Impact of excess iron on the calculated electronic, magentic, and optical properties of Gallium ferrite

Fatima IBRAHIM

supervisor :
Mébarek ALOUANI

Institut de Physique et de Chimie des Matériaux de Strasbourg (IPCMS-DMONS)

Outline

I . Introduction

- Magnetoelectric multiferroics
- Gallium ferrite: a magnetoelectric ferrimagnet

II . Method of calculation

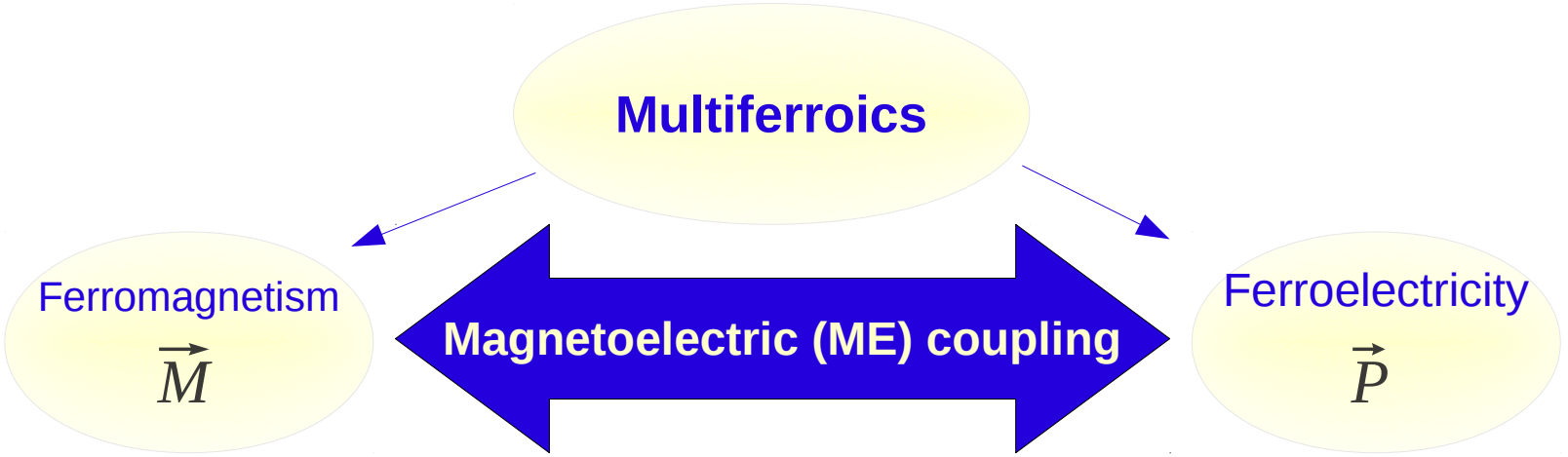
III . Results

- Optimizing calculation parameter: *U*-value
- Structural properties
- Electronic properties
- Magnetic properties
- Magnetic anisotropy
- Optical properties

IV. **Conclusion & perspective**

Magnetoelectric multiferroics

Magnetoelectric multiferroics



Magnetoelectric multiferroics

Multiferroics

Ferromagnetism $\vec{M}$

Magnetoelectric (ME) coupling

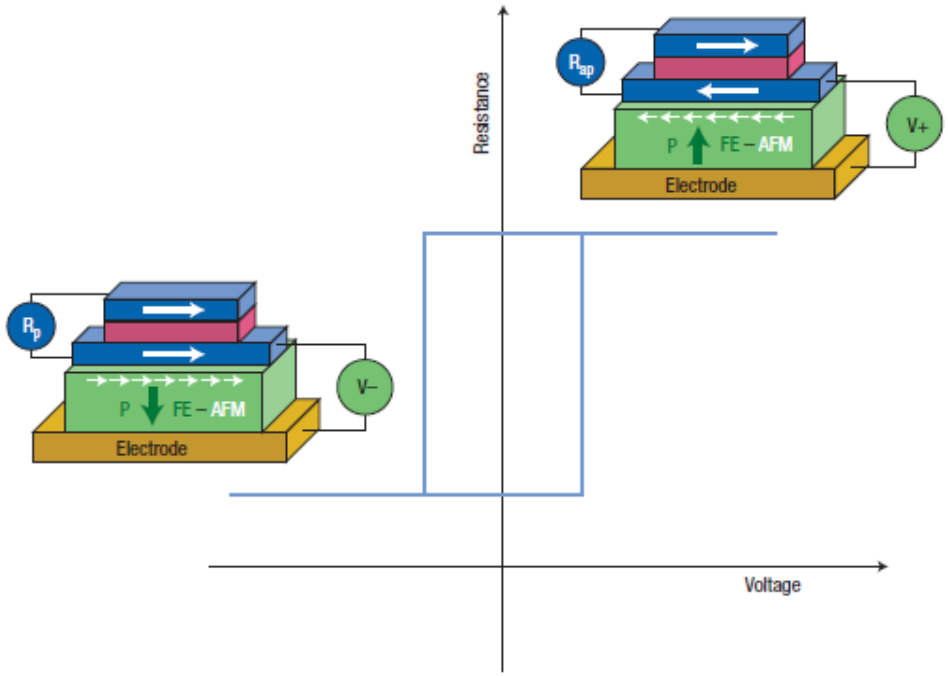
Ferroelectricity $\vec{P}$

Strong ME coupling

Possible control of:

