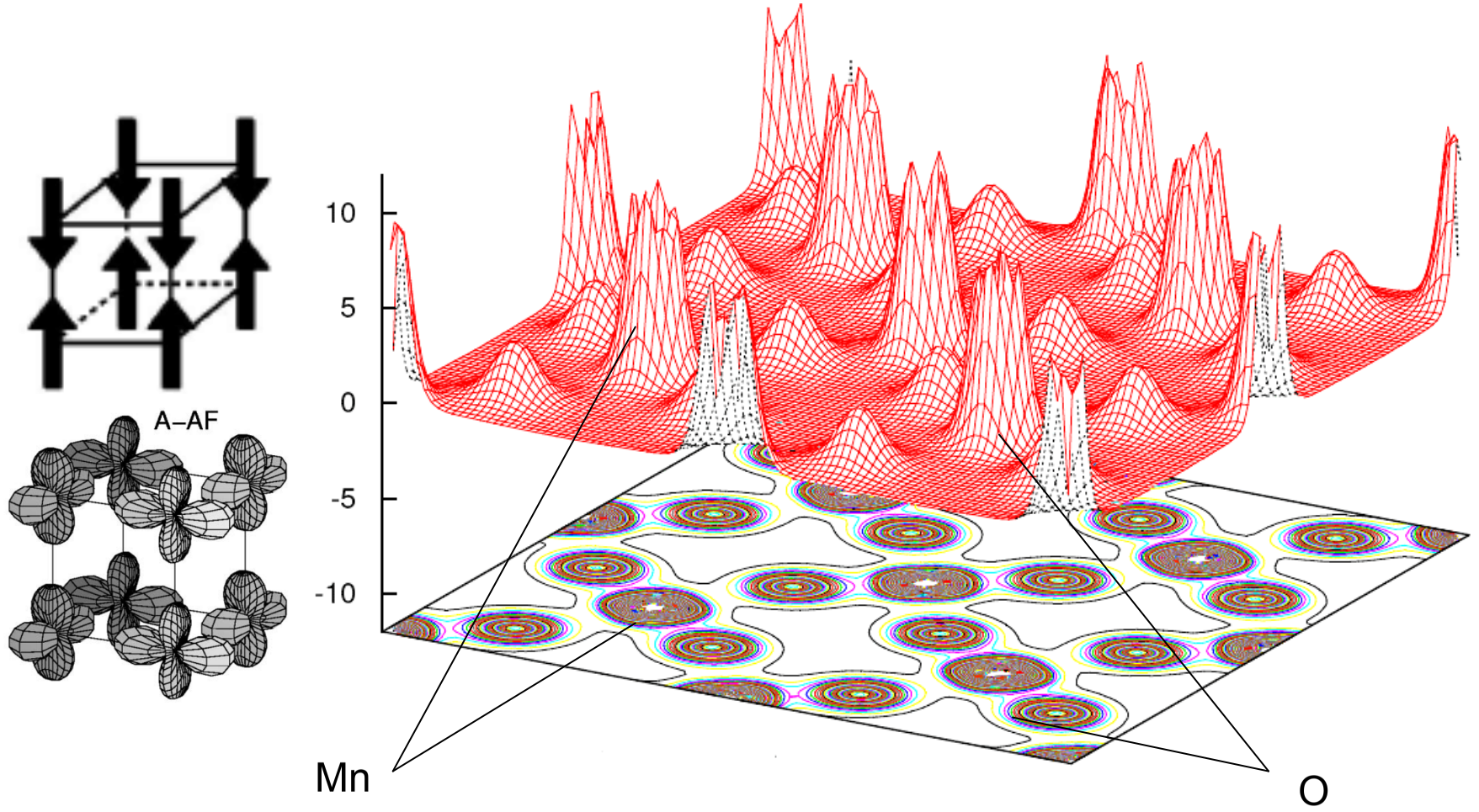


(001), spin down



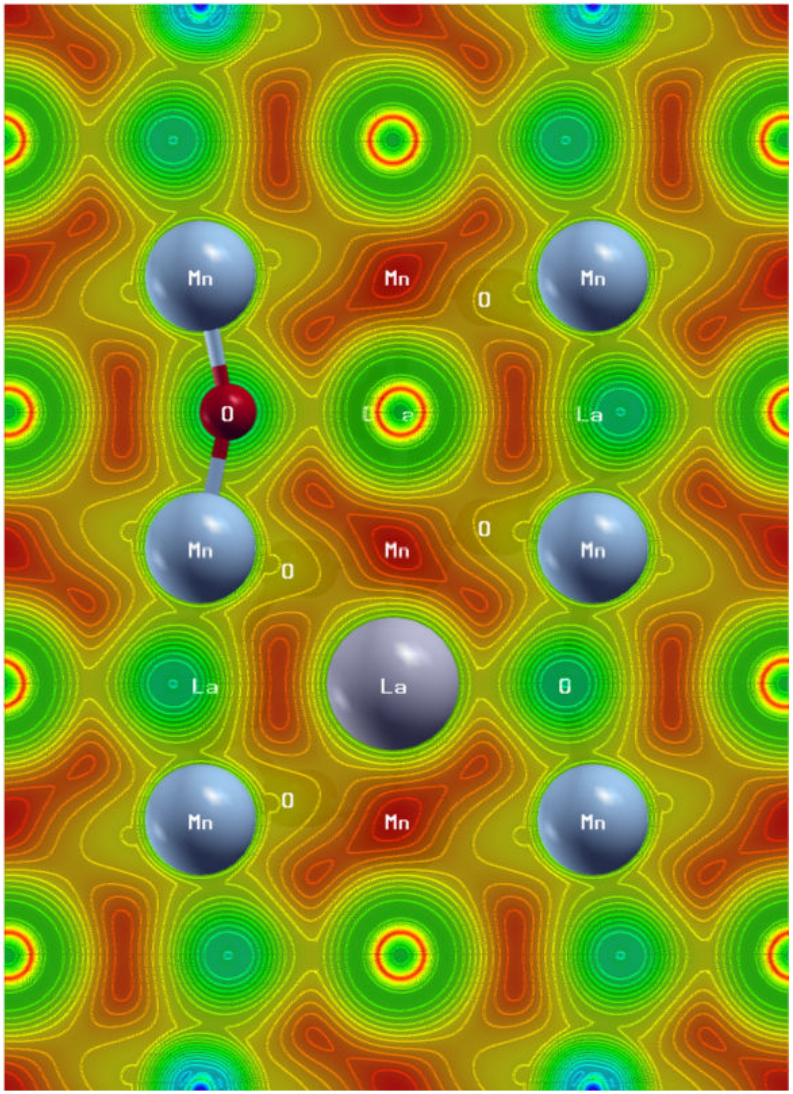


Charge density of A-AFM $LaMnO_3$

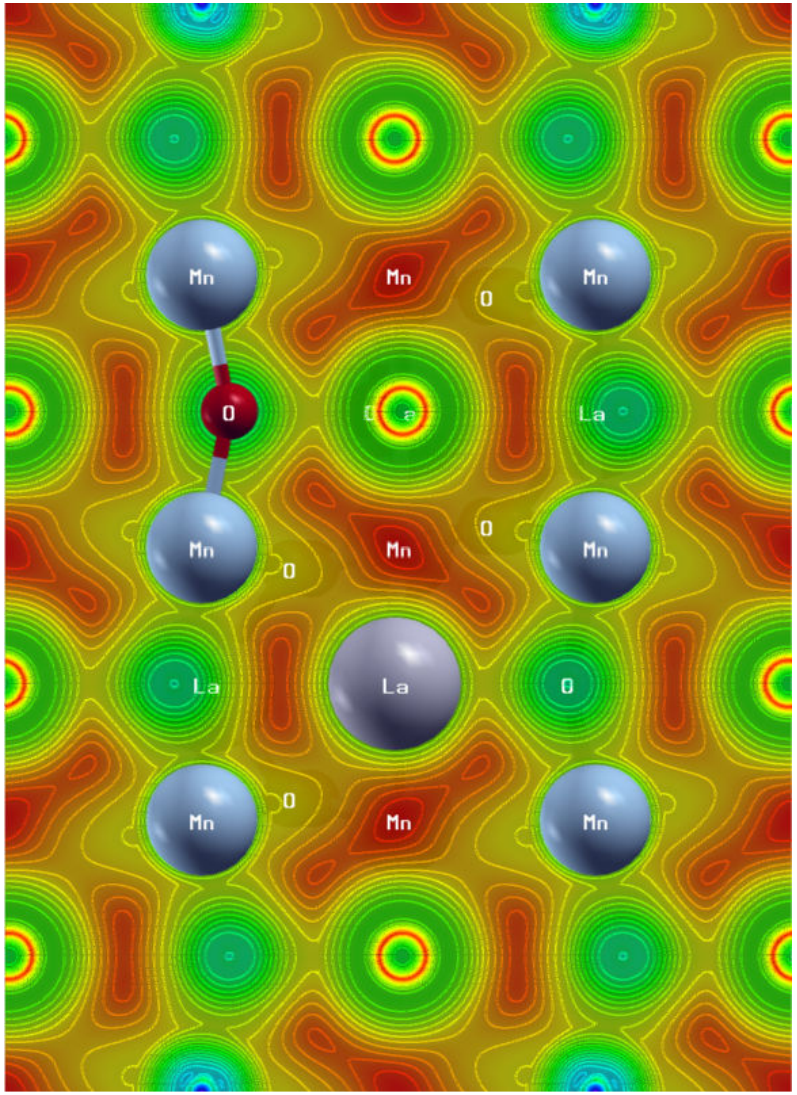


Electron density plots A-AFM $LaMnO_3$

(010), spin up

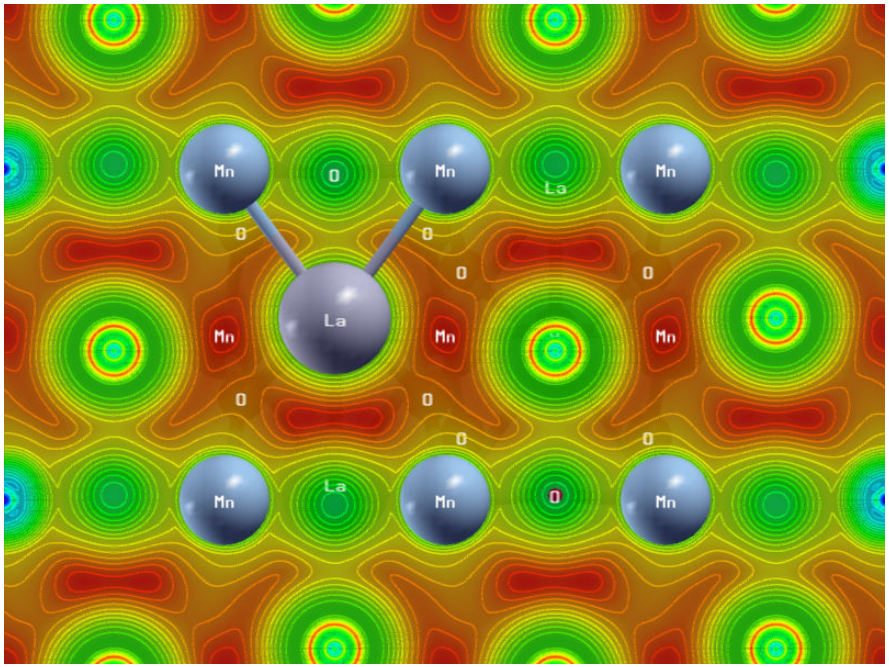


(010), spin down



Electron density plots A-AFM $LaMnO_3$

(100), spin up



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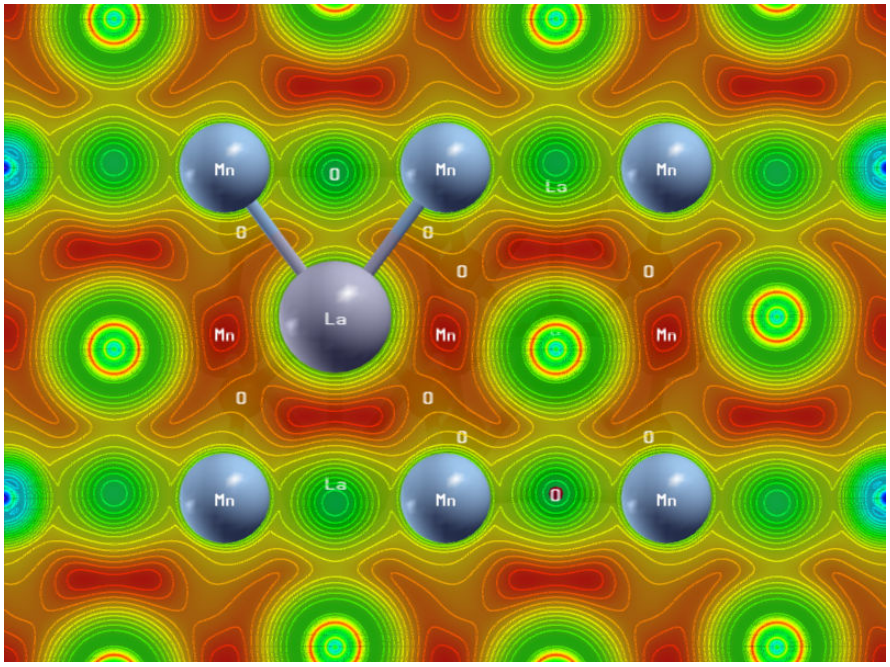
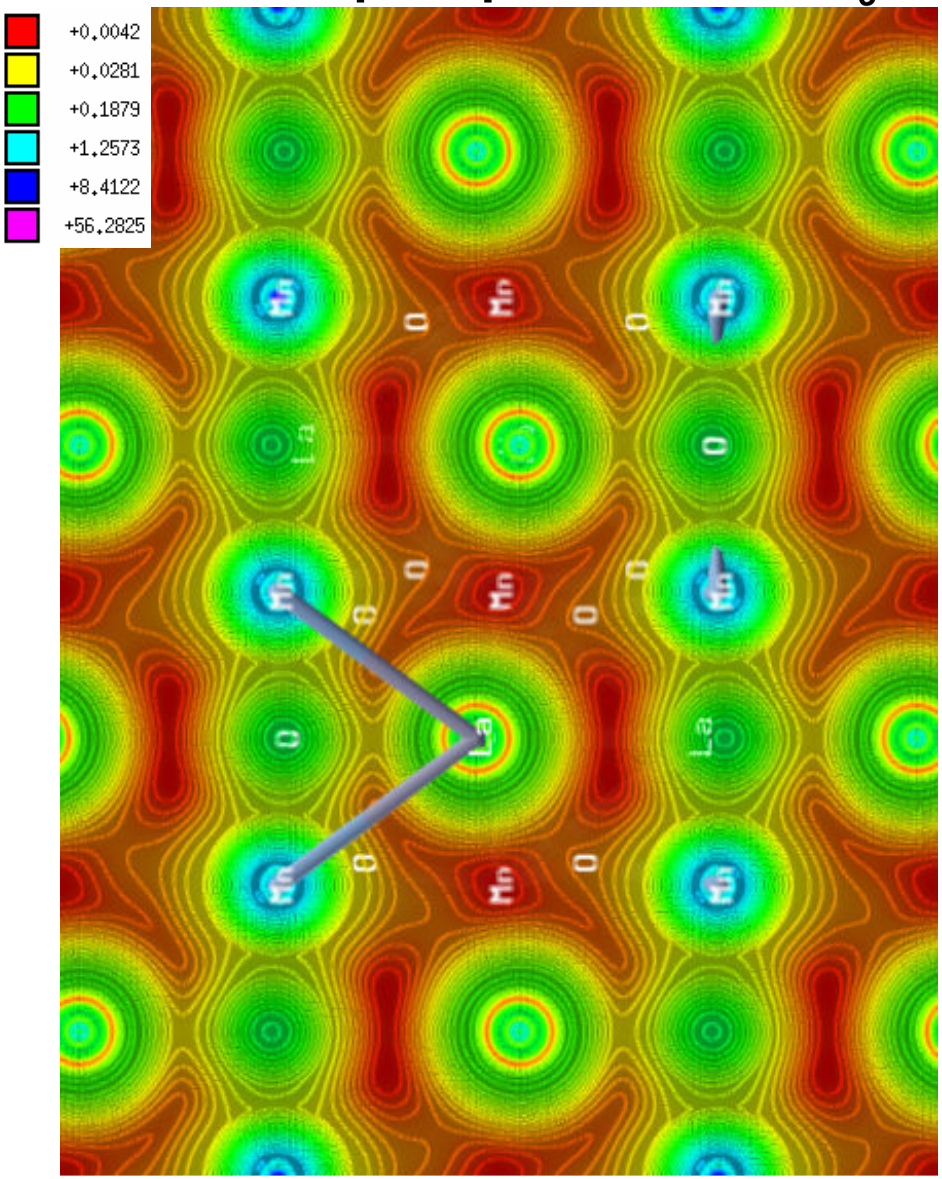
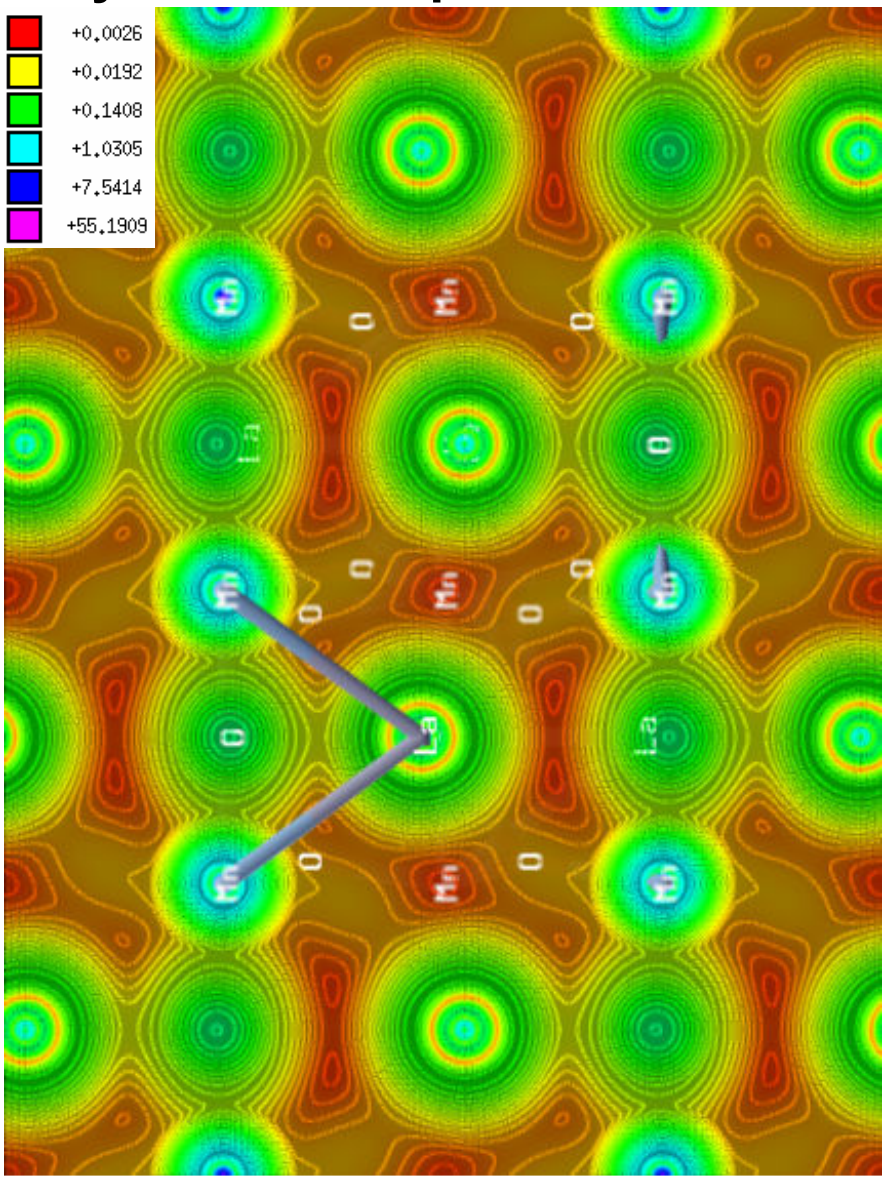


