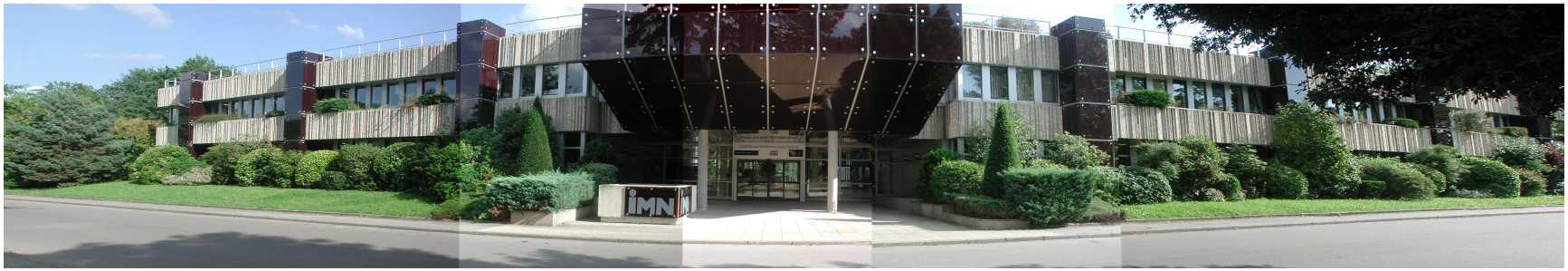
UNIVERSITÉ DE NANTES

INSTITUT DES MATERIAUX JEAN ROUXEL

IMN UMR CNRS 6502 - Université de Nantes



Insulator to metal transitions and resistive switching in the chalcogenide Mott insulator compounds AM_4X_8