$\vec{P}$ *by* $\vec{H}$ $\quad$ $\vec{M}$ *by* $\vec{E}$

ME device



Gallium ferrite : a magnetoelectric ferrimagnet

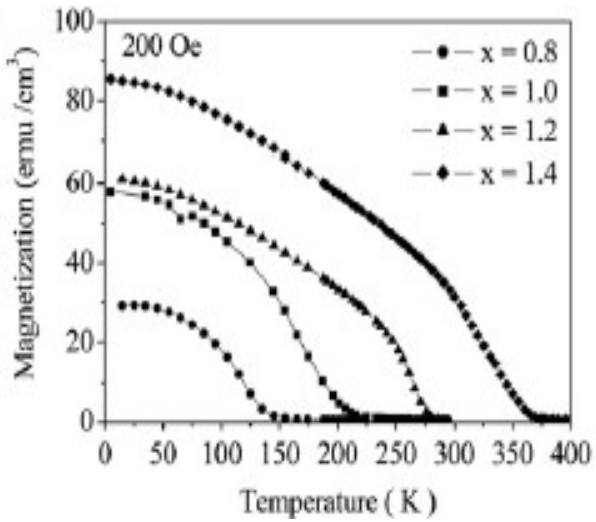
- *Experimentally demonstrated:*

Ferrimagnet
(nonvanishing net **M**)

strong ME coupling
α(GFO) >> α(Cr_2O_3)

$Ga_{2-x}Fe_xO_3$ (GFO)

Magnetic order
reaches RT for x=1.4

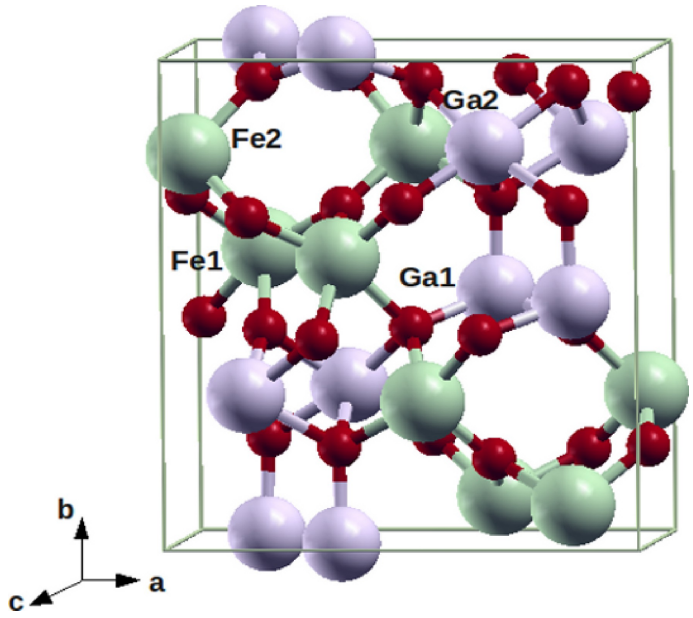


Properties are influenced by the Ga/Fe ratio

Method

VASP package: **PAW** formalism

- Including spin-orbit coupling
- Different levels of approximation (LDA - GGA)
- Correlated system → on-site Coulomb interaction (LDA+*U*)



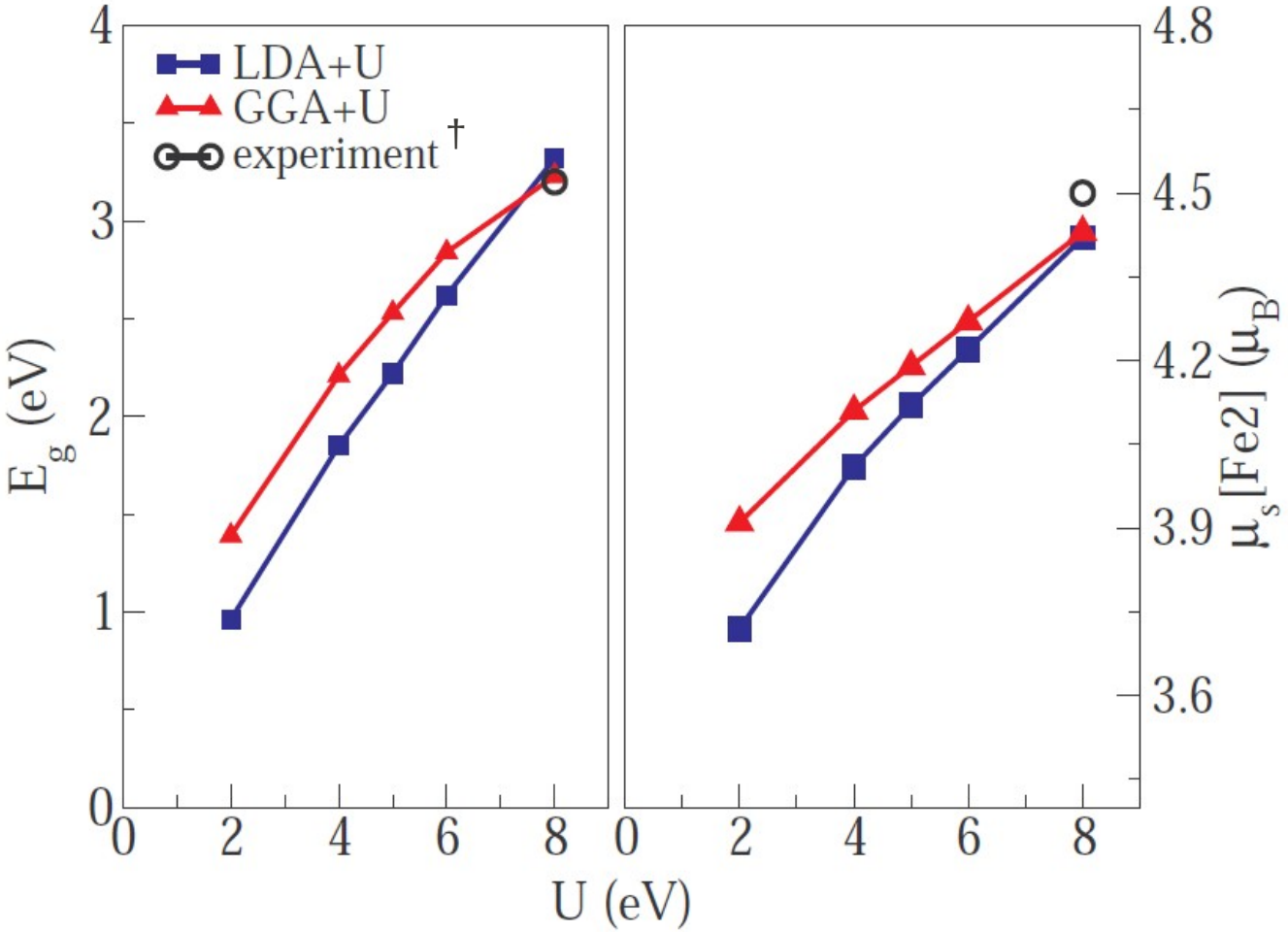
Structure

- supercell of 8 f.u.
- Orthorhombic structure
- 4 different cation sites: octahedral (Fe1,Fe2,Ga2) & tetrahedral (Ga1)
- (Atomic + volume) relaxation