Electron density plots FM $LaMnO_3$ (100) plane

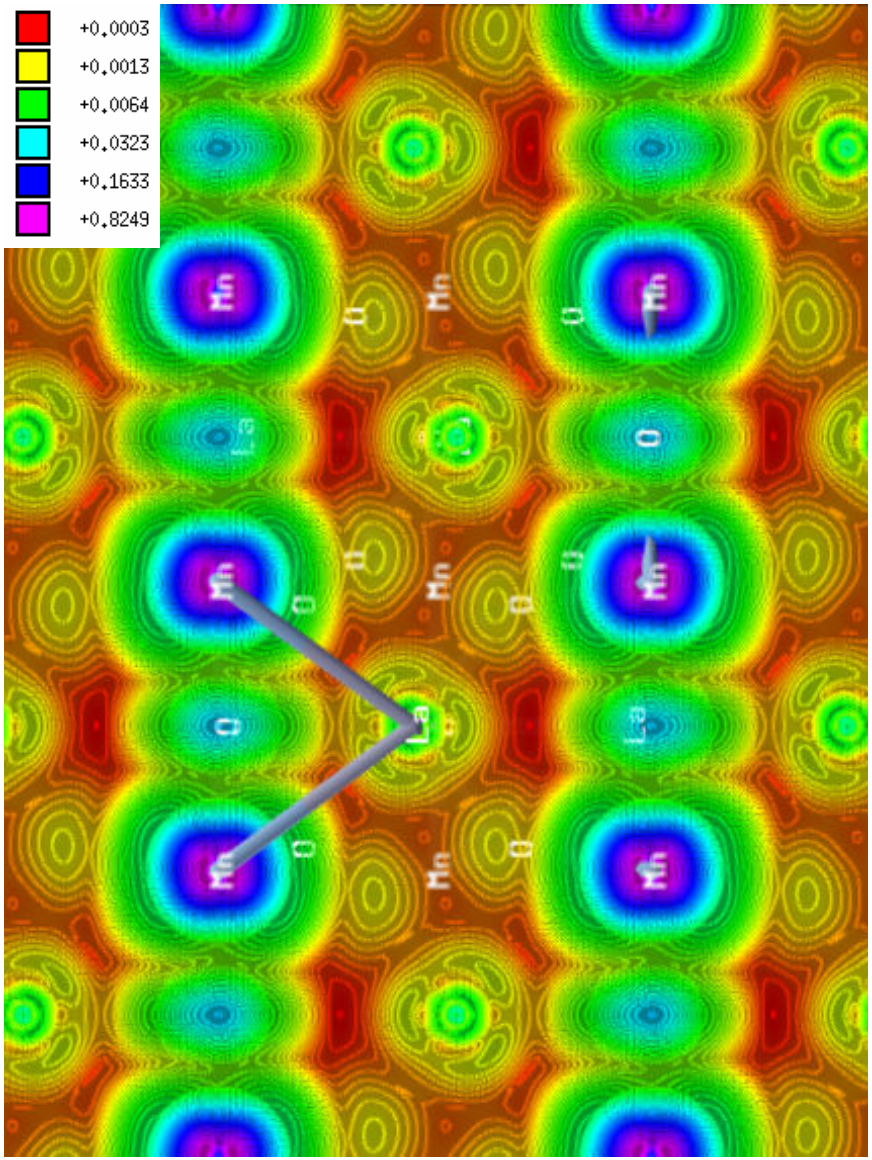
spin up E_c=0.48 Ry spin down

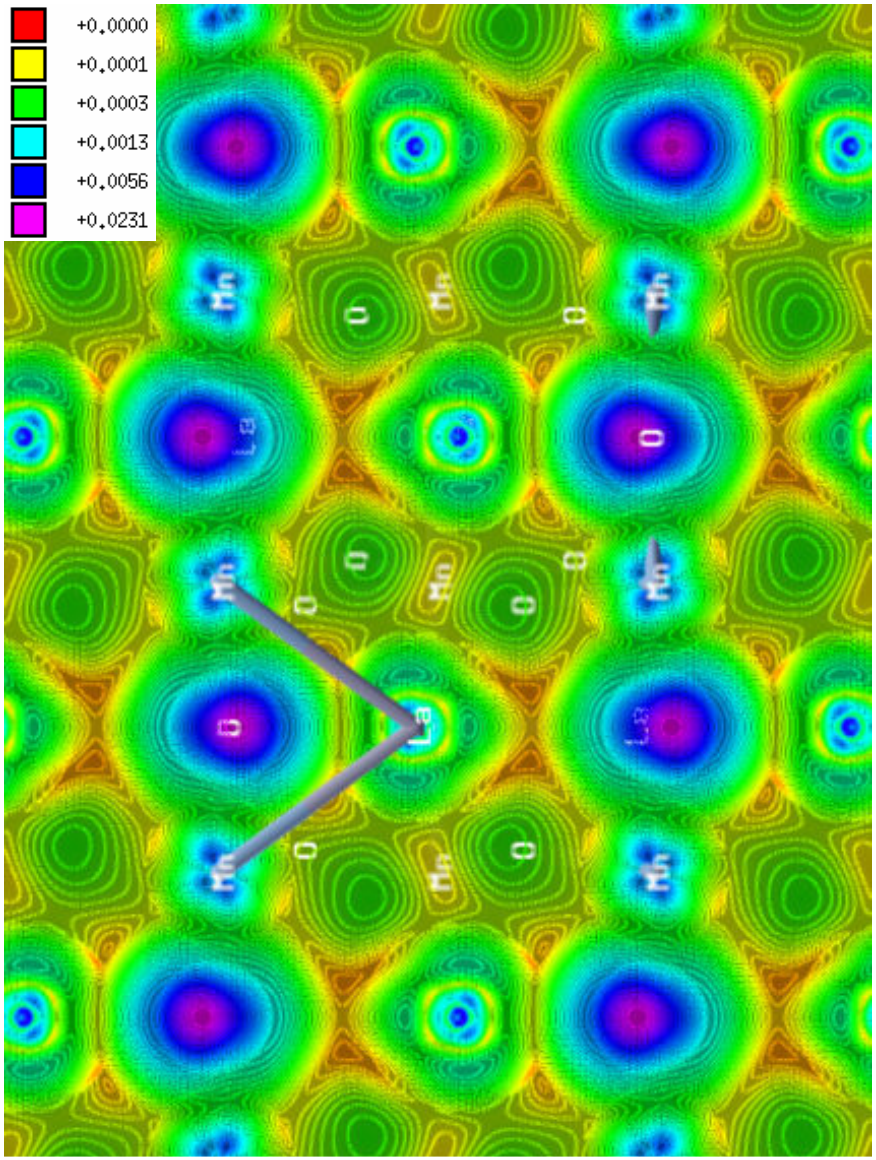




Electron density plots FM $LaMnO_3$ (100) plane

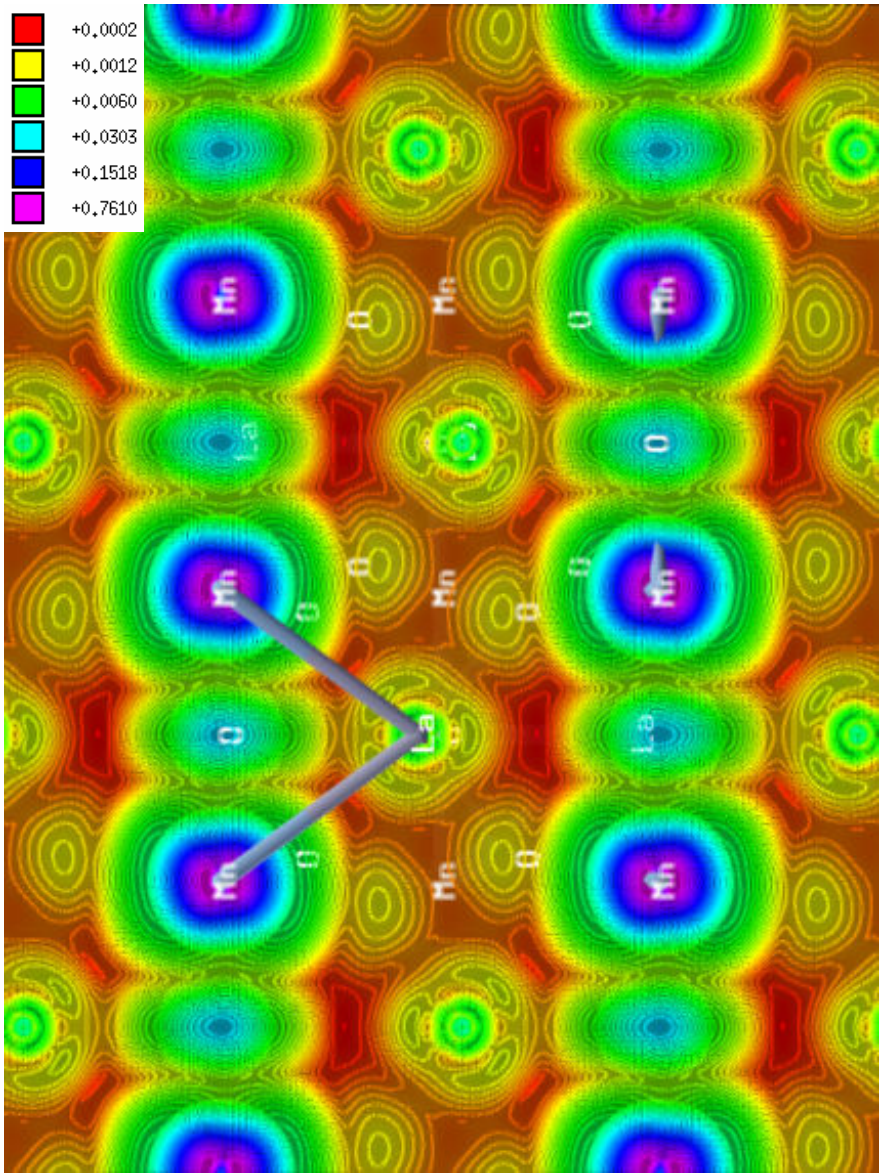
spin up E_c=0.48 Ry spin down

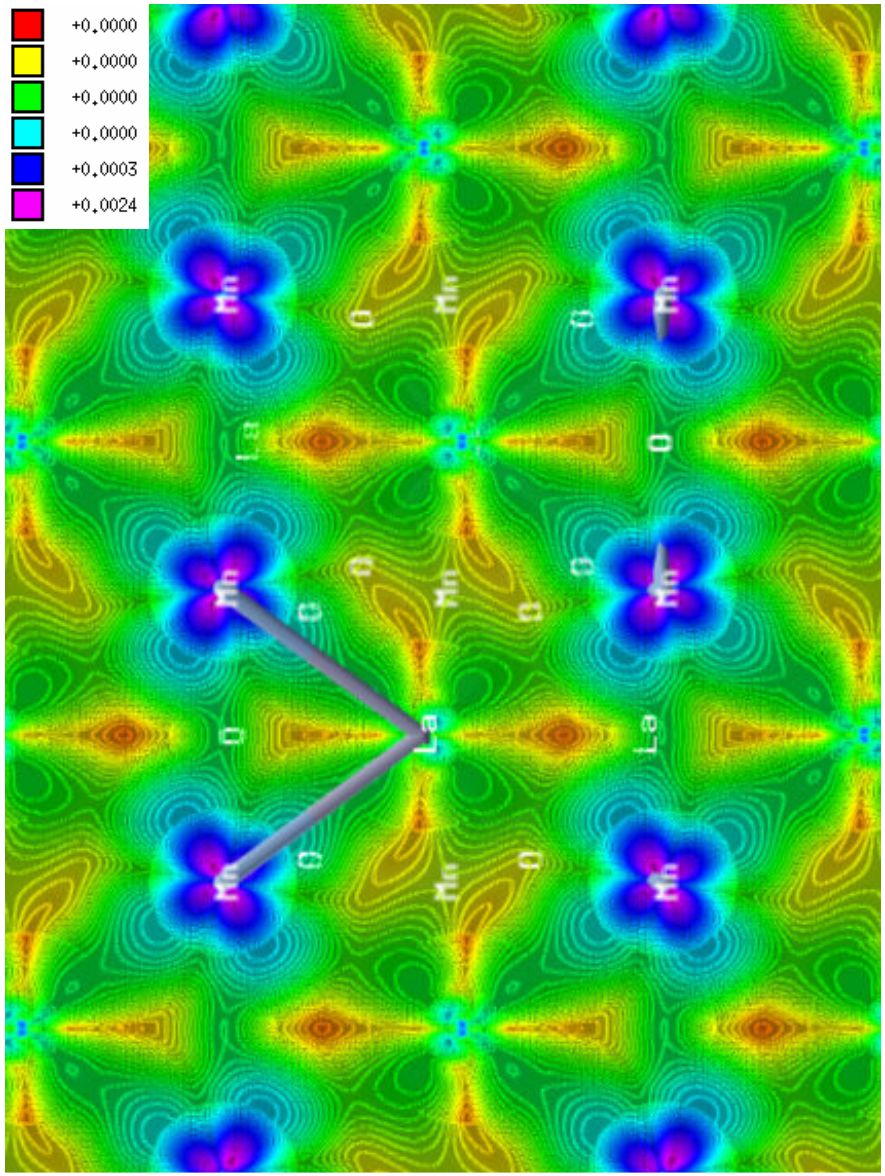




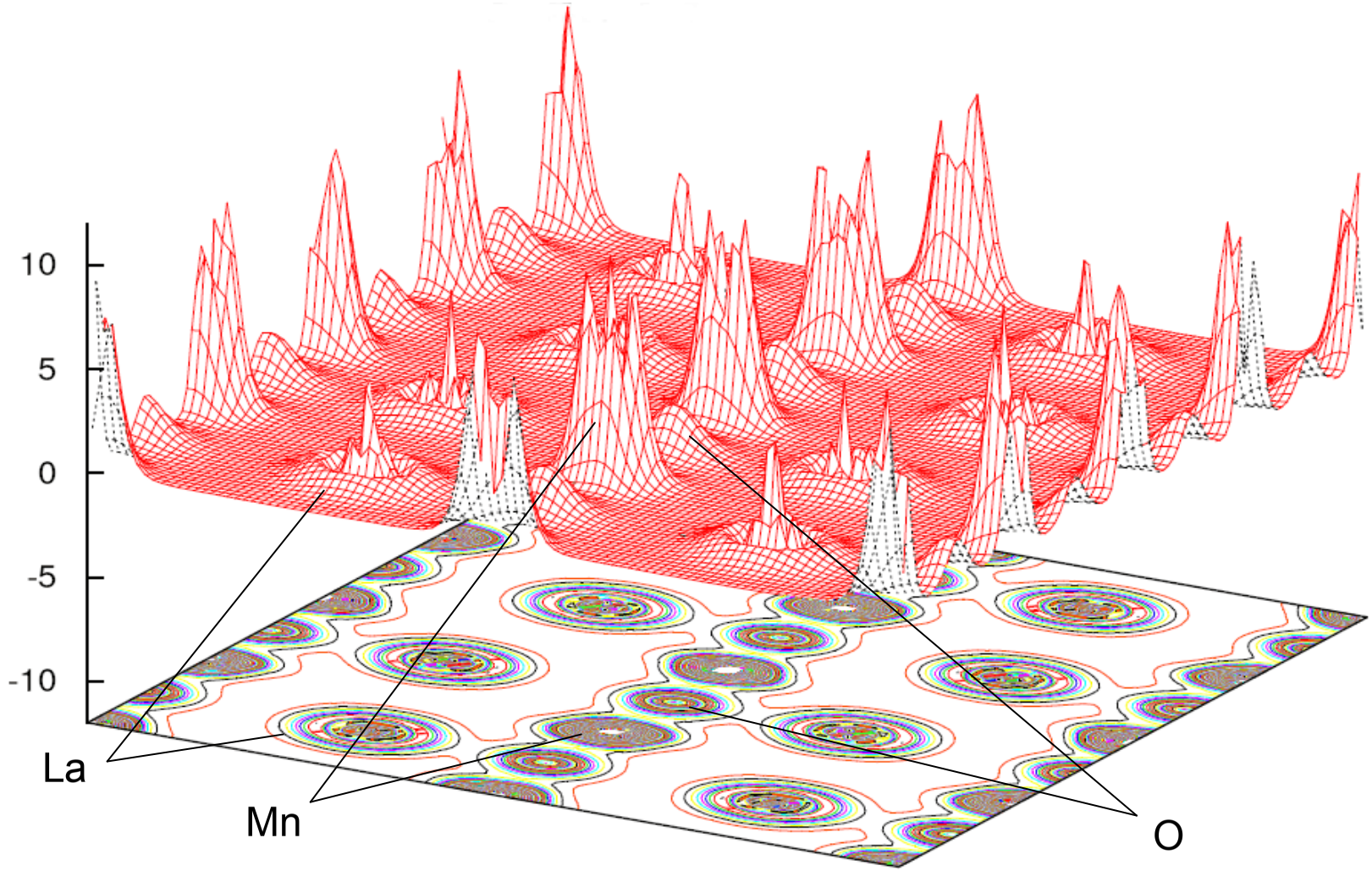
Electron density plots FM $LaMnO_3$ (100) plane