***Benoît Corraze*, Etienne Janod, Laurent Cario,**

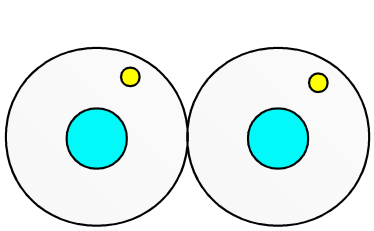
Benoit.corraze@cnrs-imn.fr

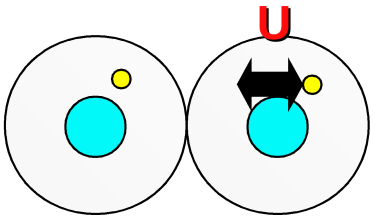
GDR MICO - Roscoff 2013

Mott Insulator

Metal

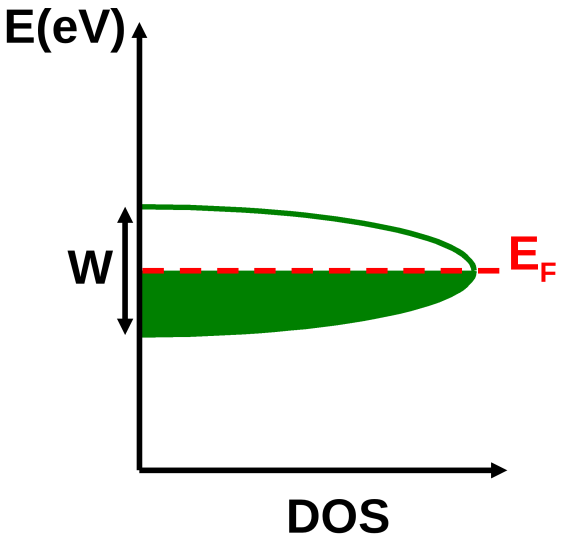
Mott Insulator

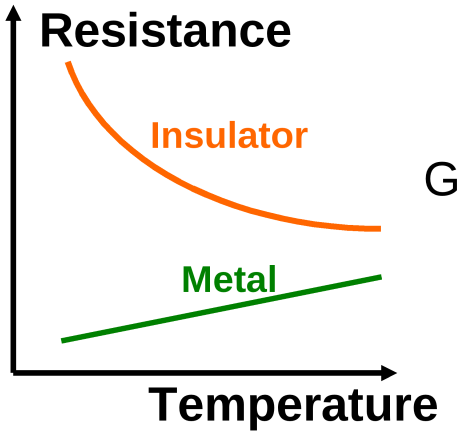


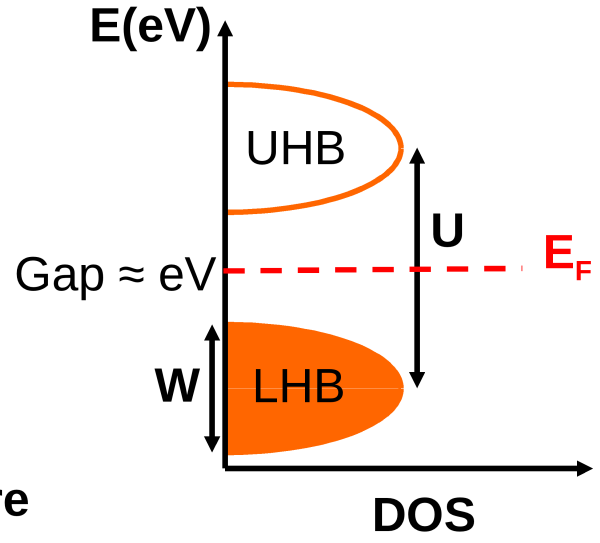


U << W

U >> W

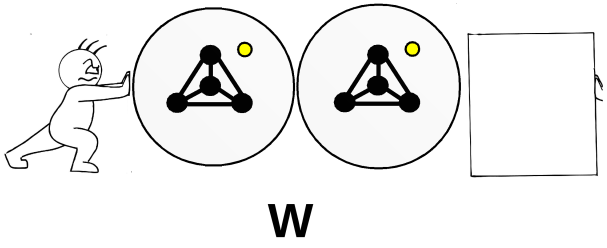


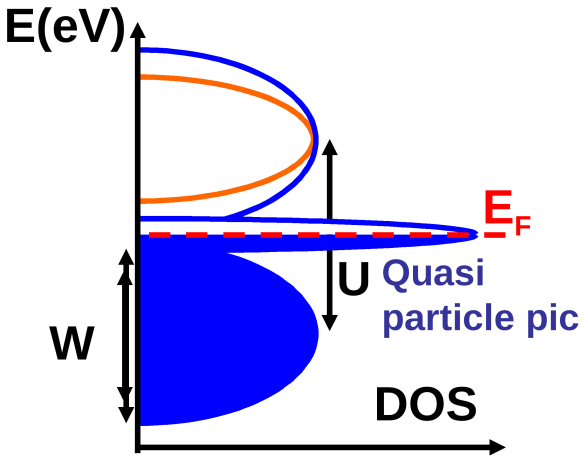