Ground state : excess Fe occupies Ga2

Optimizing Hubbard-value *U*

- Evolution of the energy band gap & spin moment as a function of *U*-value

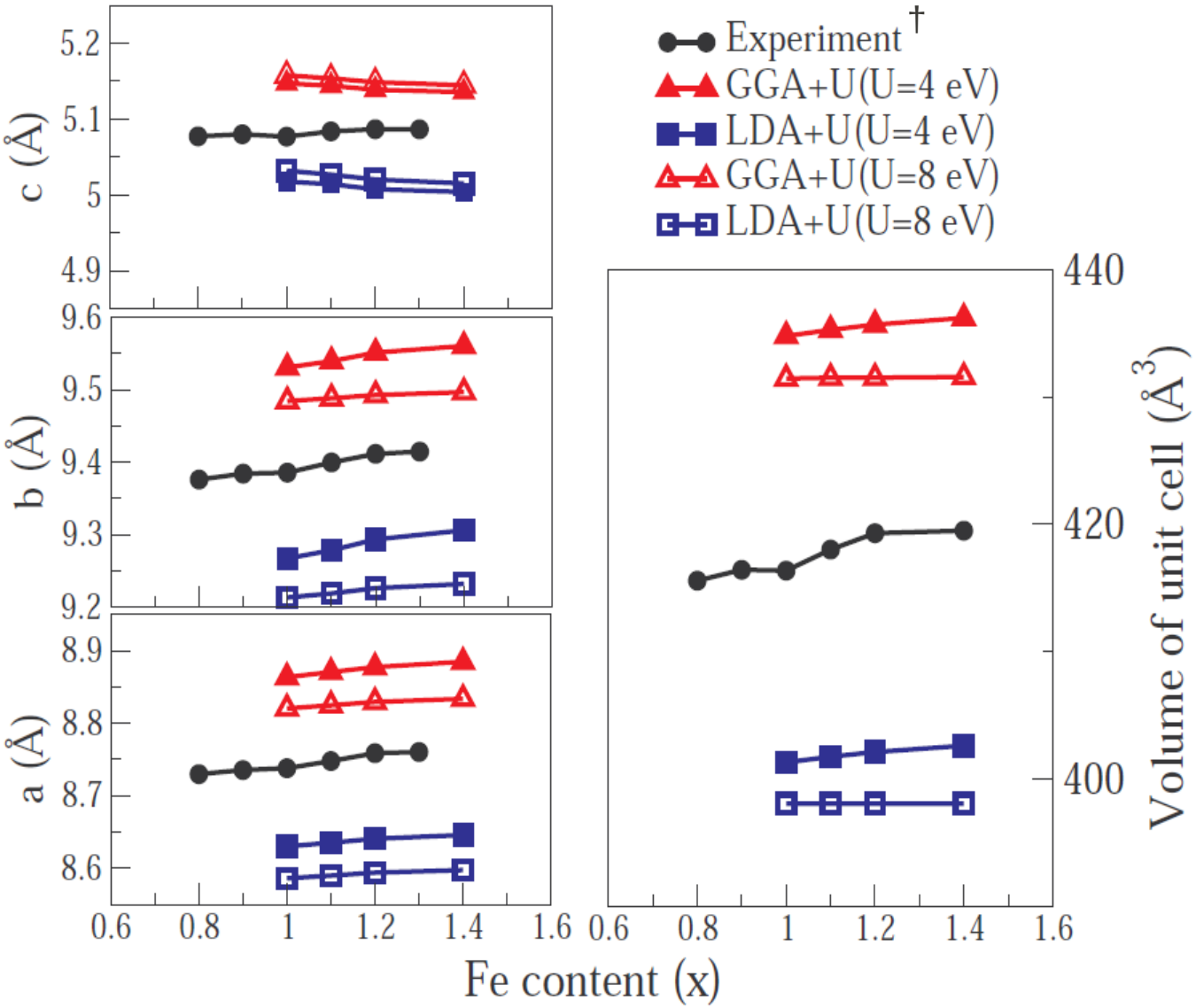


- Good agreement with experimental results reached for ***U* = 8 eV**

† A. M. Kalashnikova et al. JETP Lett. 81, 452 (2005)
T. Arima et al. PRB 70, 0644261 (2004)