spin up E_c=0.52 Ry spin down



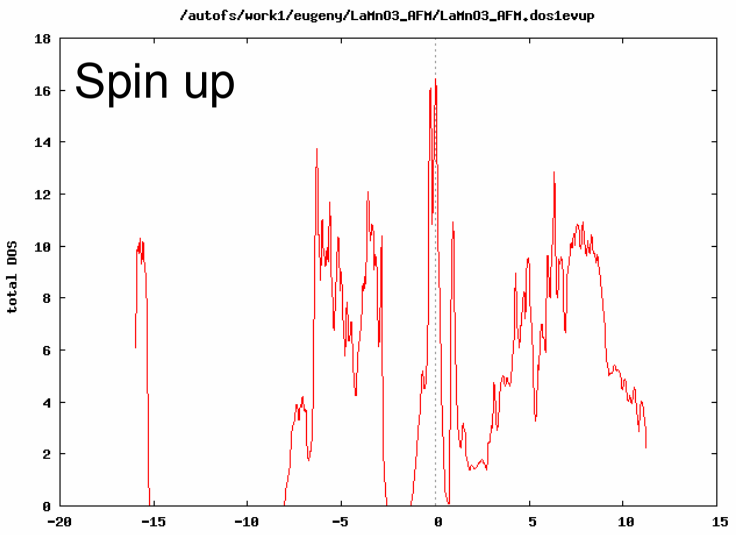


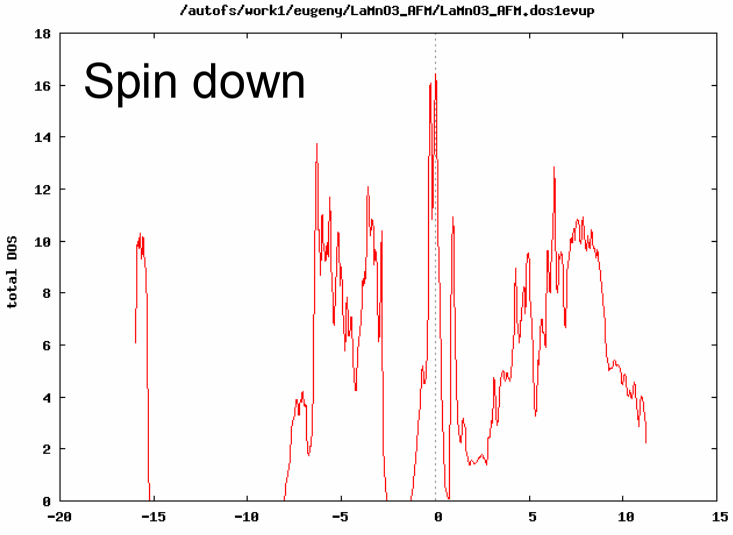
Charge density of FM $LaMnO_3$ spin up (100) plane