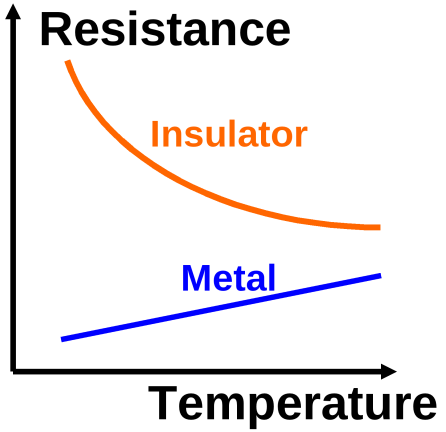


Bandwidth and filling control
Insulator to Metal Transition

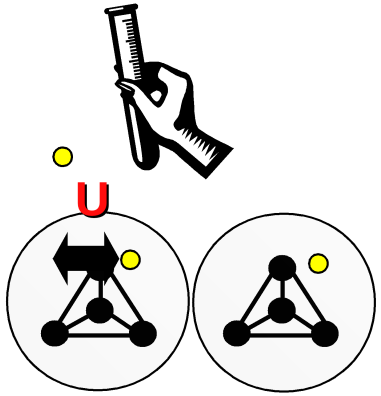
Pressure

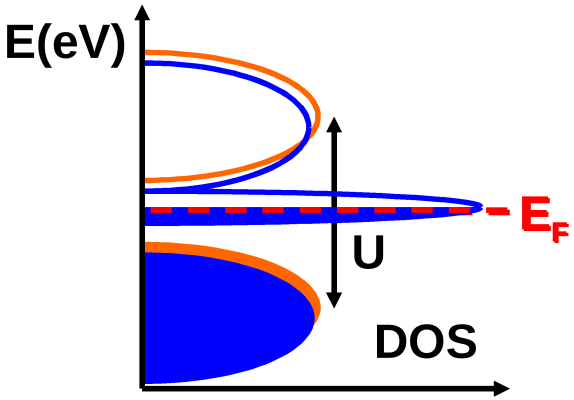


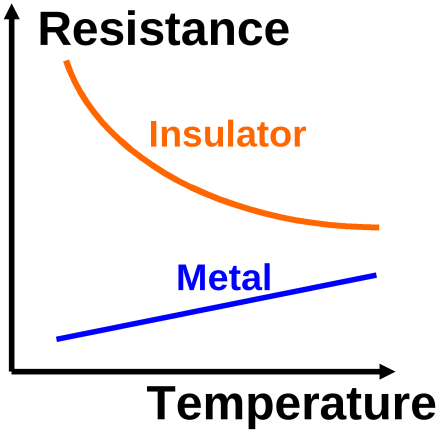




Doping x



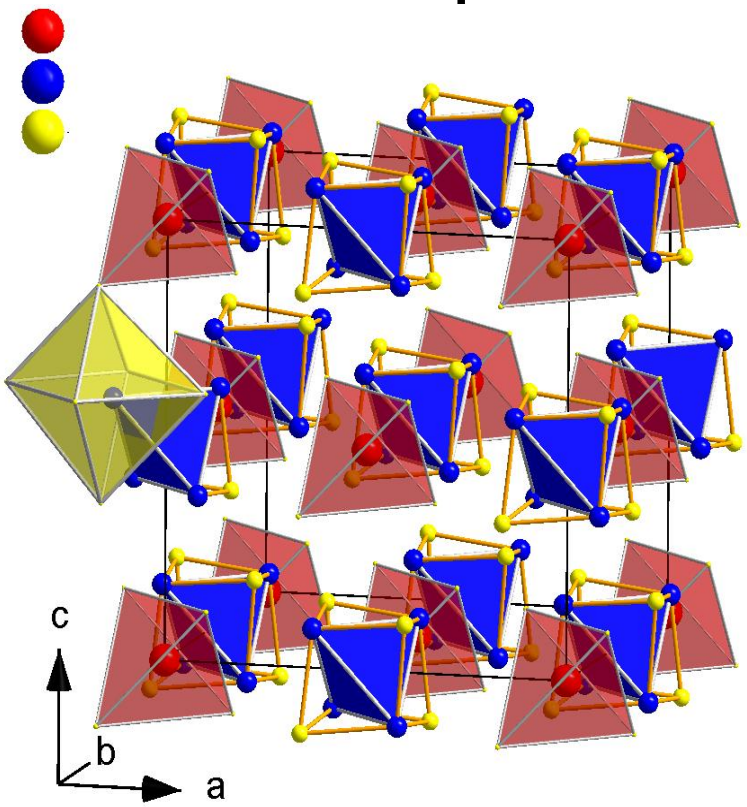


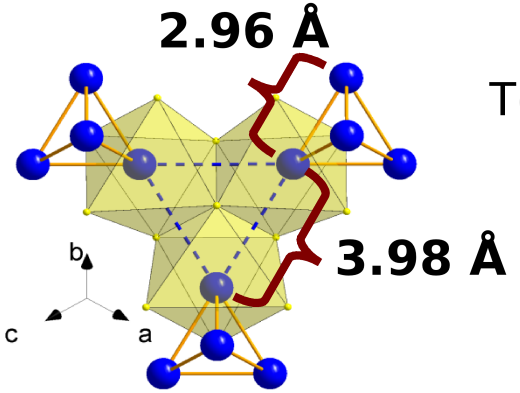


Exotic properties at the (Mott) insulator to metal

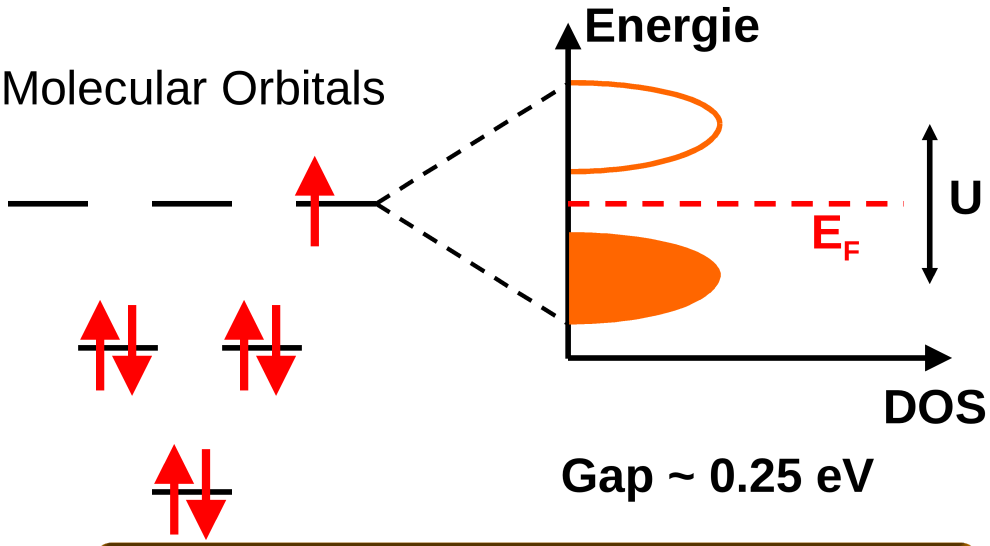