Structural properties

- Variation of the lattice parameters & volume as function of Fe content



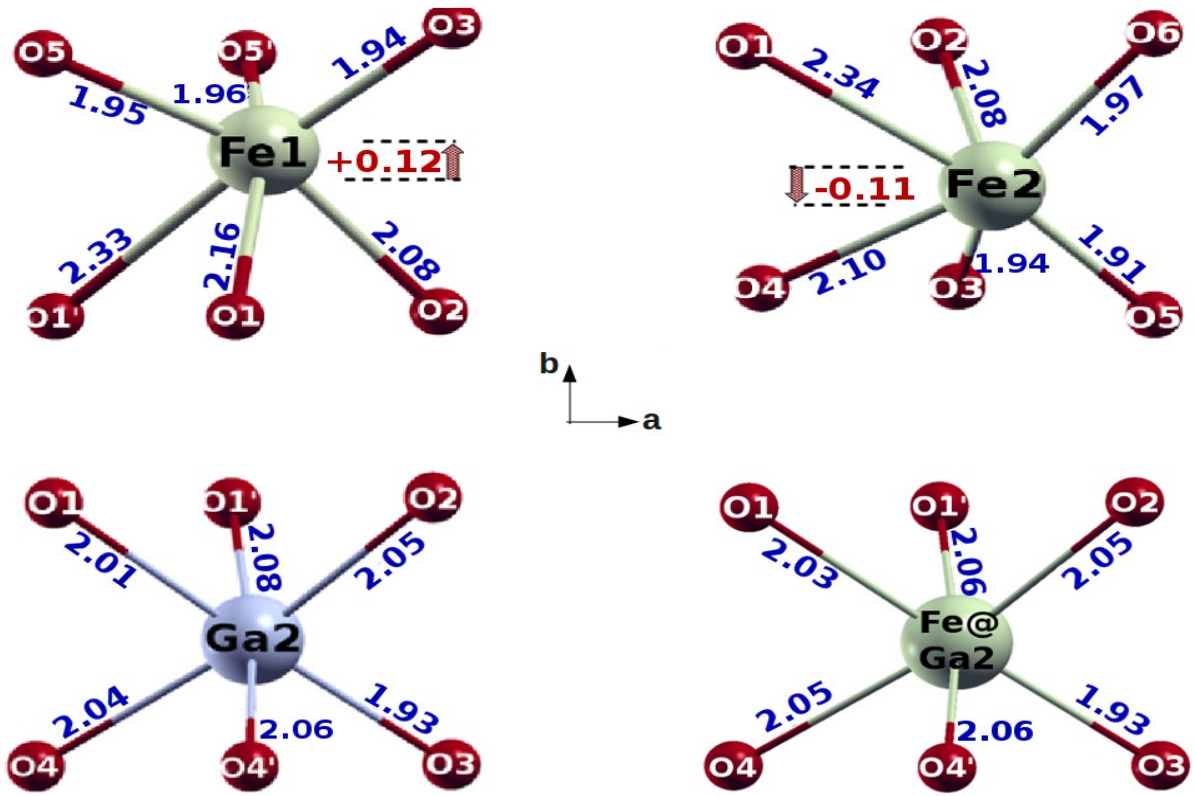
- Structural parameters are sensitive to the ex-corr and the *U*-value used
- Unit cell volume increases with the Fe content

† S. Mukherjee et al., in press (2012)

Structural properties

- Bond lengths for the different octahedral sites

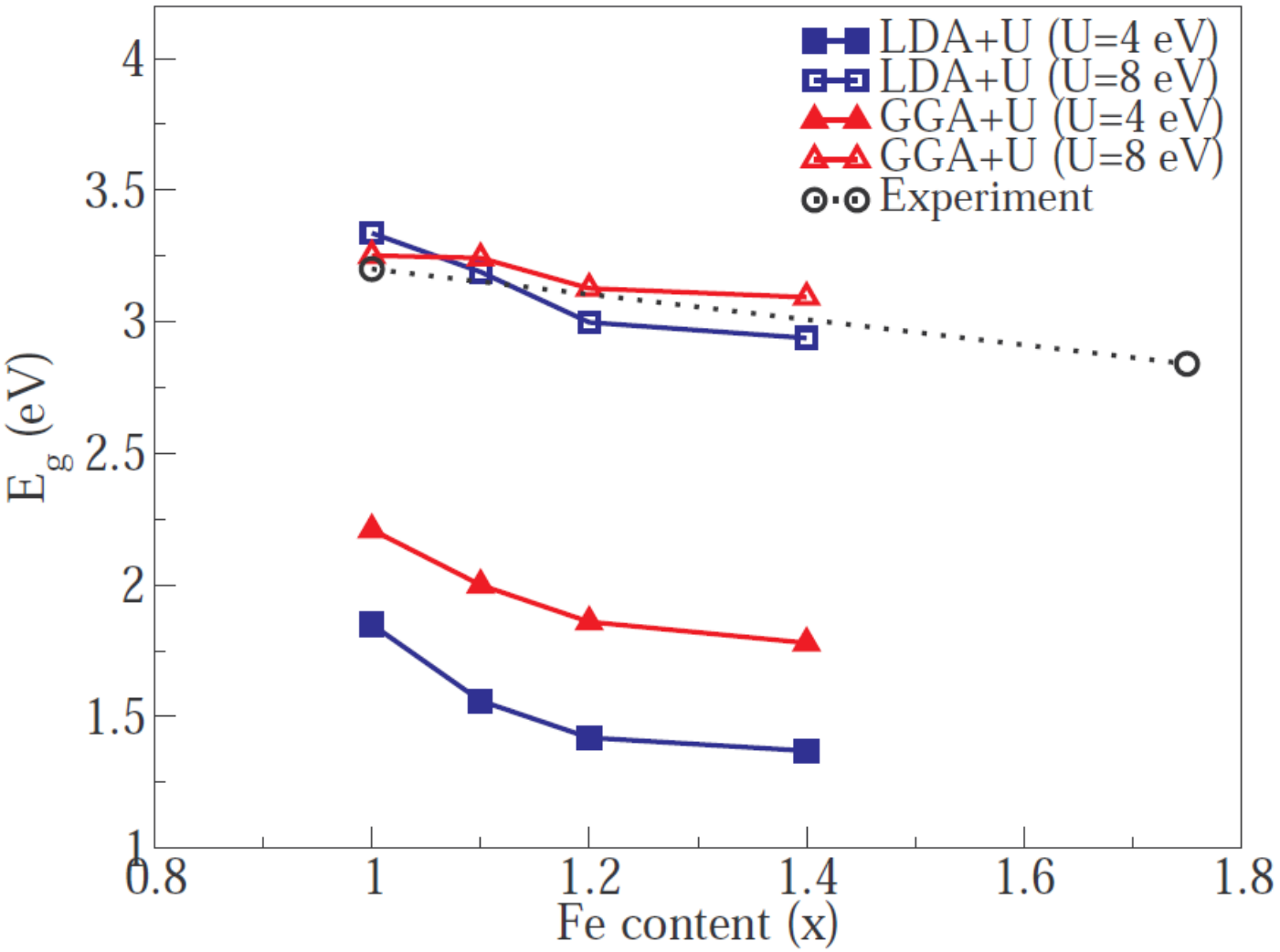
GGA+U=8 eV



- Fe1 is distorted mainly along + *b*-axis
- Fe2 is distorted mainly along - *b*-axis
- Ga2 site is almost regular