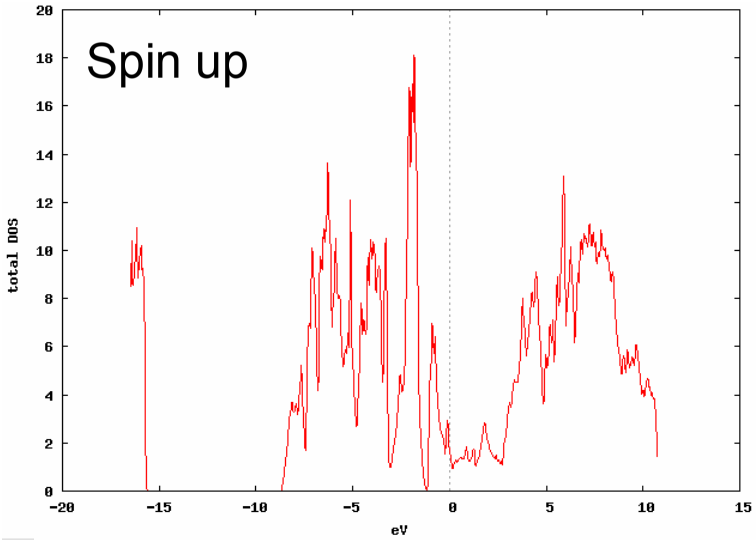
Total density of states (DOS) $LaMnO_3$

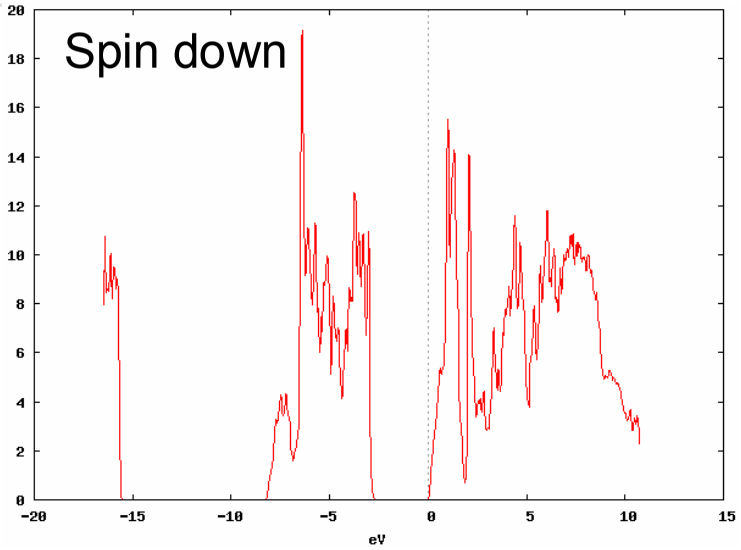
A-type Antyferromagnet





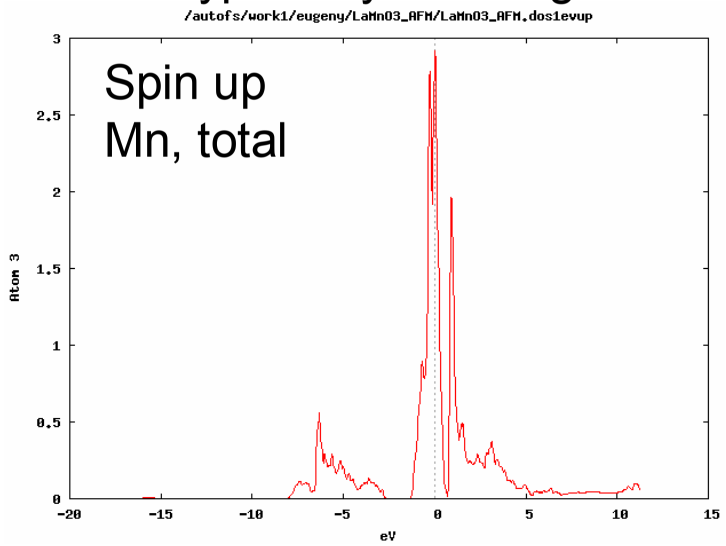
Ferromagnet

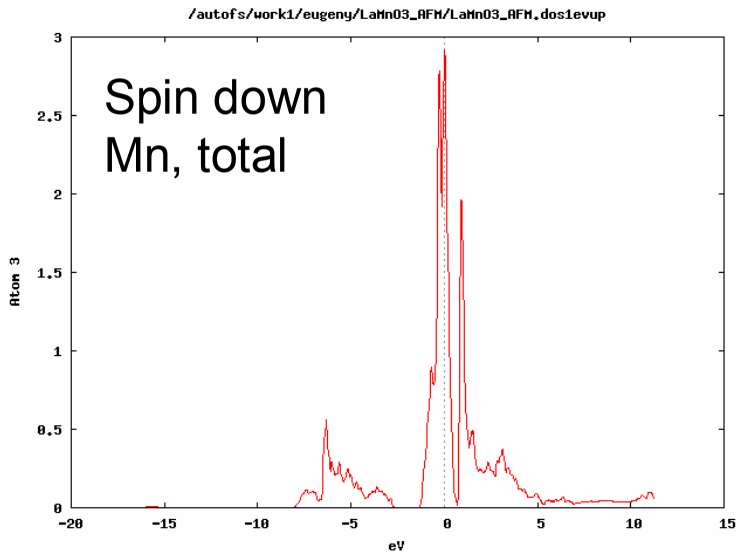




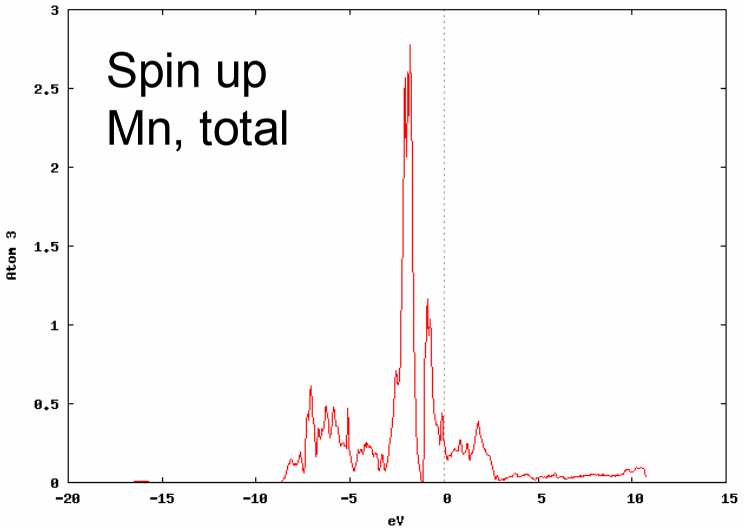
Partial DOS for Mn atoms $LaMnO_3$

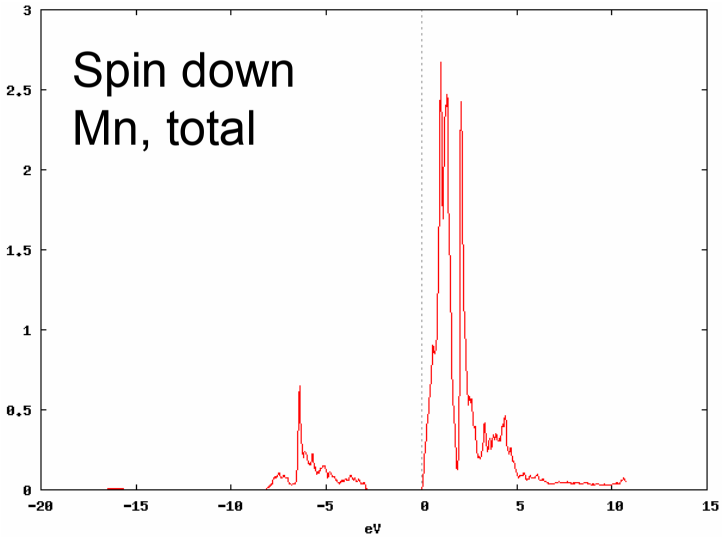
A-type Antyferromagnet





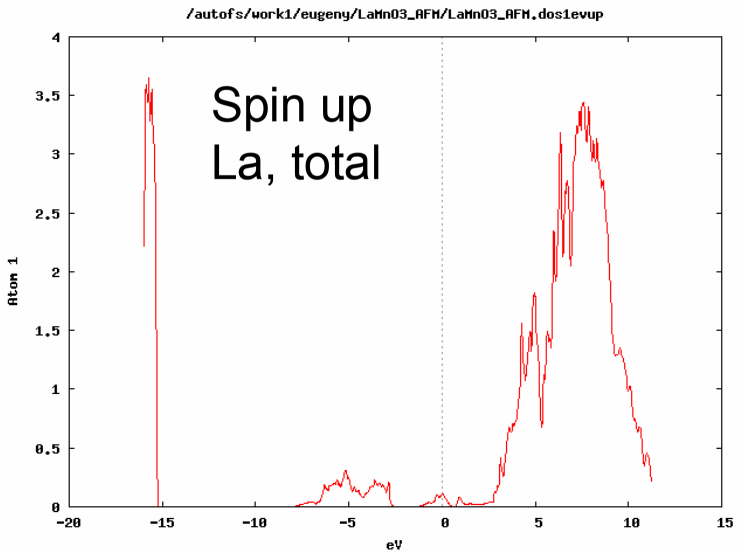
Ferromagnet

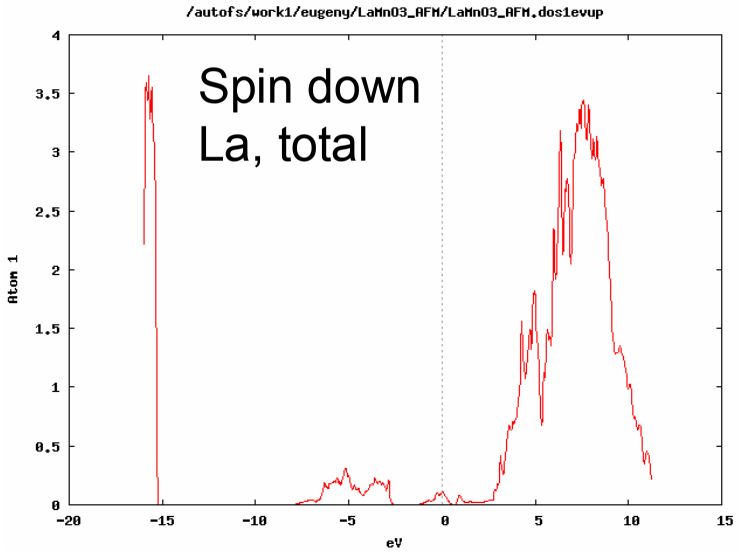




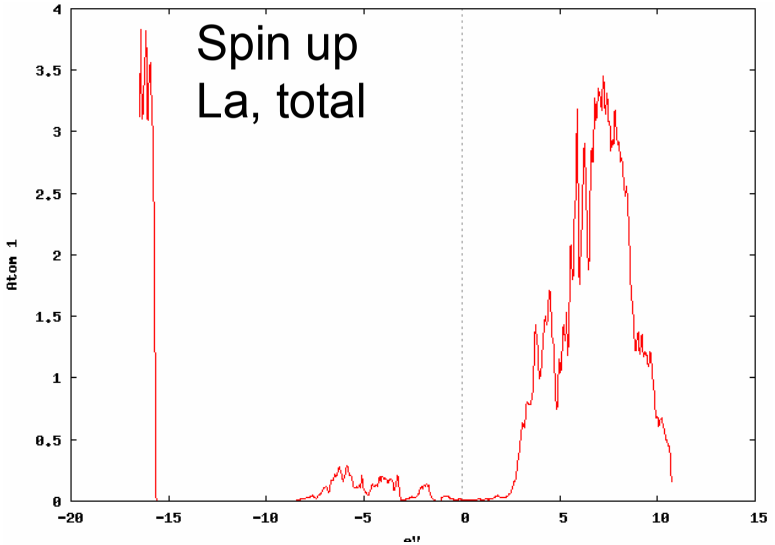
Partial DOS for La atoms $LaMnO_3$

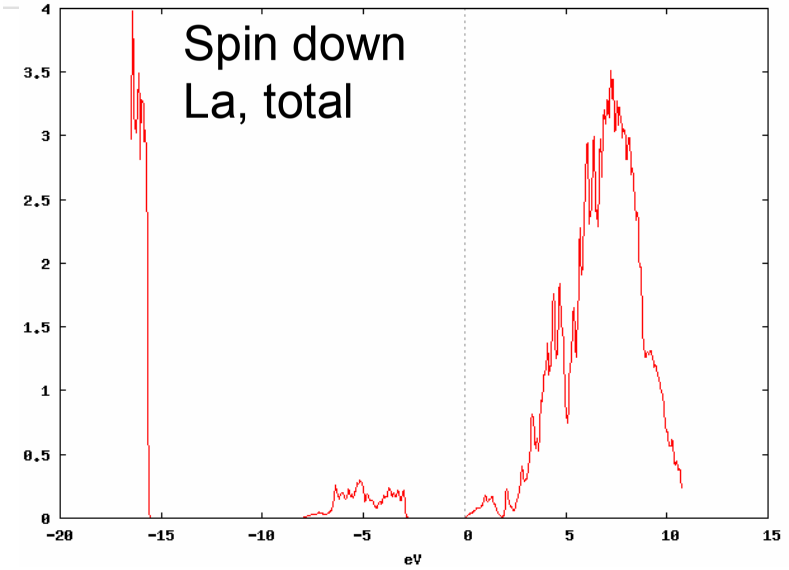
A-type Antyferromagnet





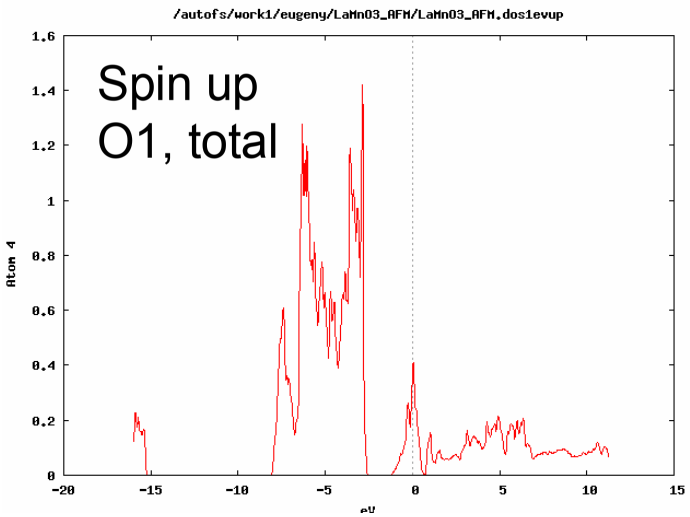
Ferromagnet

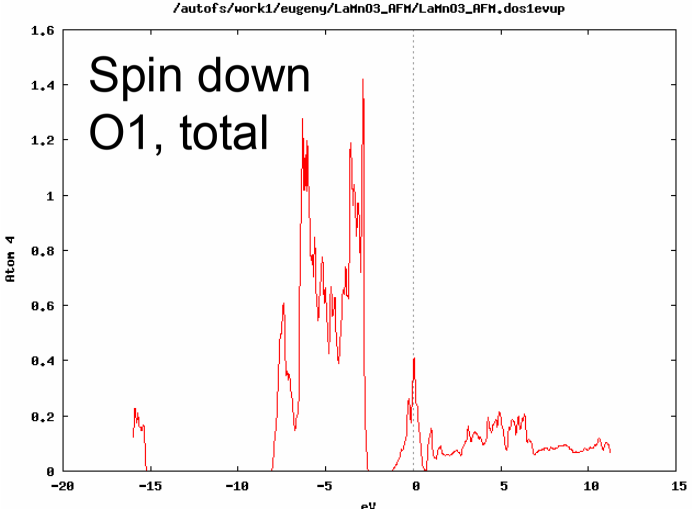




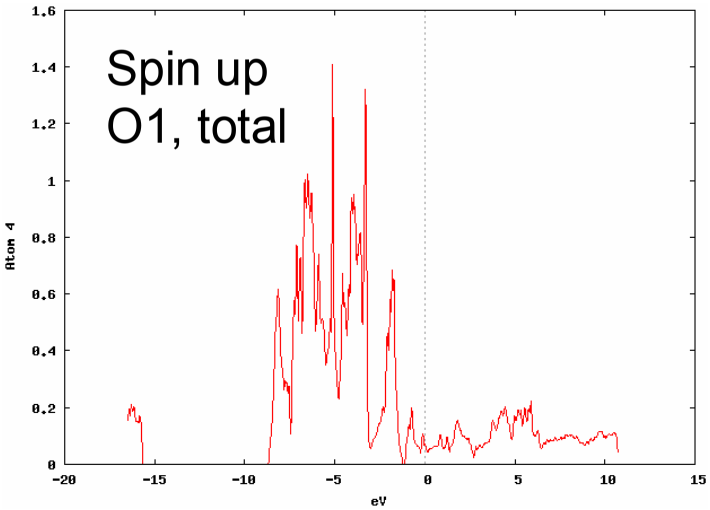
Partial DOS for O (1) atoms $LaMnO_3$

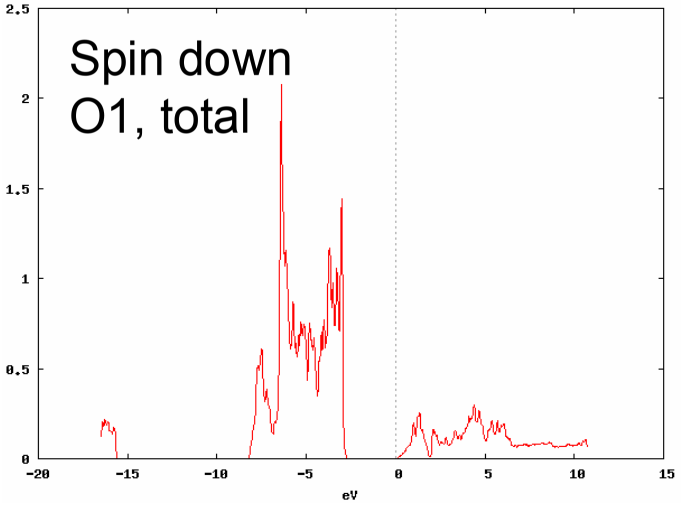
A-type Antyferromagnet





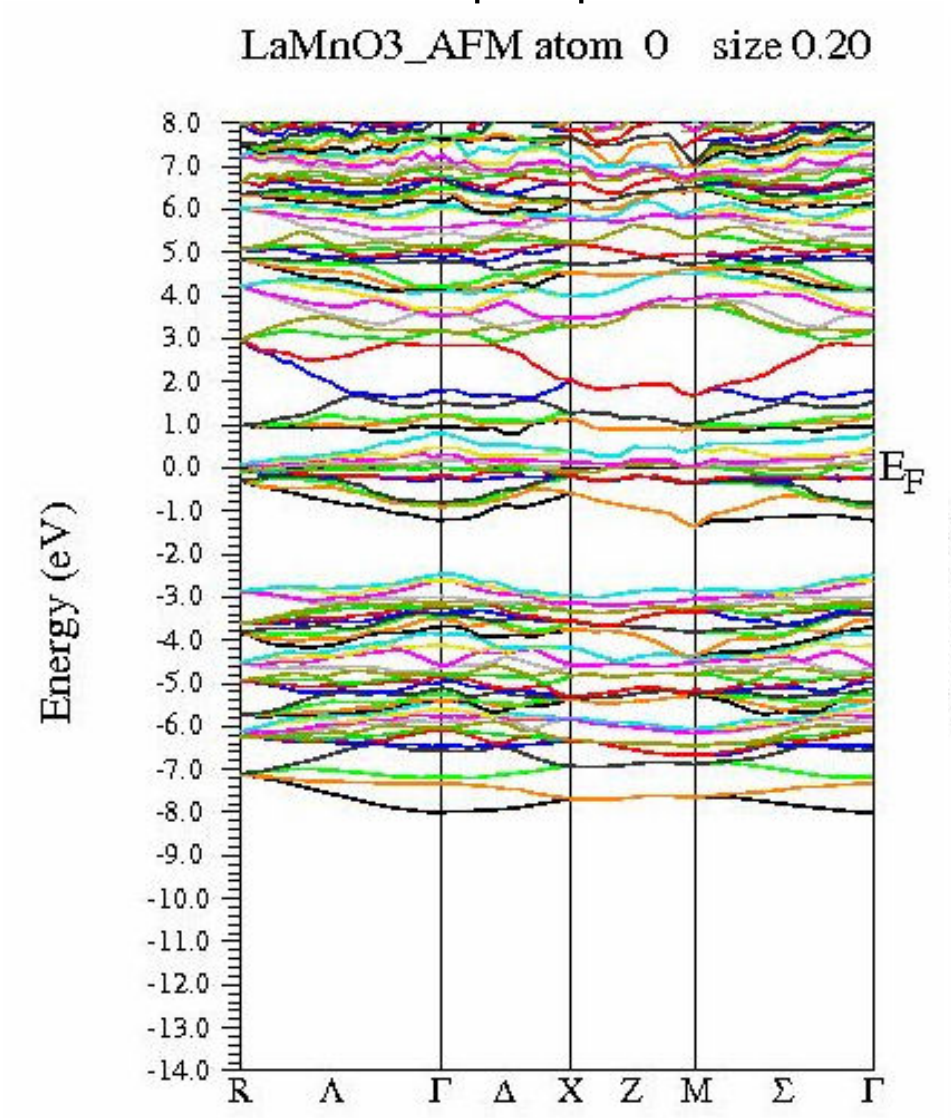
Ferromagnet



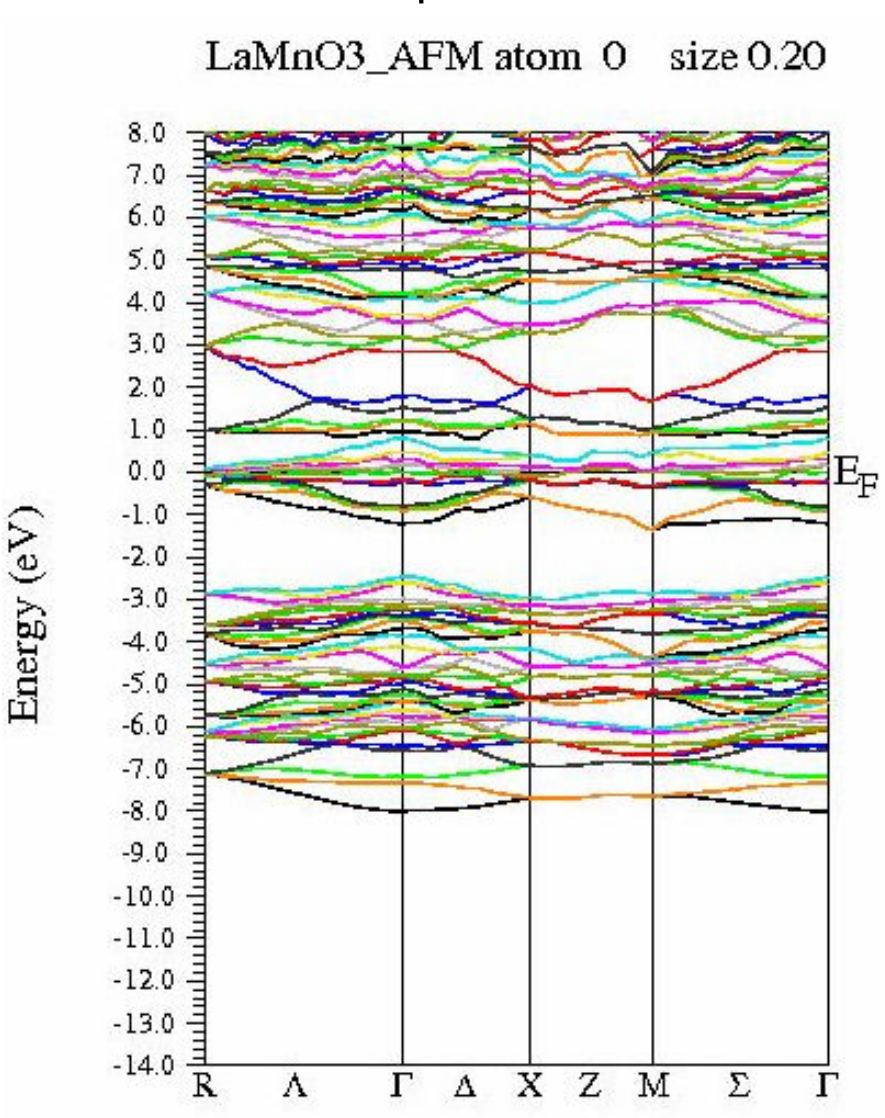


Band structure for A-AFM LaMnO3

Spin up

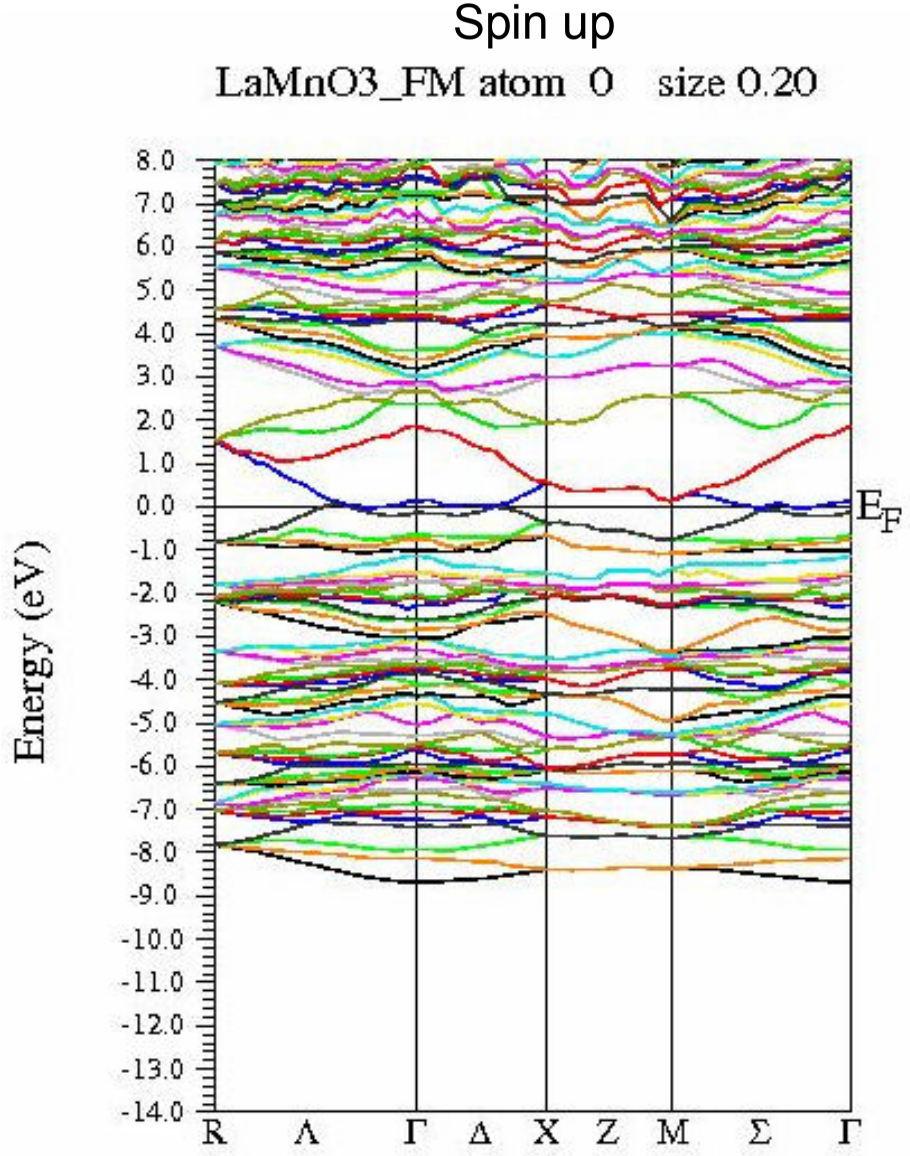


Spin down

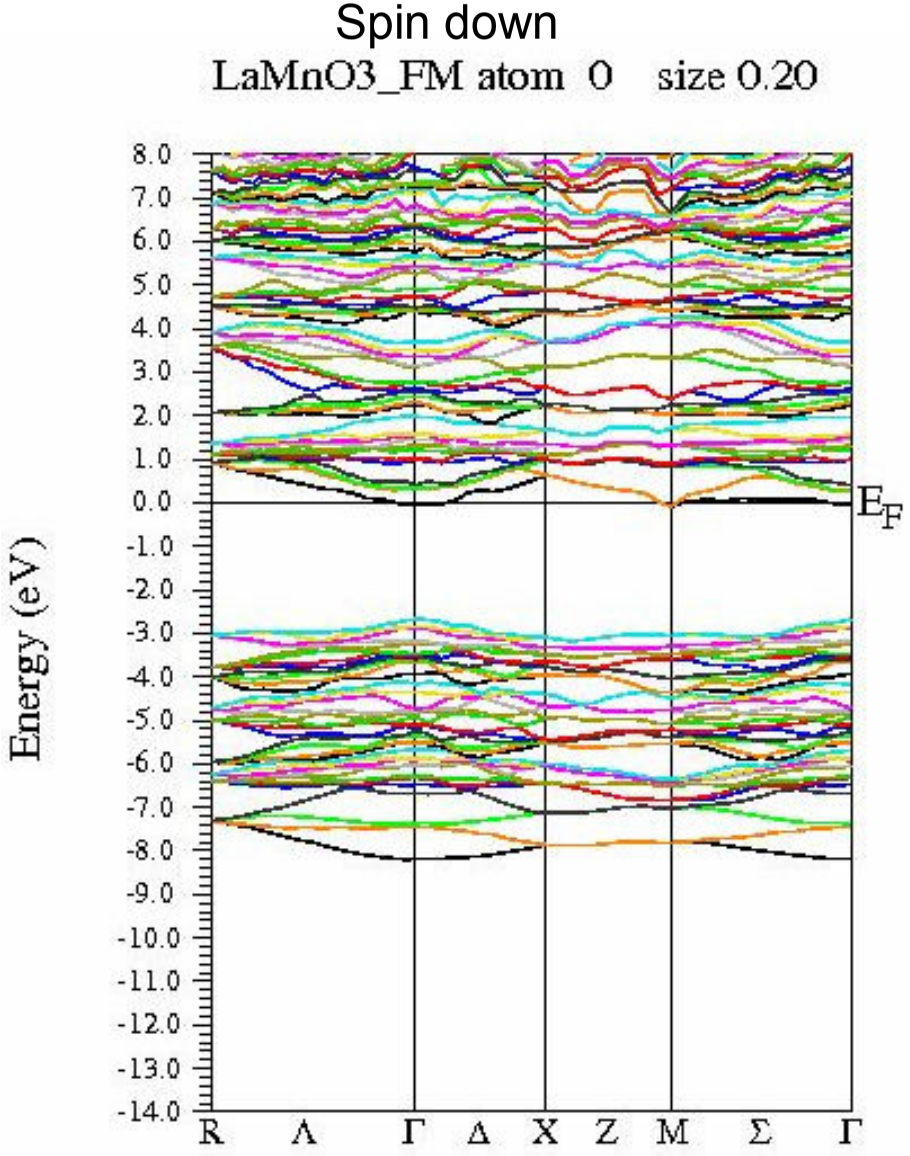


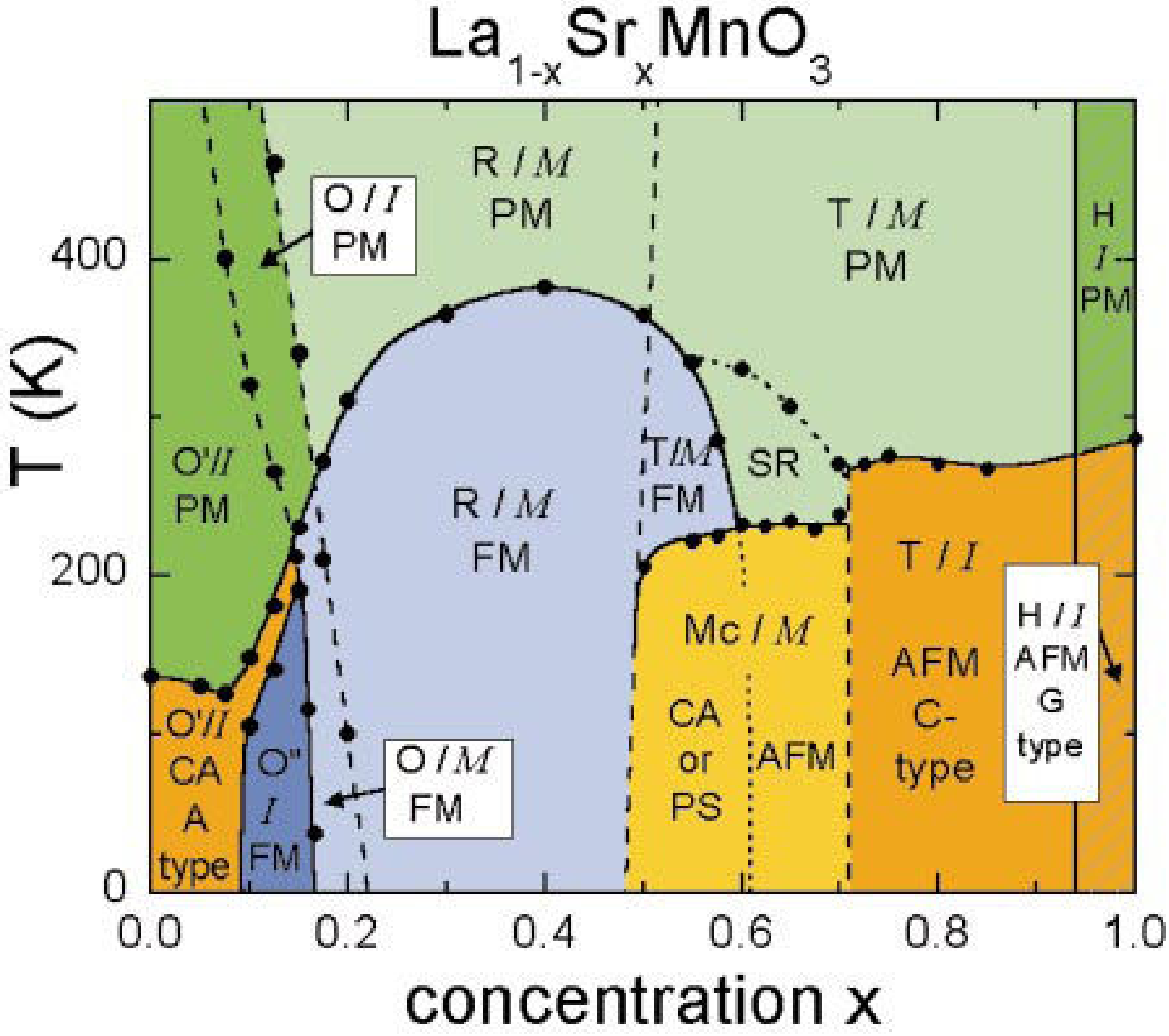
Band structure for FM LaMnO3

Spin up



Spin down

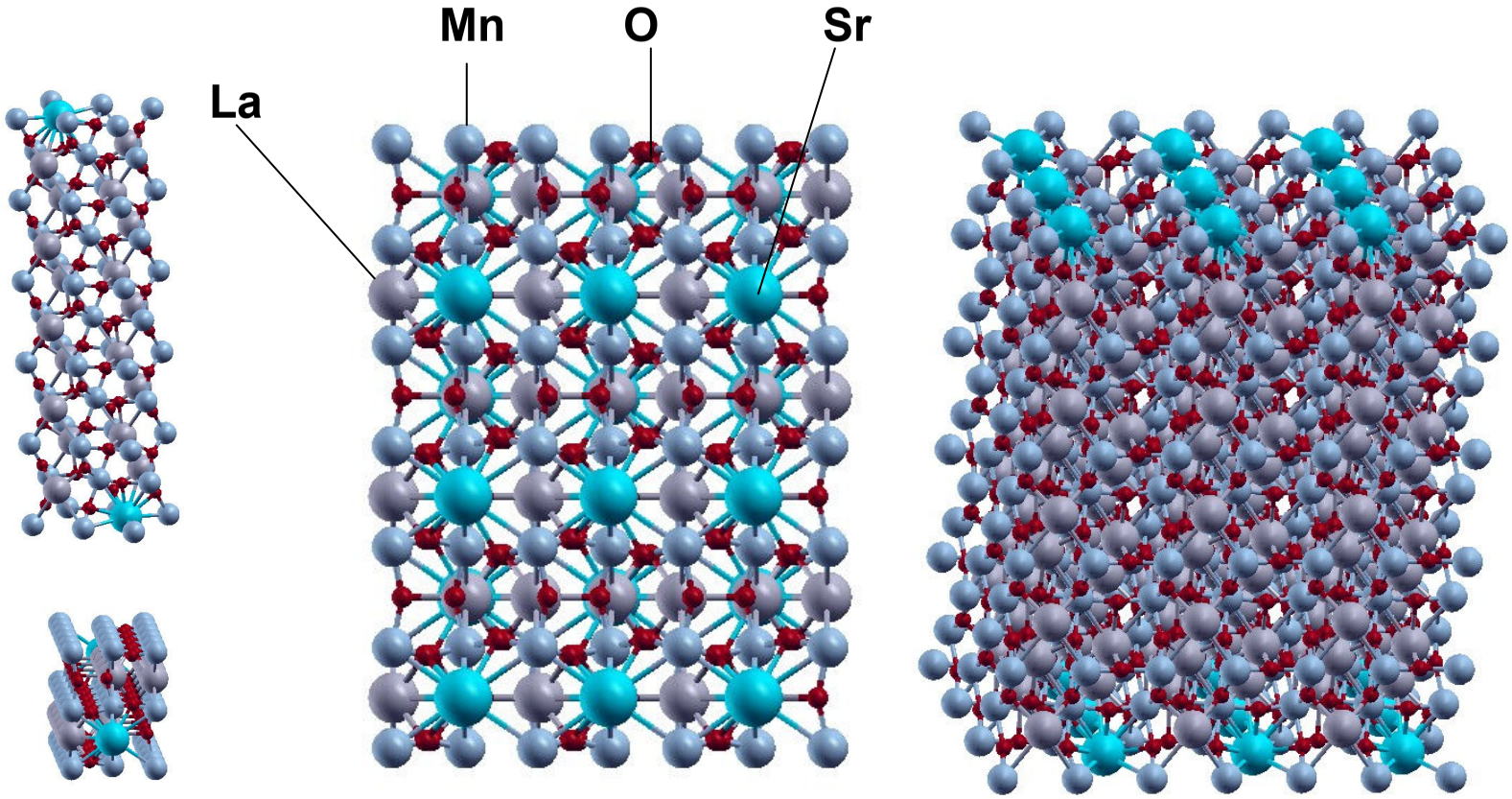



La1-xSrxMnO3
R / M
PM
O / I
PM
T / M
PM
H
I
PM
O'/I
PM
R / M
FM
T/M
FM
SR
T / I
AFM
C-
type
H / I
AFM
G
type
Mc / M
CA
or
PS
AFM
O'/I
CA
A
type
O"
I
FM
O / M
FM
T (K)
400
200
0
0.0
0.2
0.4
0.6
0.8
1.0
concentration x

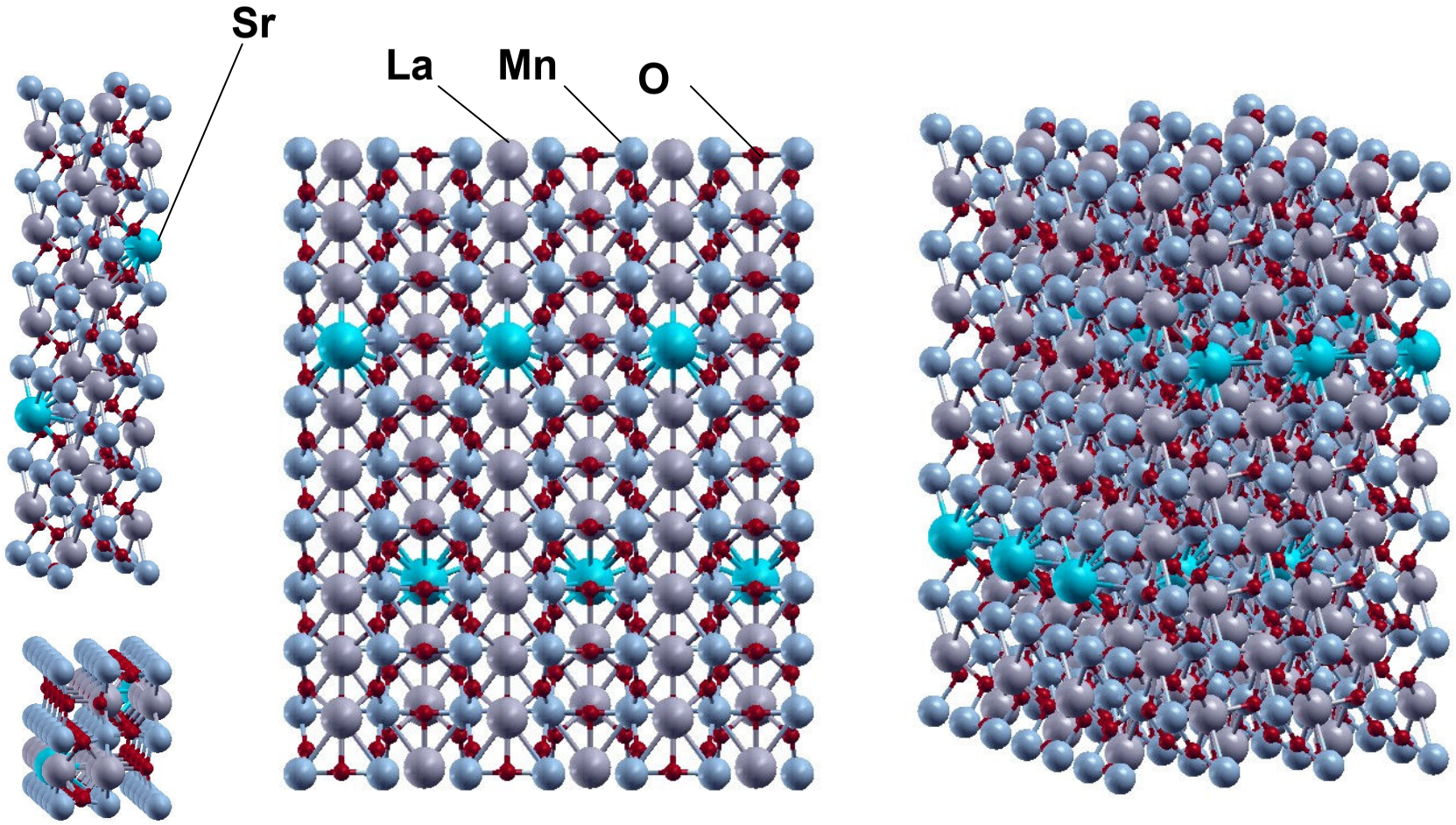
100 atoms supercell for thinly layered $La_{0.9}Sr_{0.1}MnO_3$

- **Inequivalent Atoms:** 36
- **Lattice:** Spacegroup: 11-P21/m
- **Number of symmetry operations:** 4
- **Lattice parameters:**
  a=10.45, b=54.25, c=14.49 (bohr)
  α=β=γ=90°
  Unit cell volume 8218.5
- **5 primitive cells in x direction**
- **Bravais lattice: Monoclinic primitive**
- **THE CRYSTAL SYSTEM IS ORTHORHOMBIC**
- **ORDER OF LATTICE POINT GROUP (NO BASE) : 8**
- **ORDER OF LATTICE SPACE GROUP (WITH BASE) = 4**
- **NON-SYMMORPHIC SPACE GROUP OR NON-STANDARD ORIGIN OF COORDINATES**