The Mott Insulator compounds AM_4X_8

Clustered lacunar spinel structure :





Tetrahedral Clusters
(GaV_4S_8)



A = Ga, Ge
M = V, Nb, Ta
X = S, Se

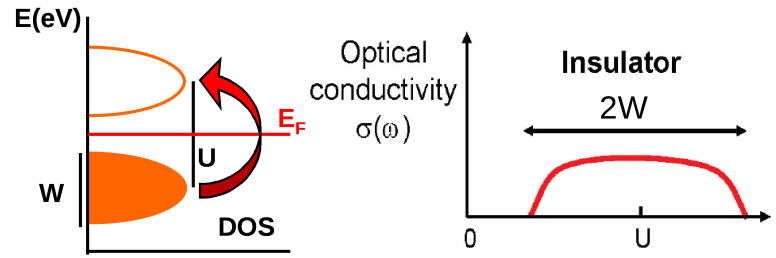
Ben Yaich, H.; Jegaden, J. C.; Potel, M.; Sergent, M.; Rastogi, A. K.;Tournier, R.
J. Less-Common Met. **1984**, *102*, 9.

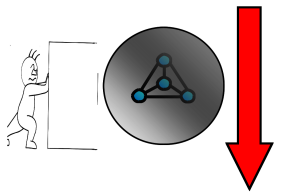
AM_4X_8 : Narrow Gap Mott Insulators

Pocha, R. et al., *J. Am. Chem. Soc.* **127**, *8732* (2005)