Electronic properties

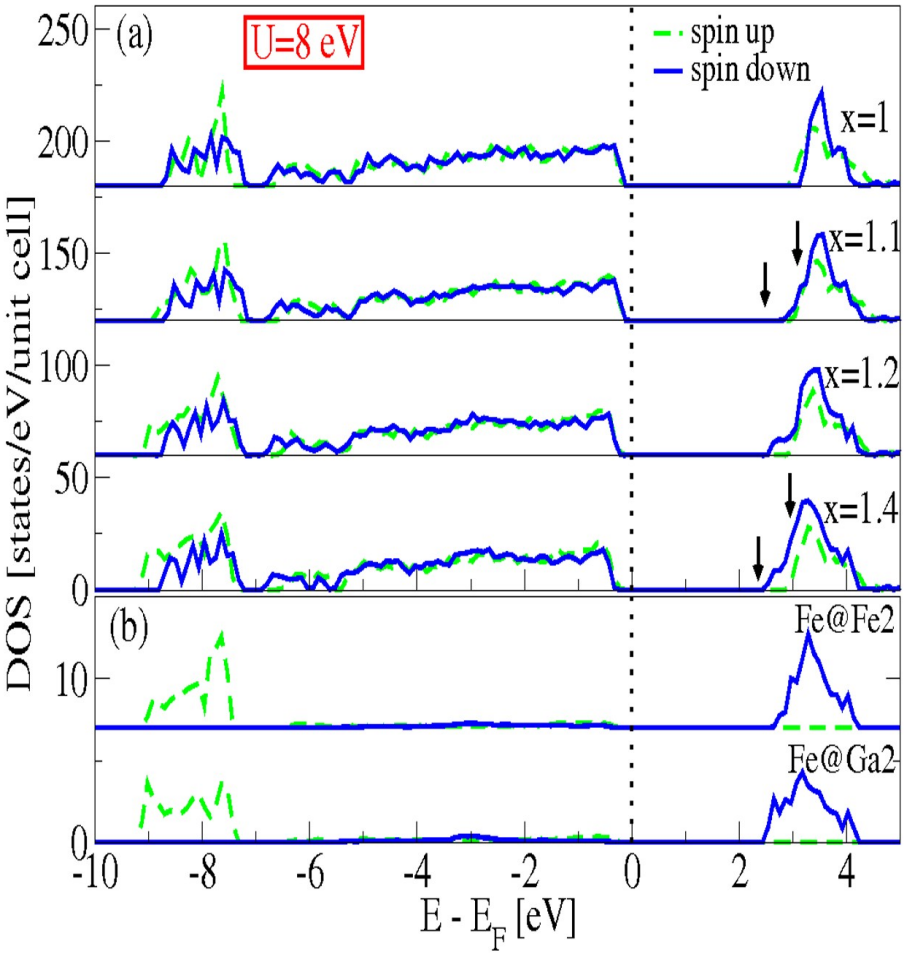
- Variation of the energy band gap as function of Fe content

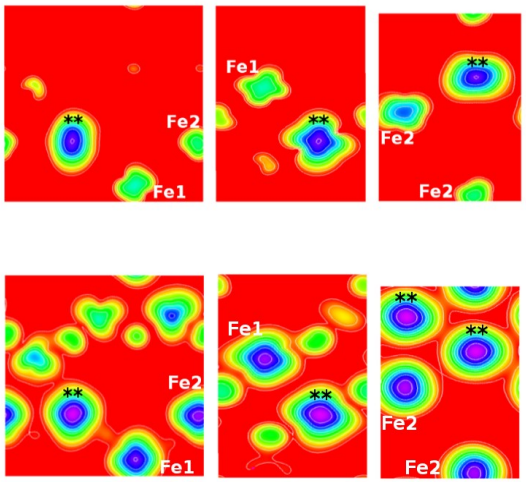


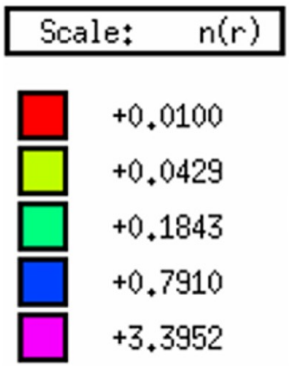
- Band gap decreases as the Fe content is increased

Electronic properties

- DOS & partial charge plots as function of Fe content







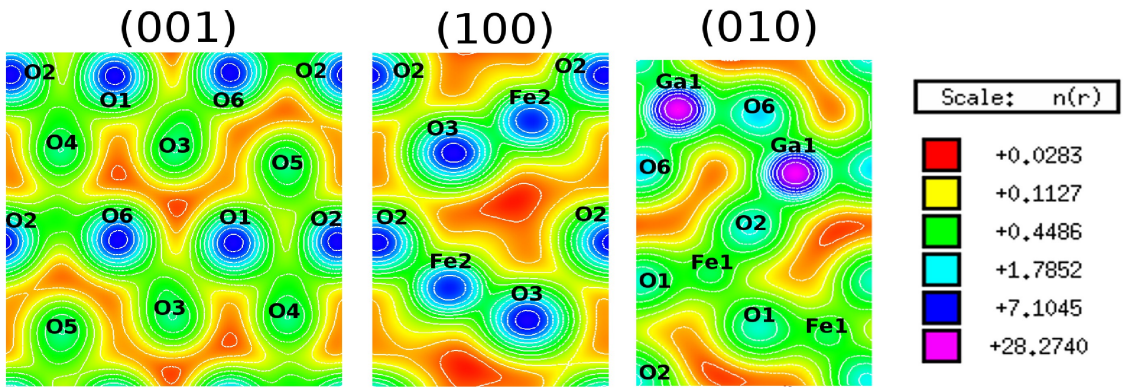
- The excess Fe ions (occupying Ga2 site) enhance the d-symmetry of the unoccupied states → reducing band gap