- **SPACE GROUP CONTAINS INVERSION**

1) full occupation of (100) plane by Sr



2) half-occupation of (001/4) and (003/4) planes by Sr



Input parameters $La_{0.9}Sr_{0.1}MnO_3$

- LDA, Perdew-Burke-Ernzerhof 96, energy to separate core and valence states: -6,5 Ry
- RMT*Kmax=4
- Temperature broadening scheme (TEMP), broadening factor 0.005
- Mixing factor 0.005
- U=4.5 eV (L= 2 U= 0.331 Ry J= 0.0 Ry), -orb, *G. Trimarchi and N. Binggeli Phys. Rev. B **71**, 035101 (2005)*
- LDA+U potential added for all Mn atoms
- 1 k-mesh before SCF (1 k-point), and 500 after achievement of the convergence (90 k-points was generated)
- Energy and charge convergence –c 0.0001 –ec 0.01
- Spin-polarized calculation

1) FULL OCCUPATION		2) PARTIAL OCCUPATION	
TOTAL ENERGY	-373985.412950 Ry	TOTAL ENERGY	-373985.419297 Ry
F E R M I – ENERGY	0.62777 Ry	F E R M I – ENERGY	0.61365 Ry
Chemical Potential	0.63050109 Ry	Chemical Potential	0.61364787 Ry
ORBITAL MOMENT: PROJECTION ON M	0.0 0.0 0.0 0.0	ORBITAL MOMENT: PROJECTION ON M	0.0 0.0 0.0 0.0
SPIN MOMENT: PROJECTION ON M	0.00 0.00 -0.36006 -0.36006	SPIN MOMENT: PROJECTION ON M	0.00 0.00 -0.36769 -0.36769

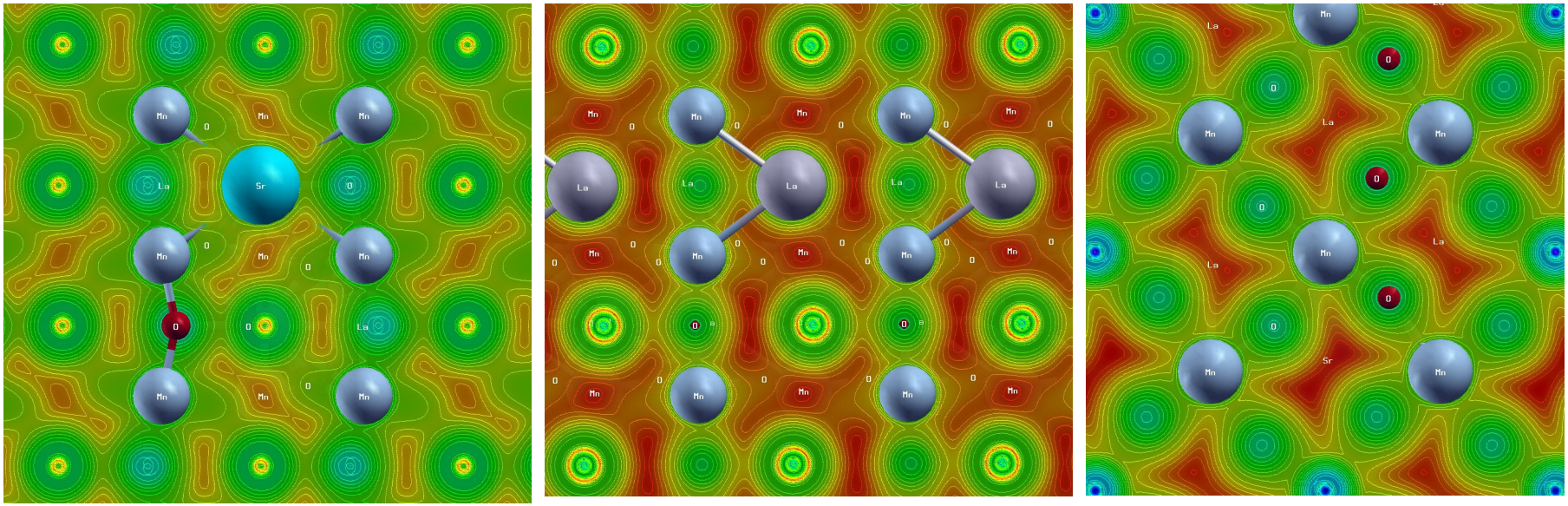
Compound	Space group	Calculation of magnetic ordering	Number of atoms in cell (supercell)	k-mesh/ k-points	E_{tot} per unit cell/ E_{tot} per atom (Ry)	M_{tot} per cell/ Mtot per atom Mn (μ_B)	E_F, eV
$LaMnO_3$	62-Pmna	nonmagnetic	20	1000 120	-79058.406 -3952.92	0	0.71504
$LaMnO_3$	62-Pmna	Spin-polarized	20	1000 120	-79058.812 -3952.94	15.99750 3.999	0.74194
$LaMnO_3$	1-P1	ferromagnetic	20	10 4	-79058.525 -3952.93	16.13940 4.034	0.73543
$LaMnO_3$	1-P1	antiferromagnetic, A-type	20	10 4	-79058.396 -3952.92	0	0.71875
$LaMnO_3$	1-P1	antiferromagnetic, C-type	20	10 4	-79058.396 -3952.92	0	0.71875
$LaMnO_3$	1-P1	antiferromagnetic, G-type	20	10 4	-79058.396 -3952.92	0	0.71875
$La_{87.5}Sr_{12.5}MnO_3$ 1 cluster (1 atom Sr)	1-P1	Spin-polarized	40	10 4	-147473.101 -3686.83	-	-0.12127
$La_{75}Sr_{25}MnO_3$ 1 cluster (1 atoms Sr)	1-P1	Spin-polarized	20	10 4	-68423.090 -4921.16	15.17455 3.79	0.67372