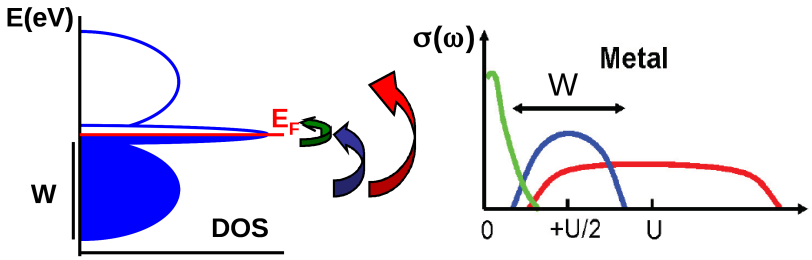
Bandwidth-controlled MIT in the AM_4X_8

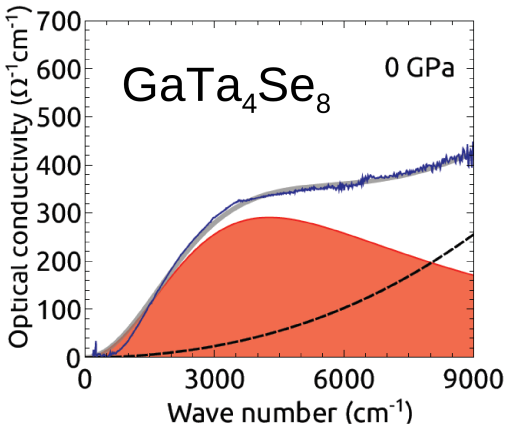
Mott Insulator



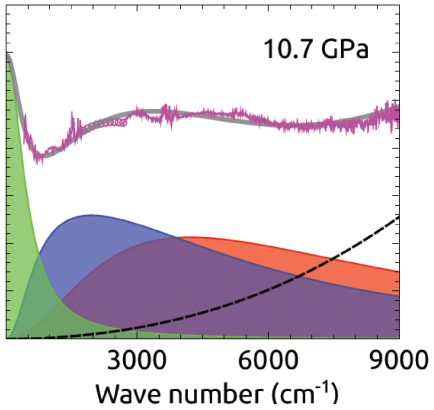


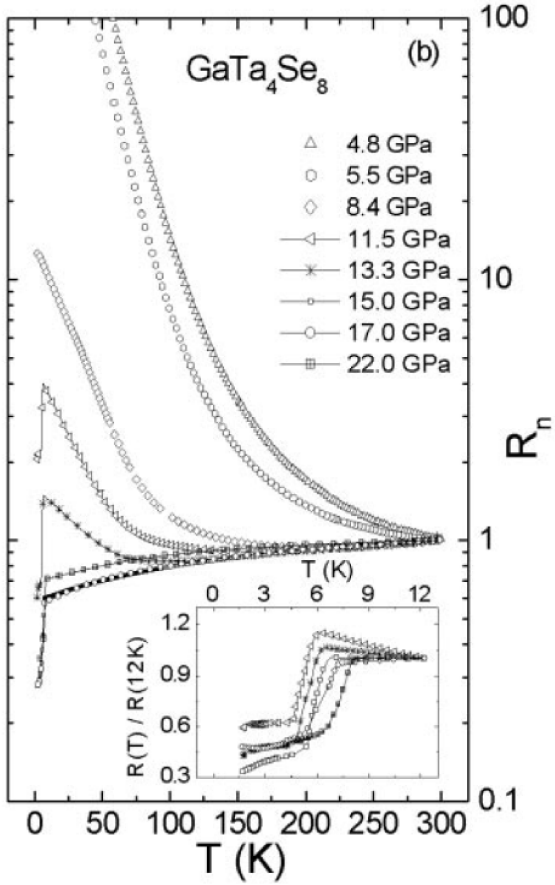
Correlated Metal





σ(ω)