Electronic properties

- Bader charges per ionic site

	$x = 1$	$x = 1.1$	$x = 1.2$	$x = 1.4$
Ga1	+1.788	+1.8	+1.796	+1.798
Ga2	+1.832	+1.85	+1.847	+1.851
Fe1	+1.633	+1.646	+1.641	+1.638
Fe2	+1.631	+1.645	+1.644	+1.646
Fe at Ga2	- -	+1.659	+1.653	+1.657
O1	−1.21	−1.2	−1.179	−1.161
O2	−1.183	−1.183	−1.175	−1.168
O3	−1.091	−1.085	−1.069	−1.057
O4	−1.198	−1.206	−1.192	−1.186
O5	−1.028	−1.04	−1.038	−1.037
O6	−1.172	−1.179	−1.178	−1.179

- Charge density plots for $GaFeO_3$



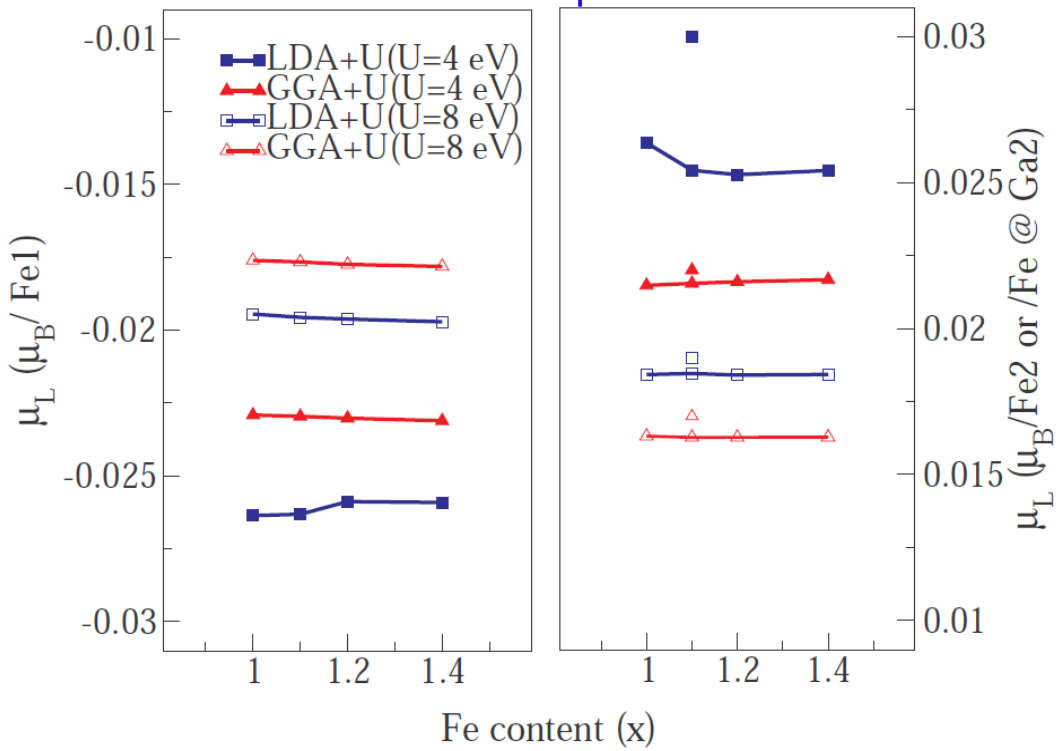
- Non trivial degree of covalency → bonding is not totally ionic
- Excess Fe @ Ga2 has charge smaller than parent Ga (related to the smaller band gap calculated)

Magnetic properties

- Calculated spin moment per ionic site

	$\mu_S[\mu_B]$	$x=1$	$x=1.1$	$x=1.2$	$x=1.4$
	Fe at Ga2		4.08	4.08	4.08
LDA + U	Fe at Fe1	−4.02	−3.98	−3.97	−3.94
	Fe at Fe2	4.01	4.01	4.02	4.02
	Fe at Ga2	(4.7)	4.15	4.15	4.15
GGA + U	Fe at Fe1	−4.11 (−3.9)	−4.10	−4.08	−4.07
	Fe at Fe2	4.10 (4.5)	4.11	4.11	4.11