Electron density plots $La_{0.9}Sr_{0.1}MnO_3$

1) Full occupation

spin up

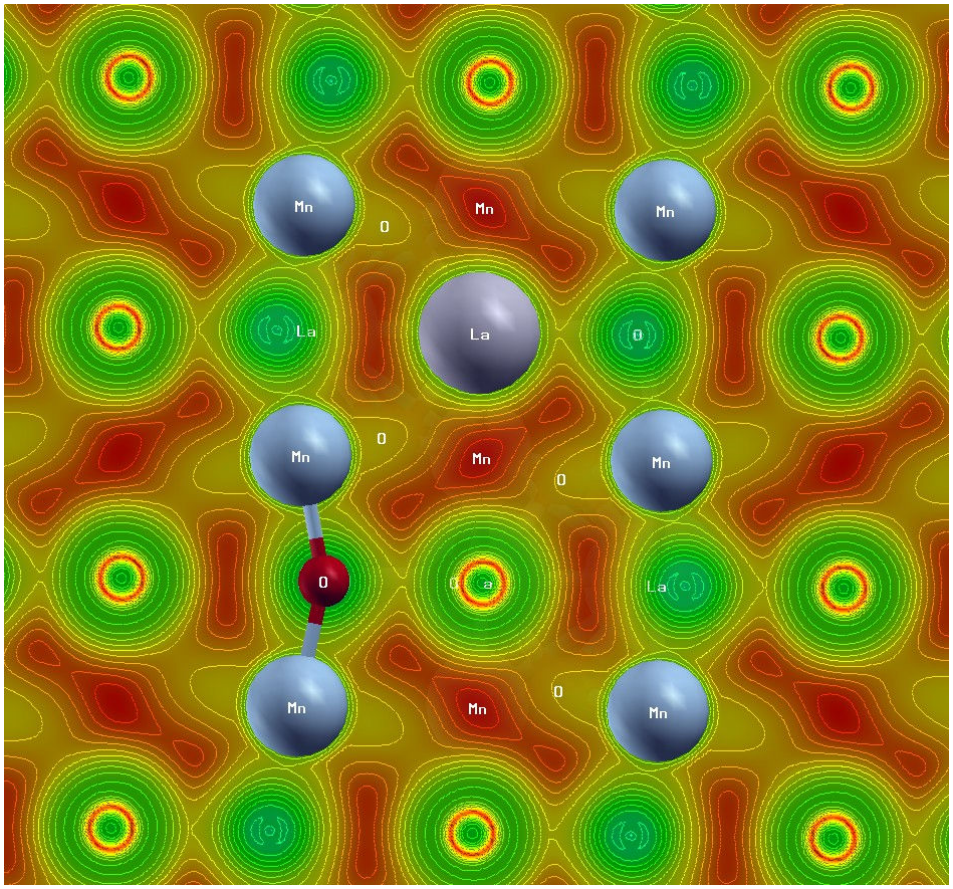
(100) (001) (010)



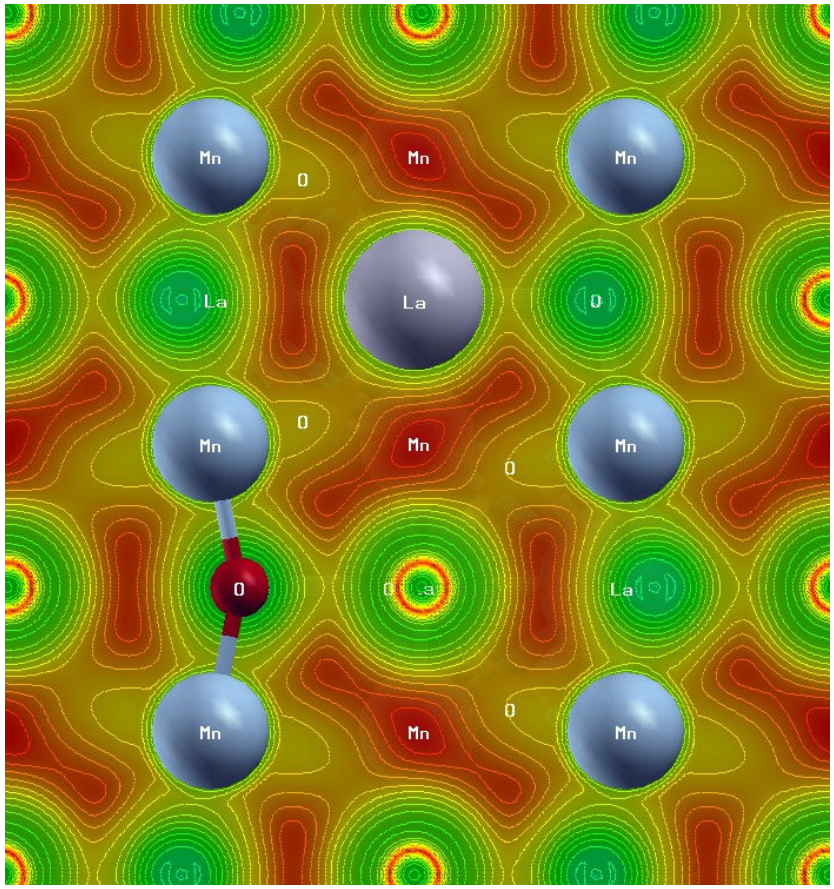
Electron density plots $La_{0.9}Sr_{0.1}MnO_3$

2) Partial occupation: view of (100) plane

spin up



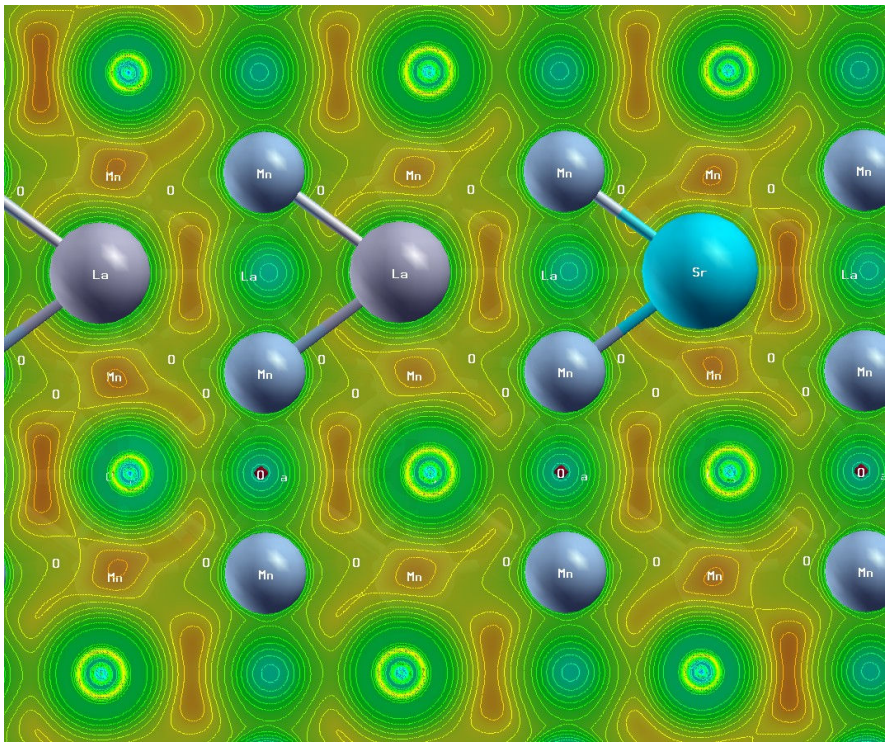
spin dn



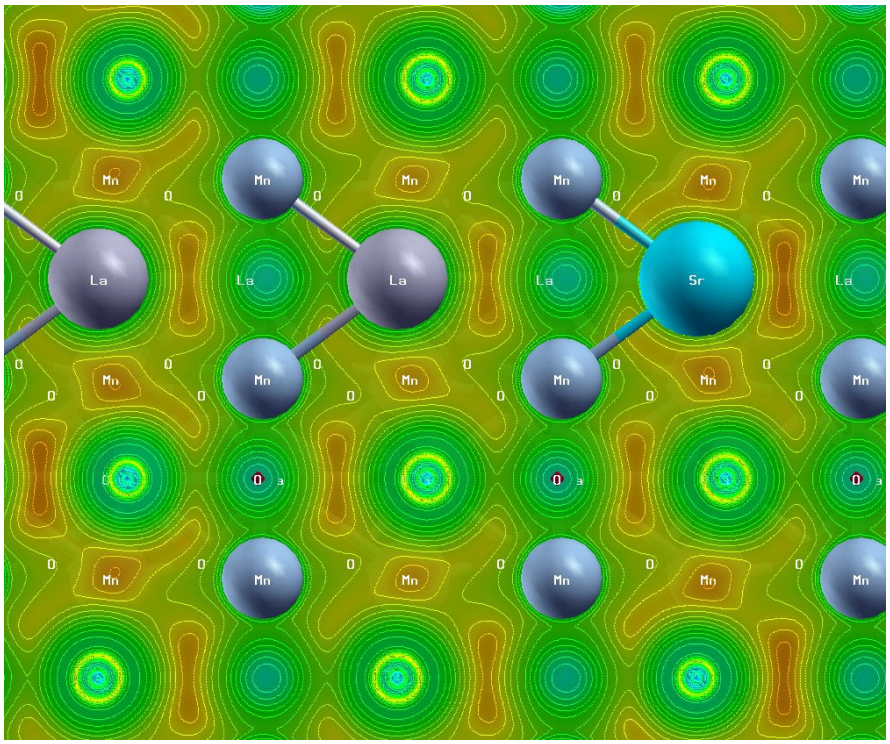
Electron density plots $La_{0.9}Sr_{0.1}MnO_3$

2) Partial occupation: view of (001) plane

spin up



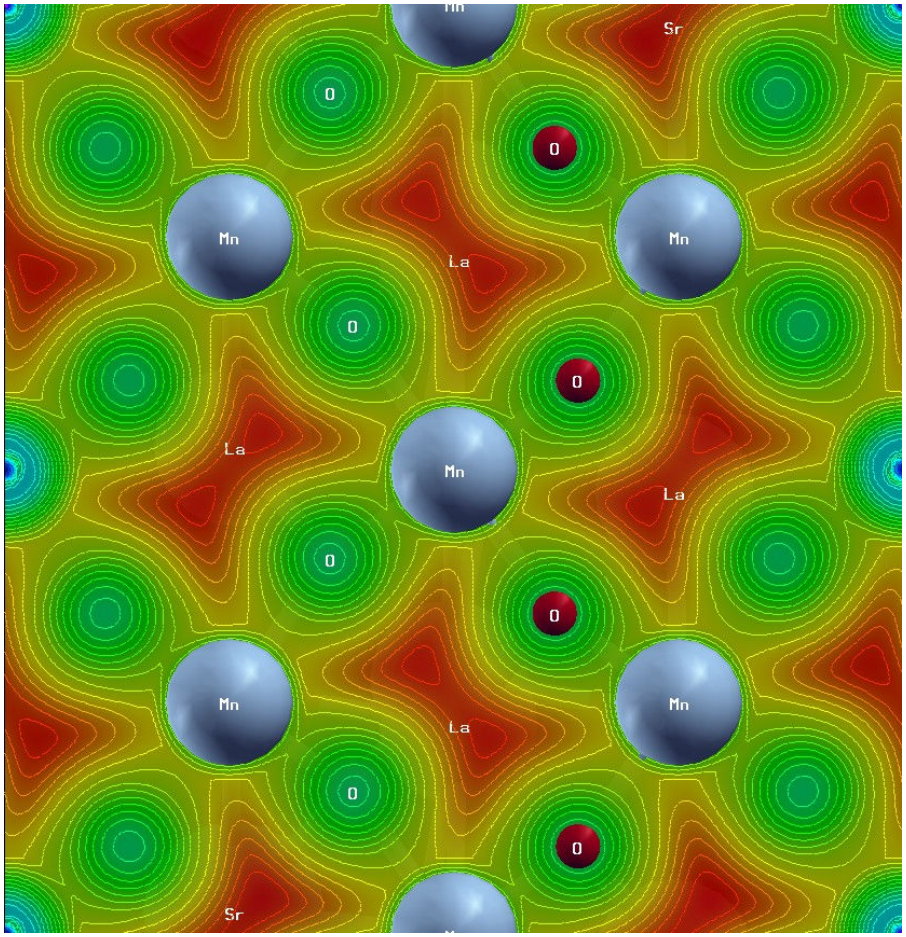
spin dn



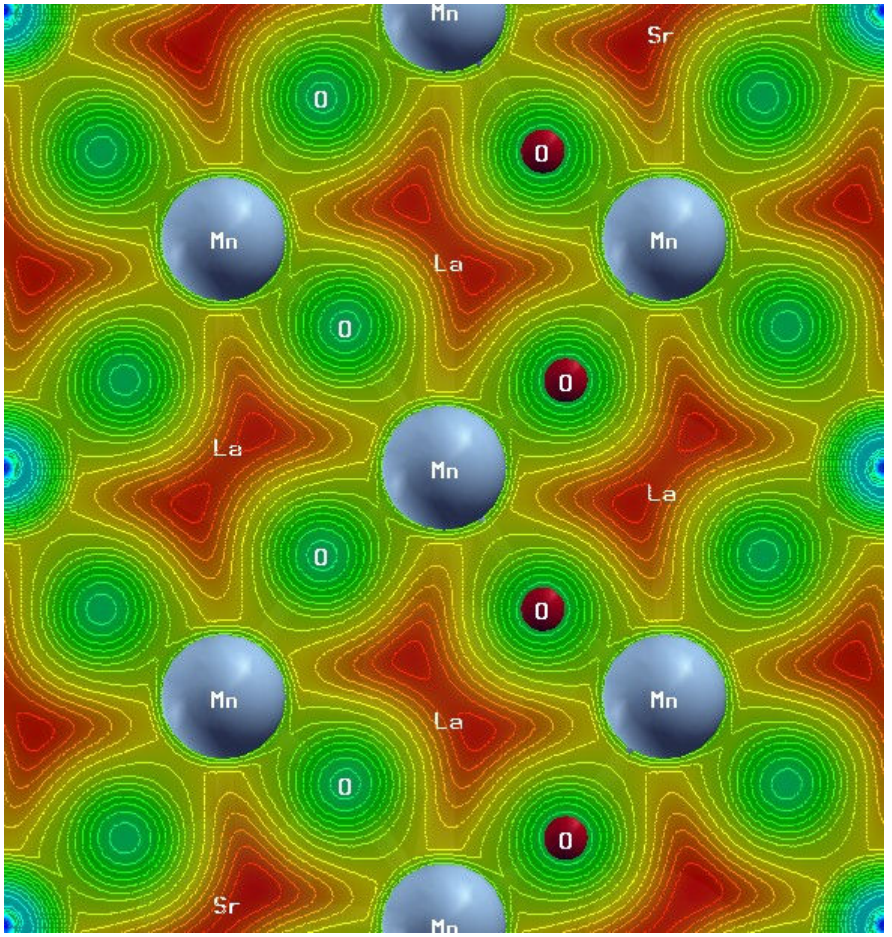
Electron density plots $La_{0.9}Sr_{0.1}MnO_3$