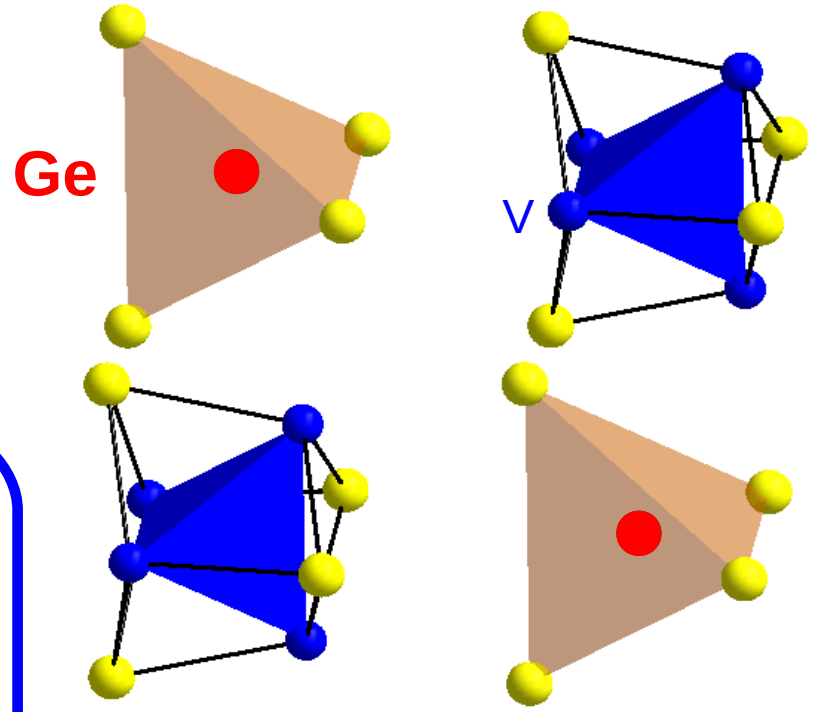
Abd-Elmeguid et al.,
Phys. Rev. Lett. **93**, 126403 (2004)

R. Pocha *et al.*,
J. Am. Chem. Soc. **127**, *8732* (2005)

Collaboration Vinh Ta Phuoc (V. Ta Phuoc *et al., accepted*

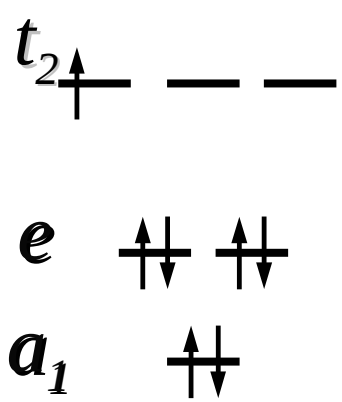
$GaTa_4Se_8$: canonical Mott Insulator to Metal Transition under pressure (+ superconductivity)

Filling-controlled MIT in the AM_4X_8 compounds ?