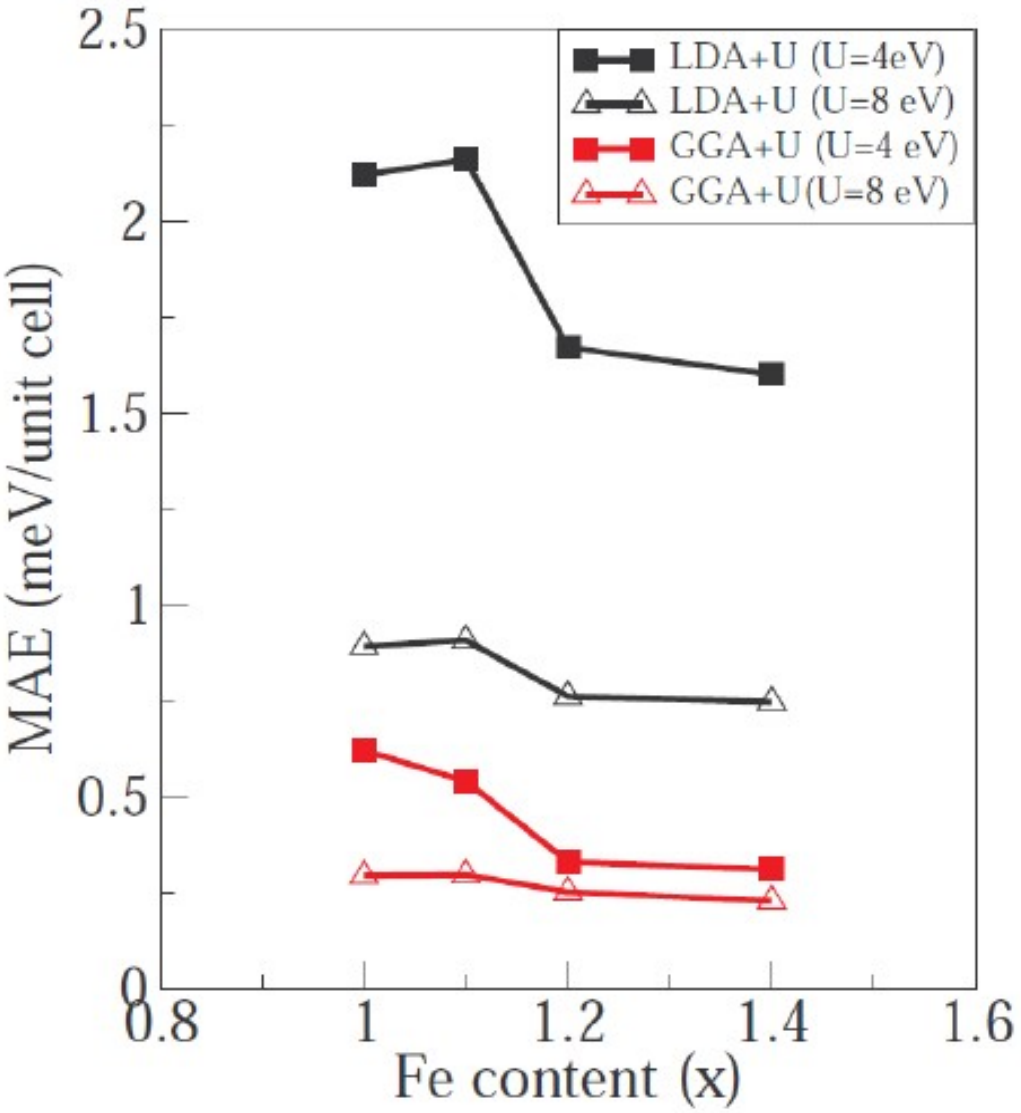
- Calculated orbital moment per ionic site



- Excess Fe ion (occupying Ga2 site):
  - is FM coupled to Fe2
  - holds larger spin & orbital moment than parent Fe sites
- Larger *U*-value results in smaller orbital moments

Magnetocrystalline anisotropy

- Magnetic anisotropy energy (MAE) = $E_{total}(\vec{M}$ // *b*-axis) - $E_{total}(\vec{M}$ // *c*-axis)

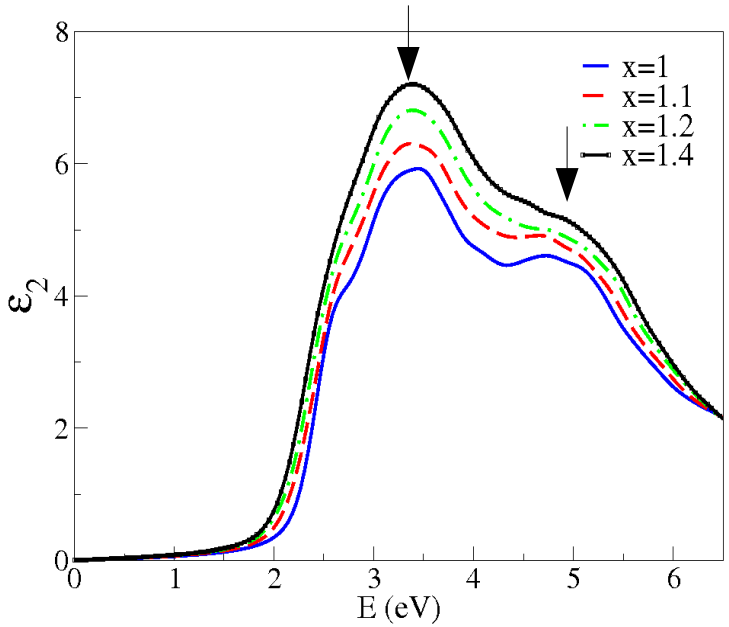


- MAE > 0 → *c*-axis magnetization easy axis (agreement with expt.)
- Direction of the easy axis linked to structure (distortion of parent Fe sites in *ab*-plane)
- MAE value drops as Fe content increases: excess Fe ions occupy Ga2 site which is more regular i.e. less anisotropic.

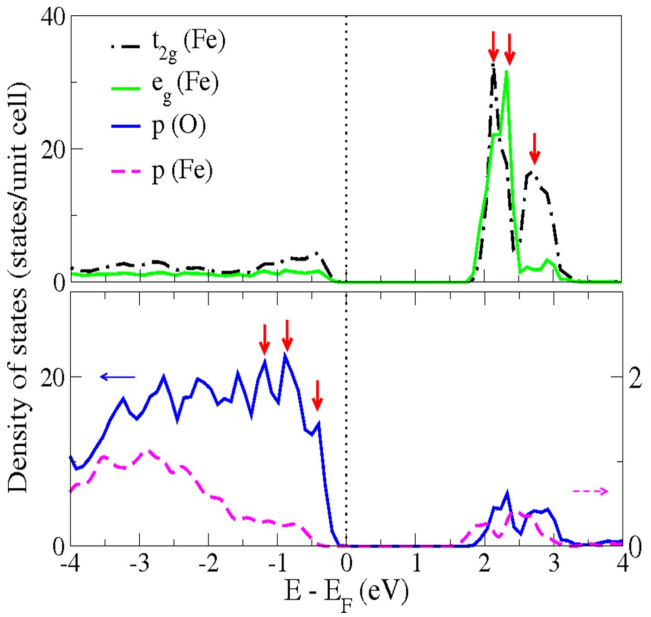
F. Ibrahim & M. Alouani, PRB 85, 174411 (2012)