2) Partial occupation: view of (010) plane

spin up

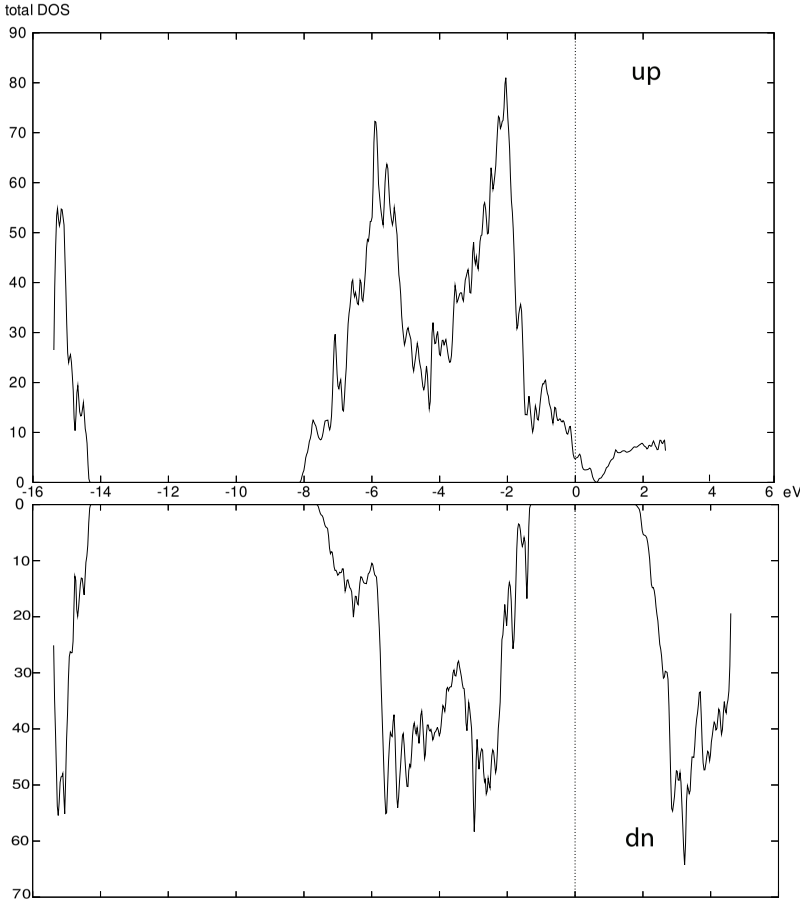


spin dn

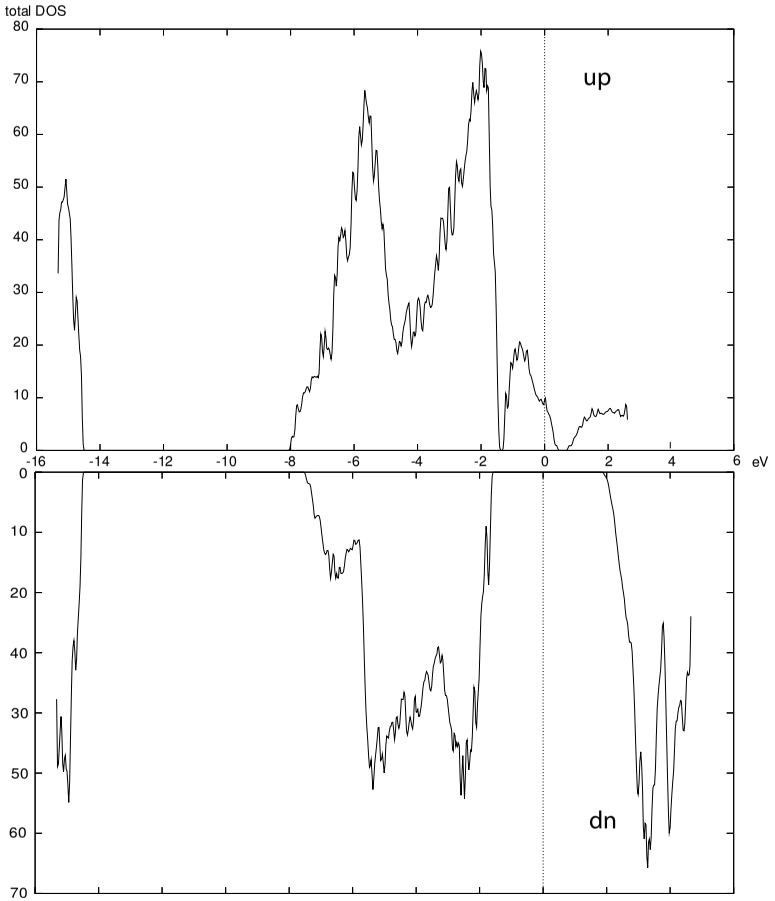


Total DOS $La_{0.9}Sr_{0.1}MnO_3$

1) Full

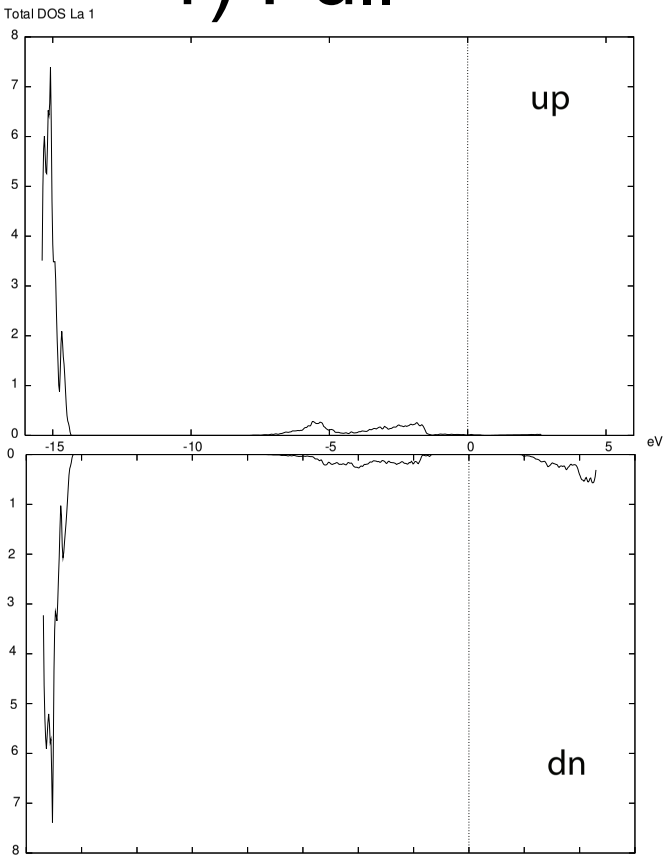


2) Partial

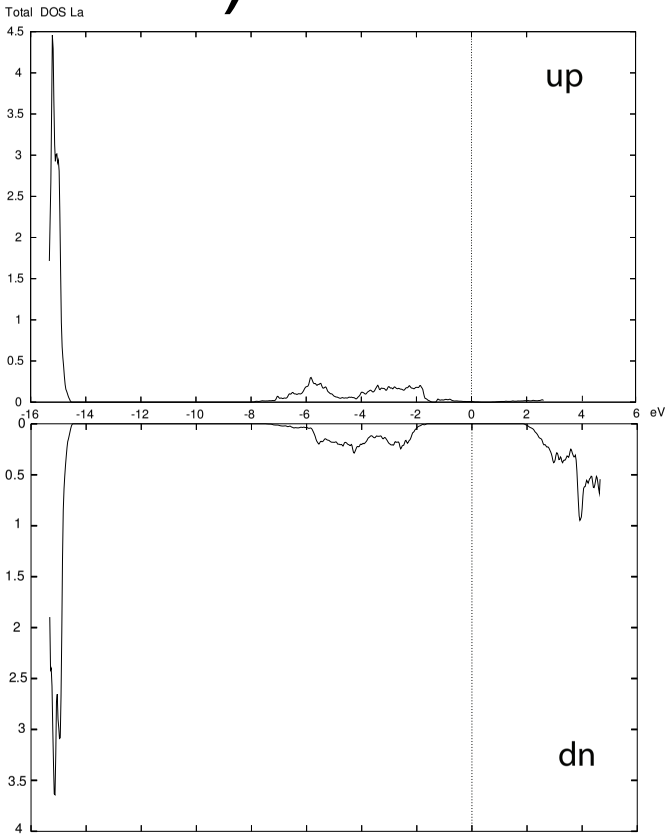


Total DOS La

1) Full

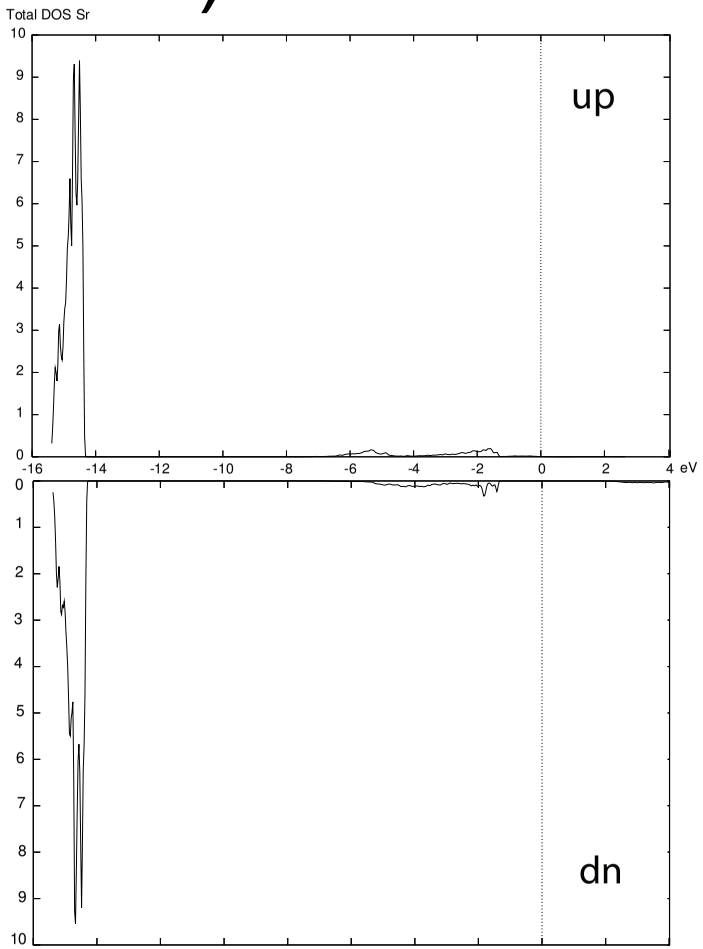


2) Partial

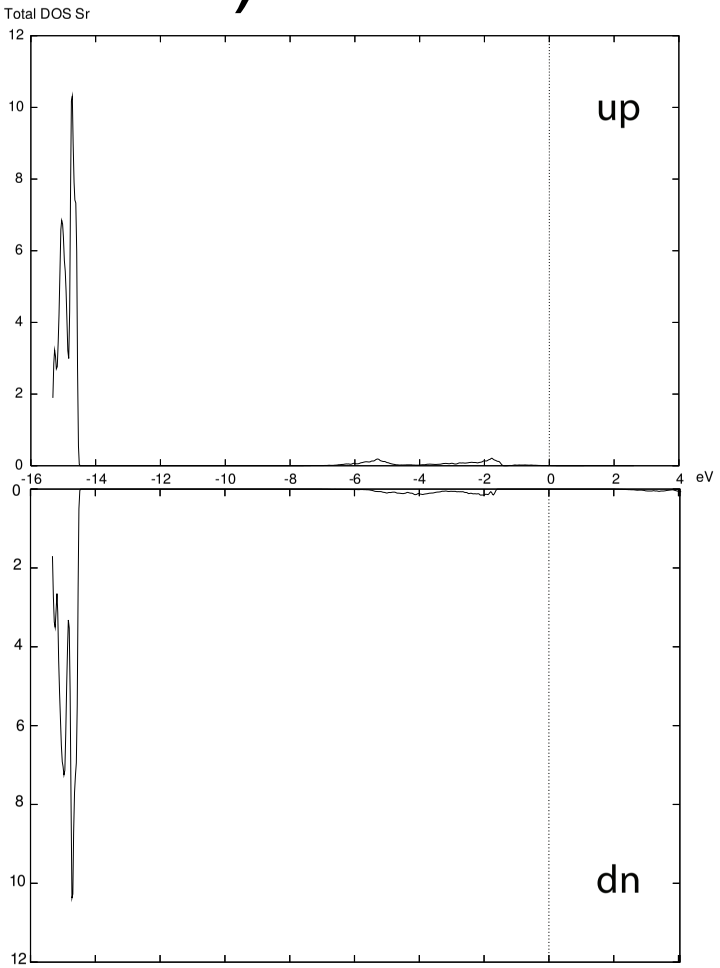


Total DOS Sr

1) Full

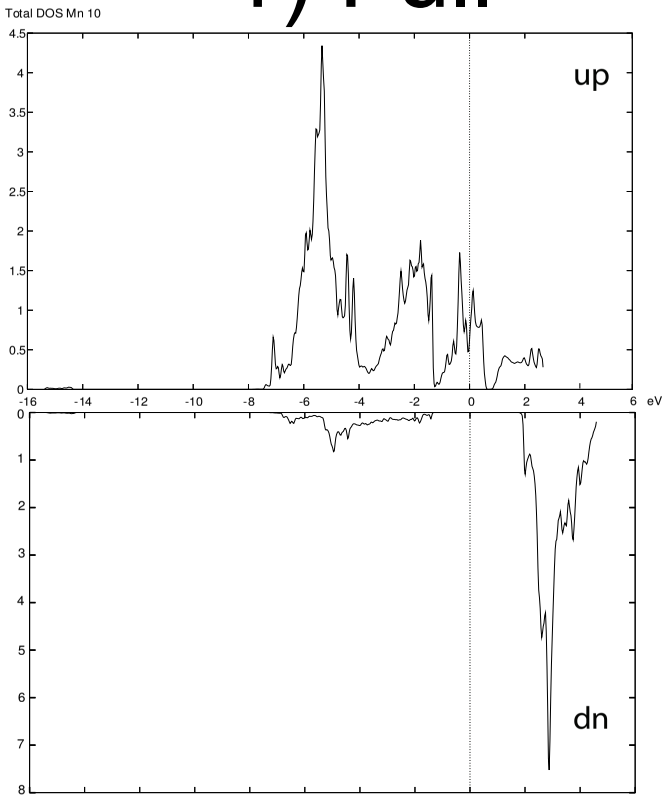


2) Partial

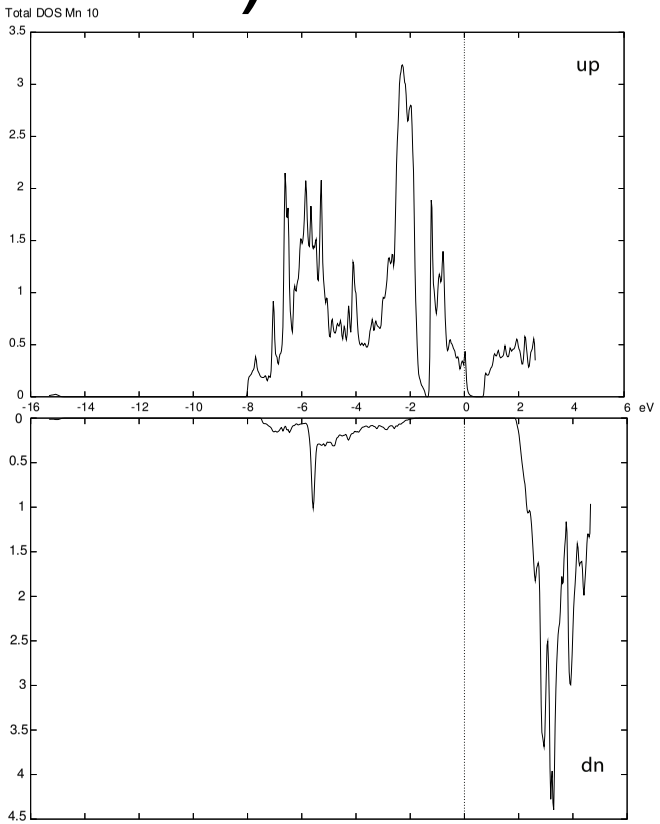


Total DOS Mn (1)

1) Full



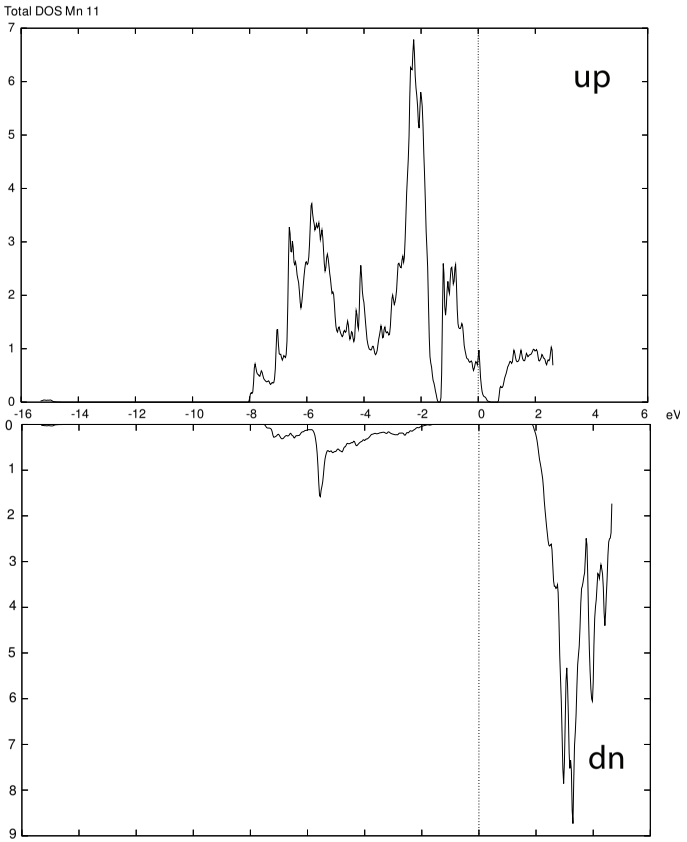
2) Partial



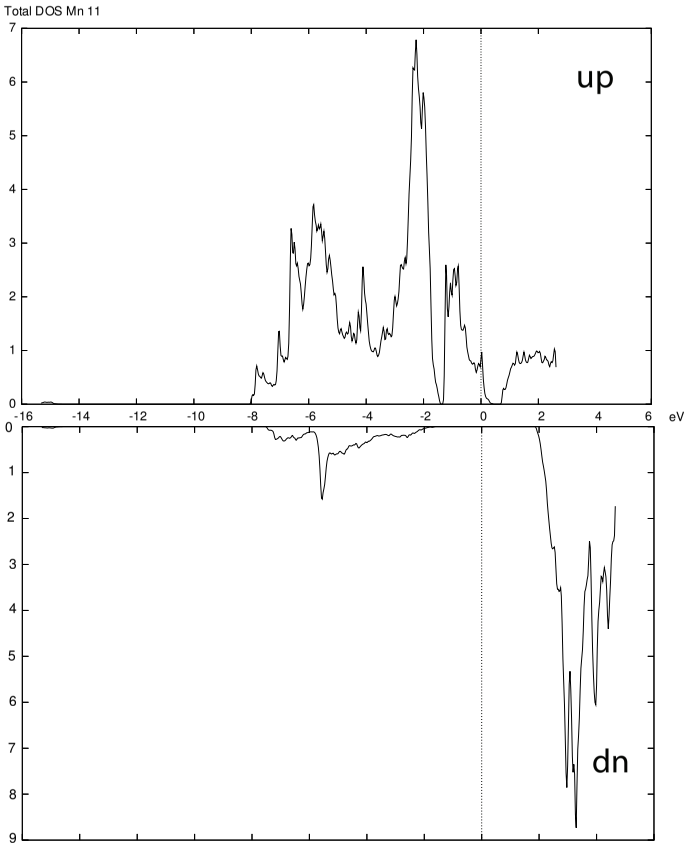
Coordinates of Mn
x=0.0 y=0.0 z=0.0
x=0.0 y=0.0 z=0.5

Total DOS Mn (2)