$Ga^{3+}V_4S_8$

7 e^- / V_4 cluster

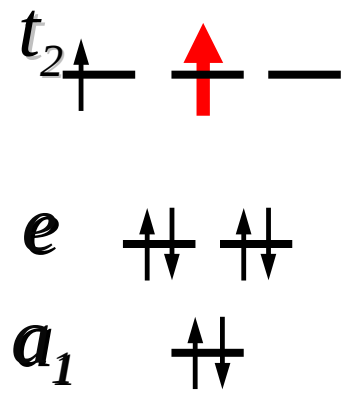


Doping on A site

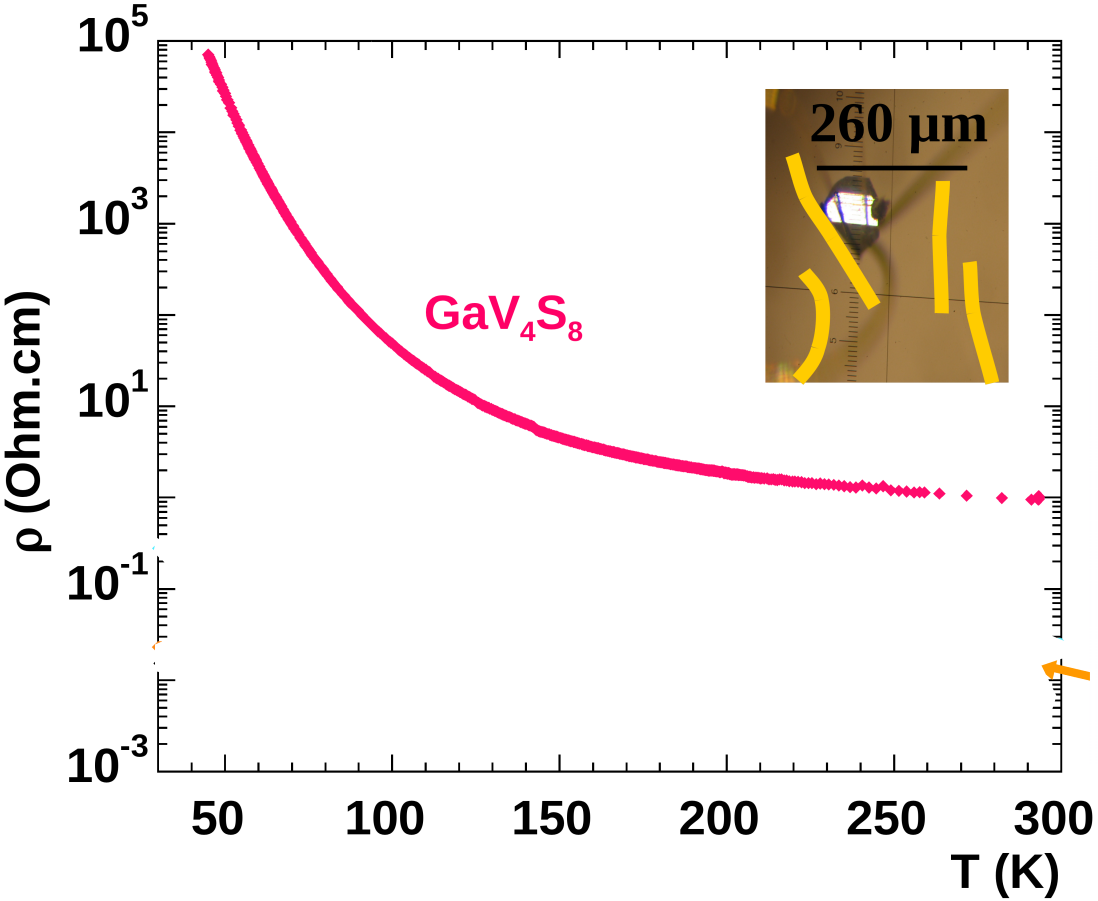
Substitution Ga^{3+} by Ge^{4+} : adding electrons (n doping)