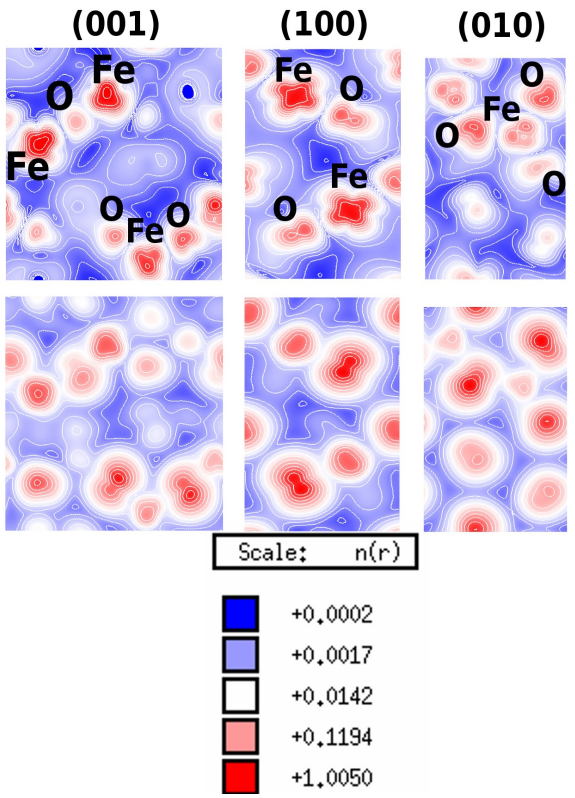
Optical properties

- Evolution of the dielectric function as a function of the Fe content



- PDOS and charge density plots for the valence and conduction bands





- Two main optical features whose energy positions are independent of x
- Oscillatory strength increases with the Fe content due to enhanced Fe unoccupied states

- Fe-d states in conduction band and O-p states in the valence band show energy and spatial overlap → optical features ocrrespond to CT transitions from O-p to Fe-d states.

*A. Thomasson et al., RSC advances **3**, 3124 (2013)*

Conclusion & perspective

Conclusions

- Setting on-site Coulomb interaction U=8 eV better describes the experimental results on GFO properties

- Bonding in GFO is not completely ionic

- Properties are influenced by increasing Fe concentration :

  - increase of the unit cell volume
  - decrease of the energy band gap
  - decrease of the MAE (discussed in relation to structure)
  - altering optical spectra's features

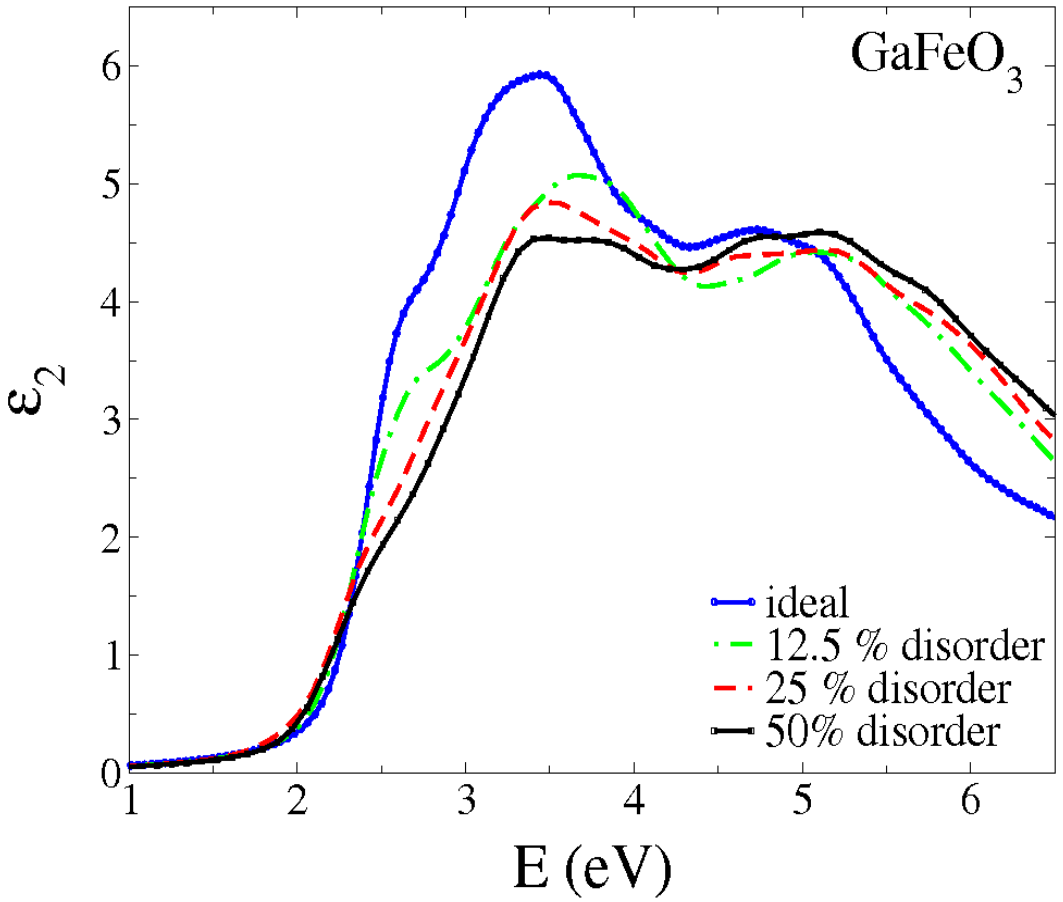
Perspective

- Exploring the relation between polarization & magnetism in GFO (magnetoelectric effect)

Thanks for your attention !

Optical properties

- Evolution of the dielectric function as a function of the Fe/Ga disrorder percentage



- Intensity of the first peak shifts toward lower energies as the disorder percentage in promoted
- Intensity of the second peak almost doesn't change while it is boradened.