1) Full

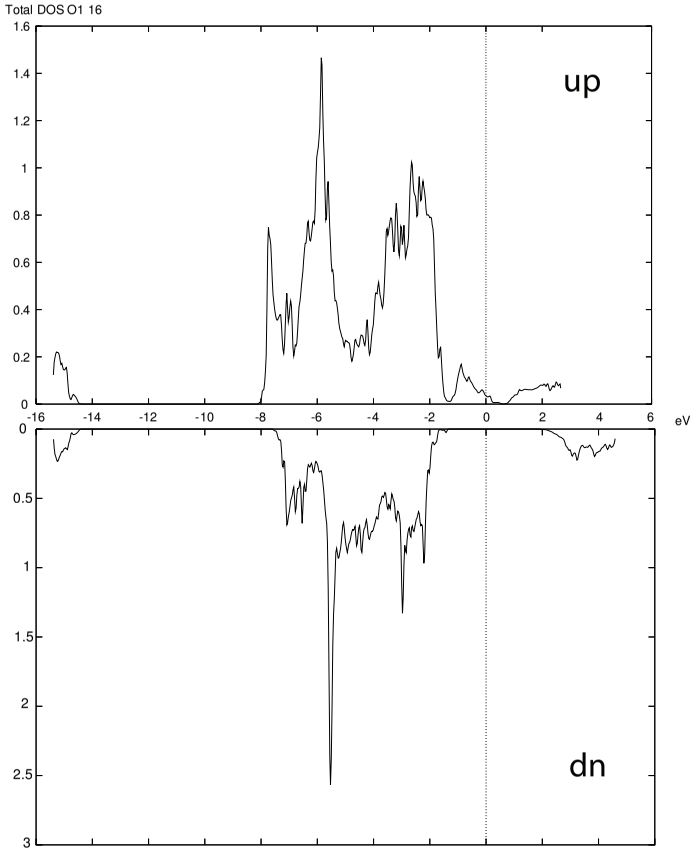


2) Partial

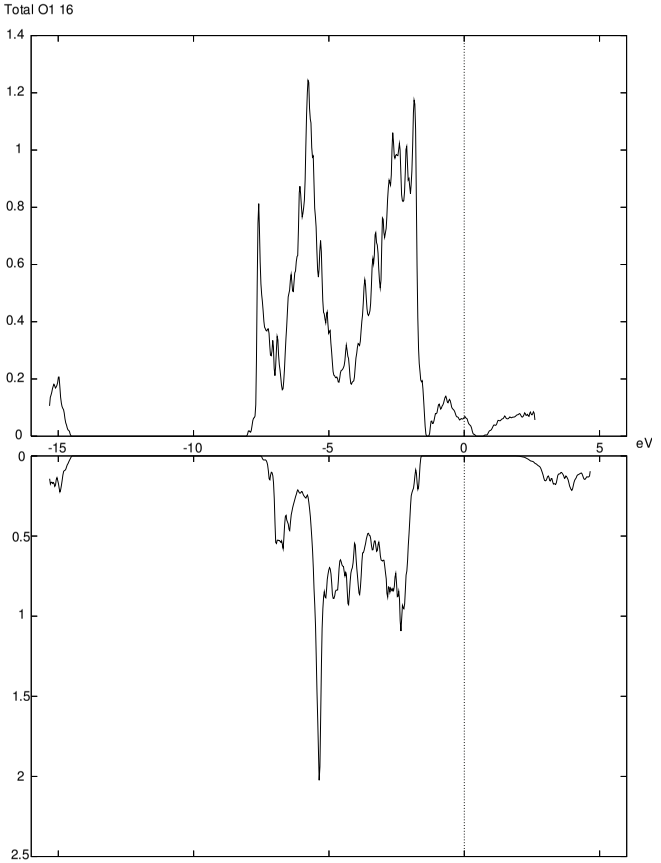


Total DOS O (1)

1) Full

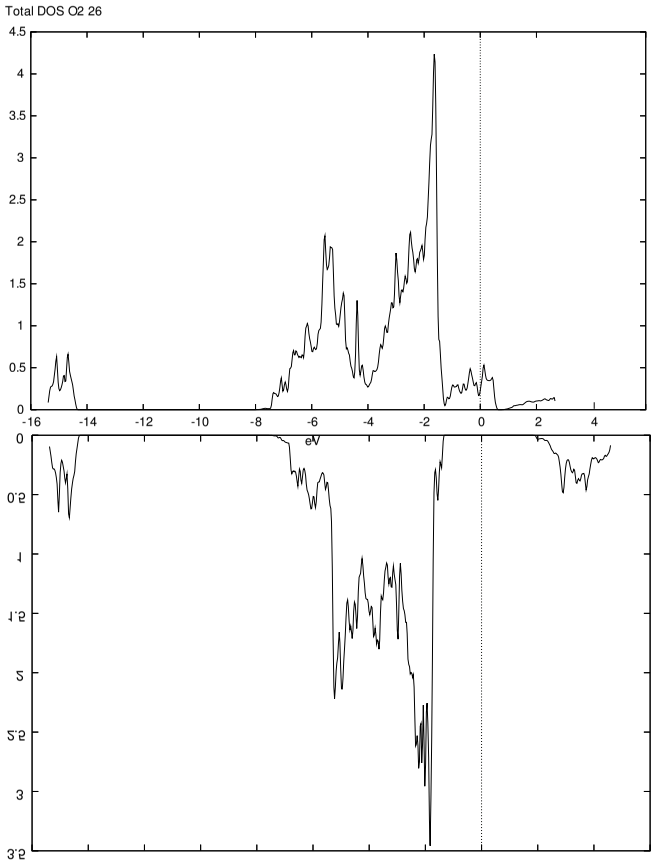


2) Partial

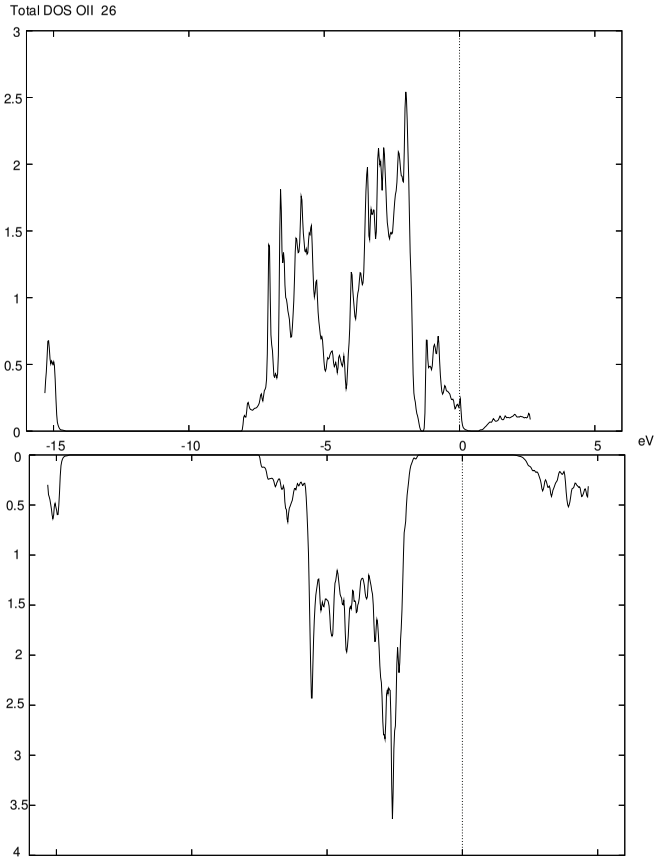


Total DOS O (2)

1) Full

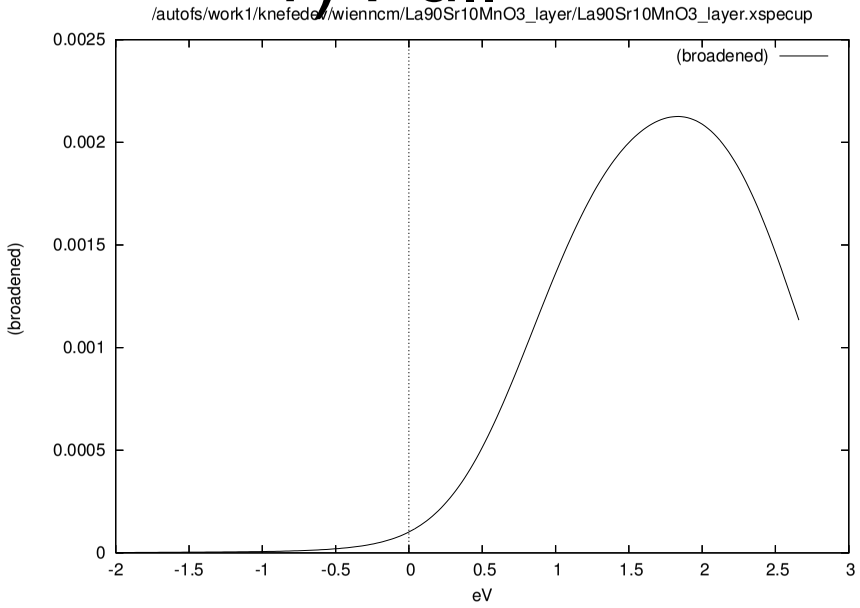


2) Partial

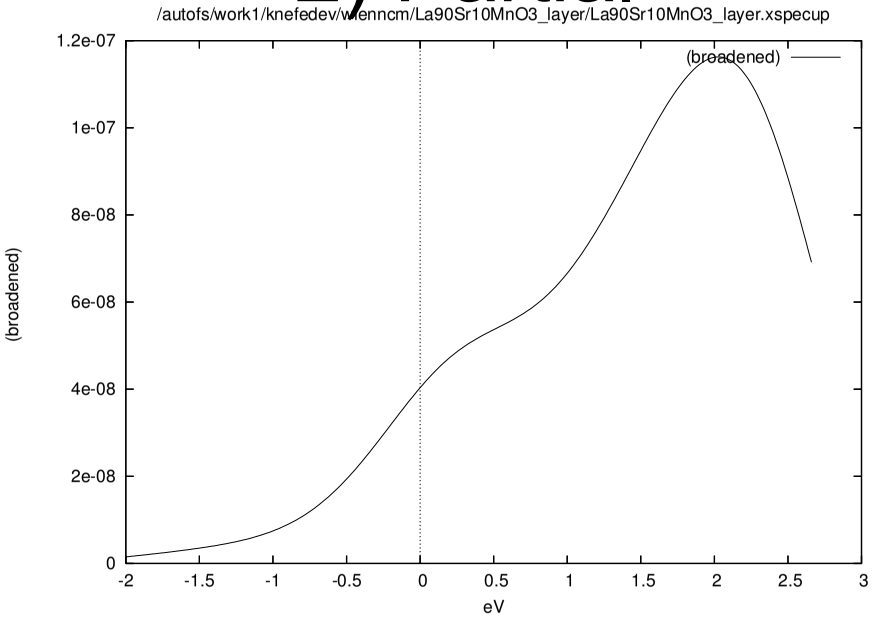


X-spectrum $La_{0.9}Sr_{0.1}MnO_3$

1) Full



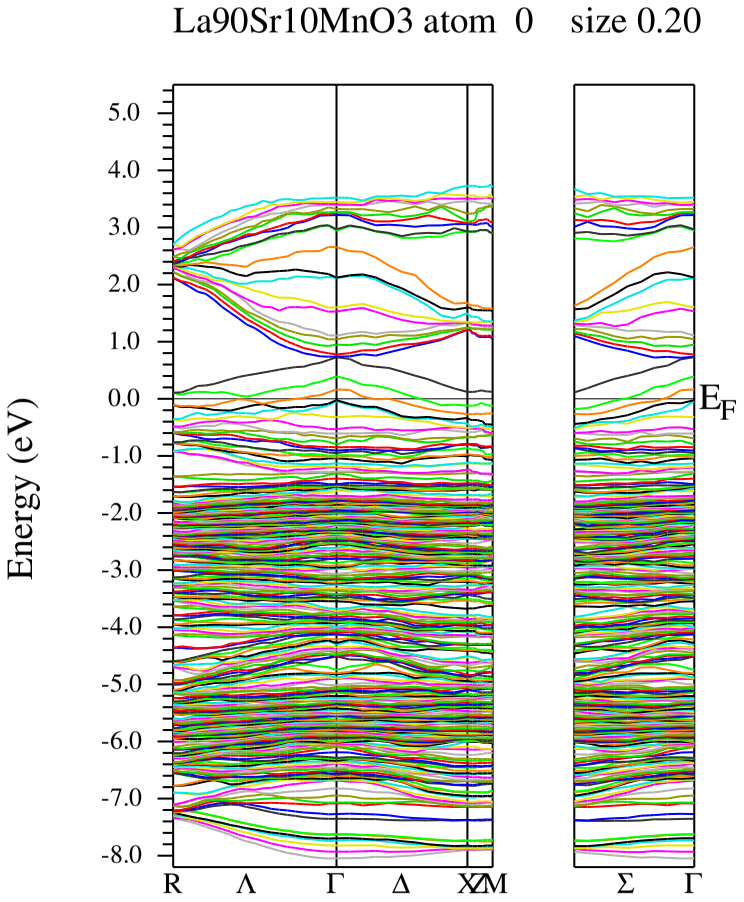
2) Partial



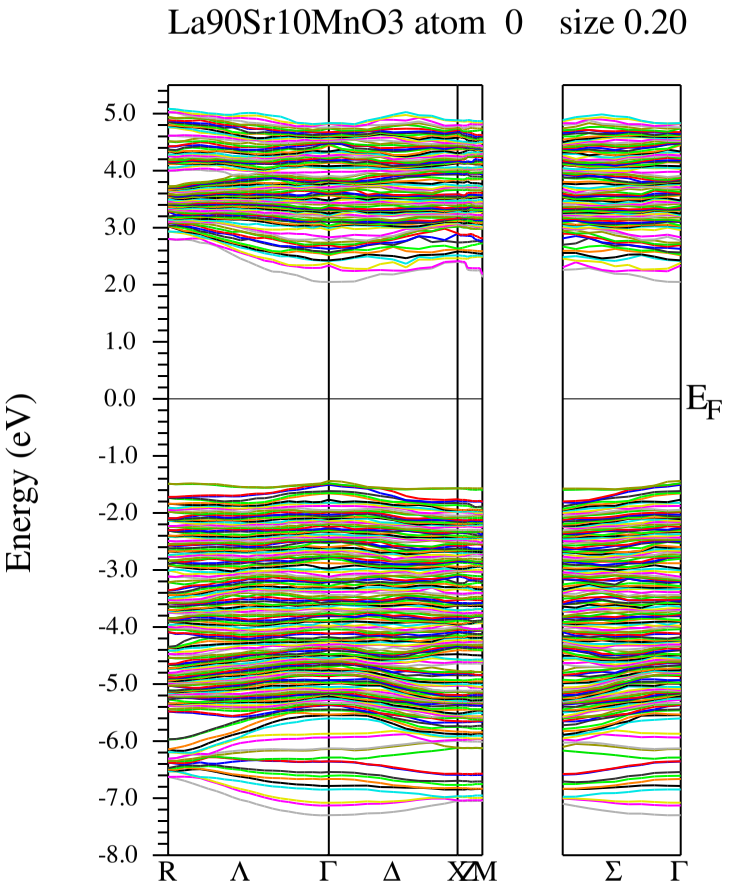
Band Structure $La_{0.9}Sr_{0.1}MnO_3$

1) Full occupation

spin up



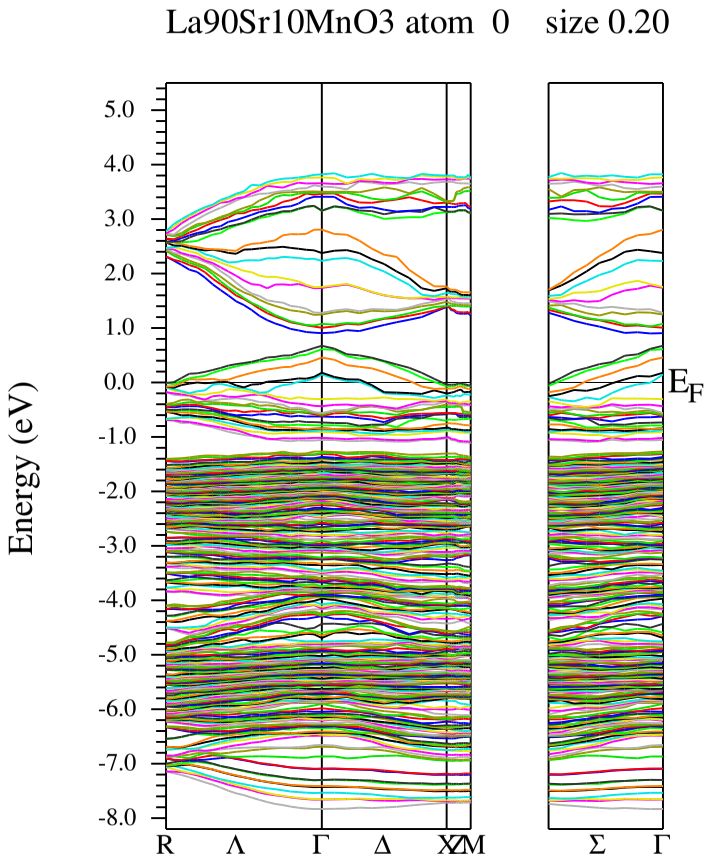
spin dn



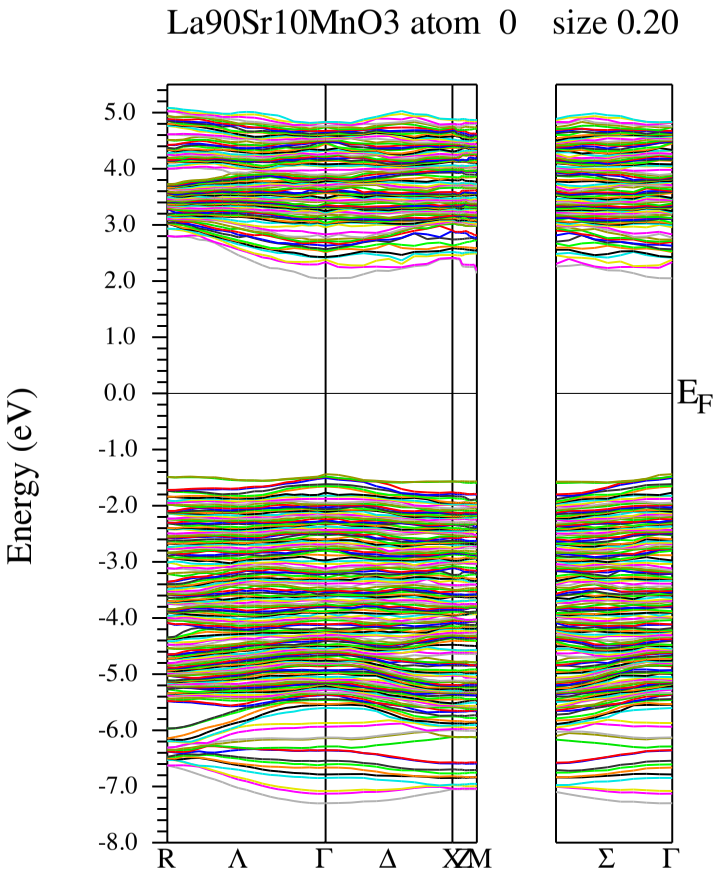
Band Structure $La_{0.9}Sr_{0.1}MnO_3$

2) Partial occupation

spin up



spin dn



Summary

- DFT gives us an exact and powerful tool for theoretical research in condensed matter physics, chemistry, materials science

- WIEN2k program package is interesting and helpful implement for a*b initio* calculations of magnetic superstructures

- There is possibility to calculate different magnetic structures, but the choice of magnetic order type for the given crystal structure is made by hand.

Thank you!