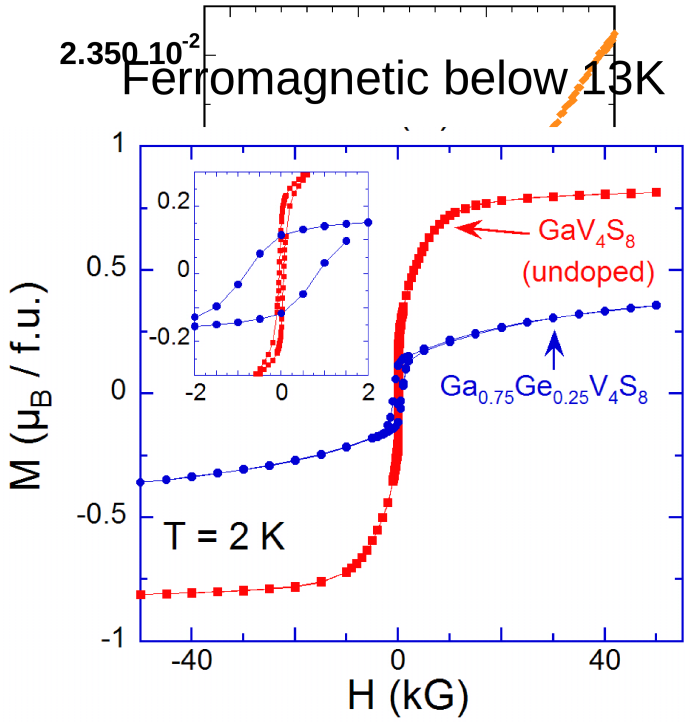
$Ge^{4+}V_4S_8$

8 e^- / V_4 cluster



Insulator to Metal Transition in the FM Mott Insulators $Ga_{1-x}Ge_xV_4S_8$



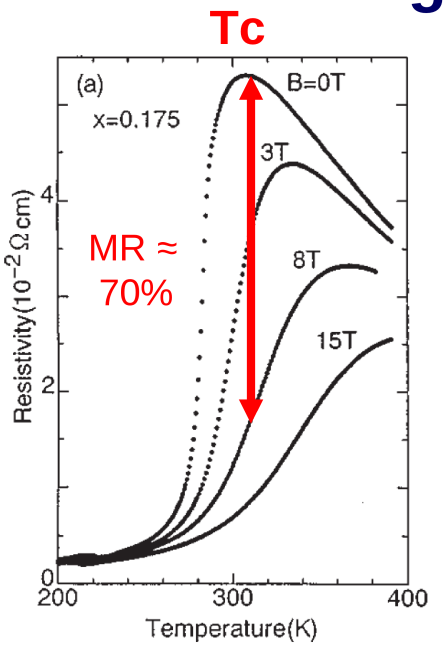


$Ga_{1-x}Ge_xV_4S_8$ a Mott transition in a Ferromagnetic

Negative CMR in the ferromagnetic $Ga_{1-x}Ge_xV_4S_8$

Manganites

→ **negative CMR**

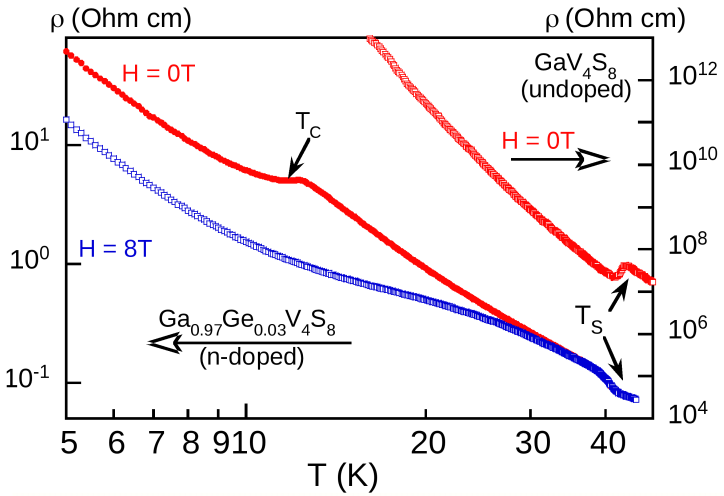


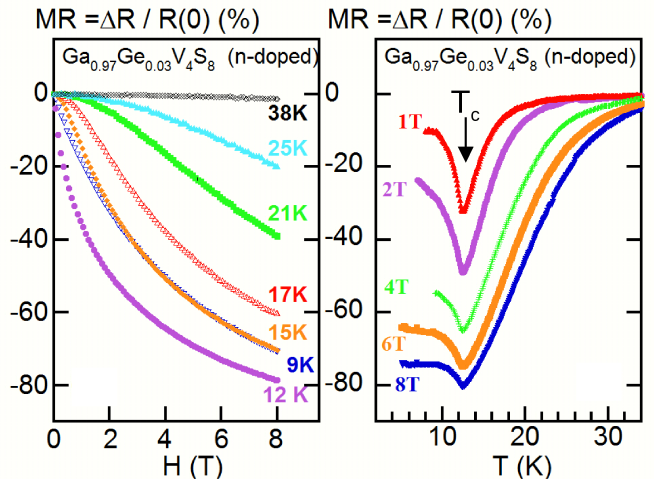
$La_{1-x}Sr_xMnO_3$ (x=0.175) crystal

Tokura *et al.*,

J. Phys. Soc. Jpn. **63**, 3931 (1994)

Ge-doped GaV_4S_8





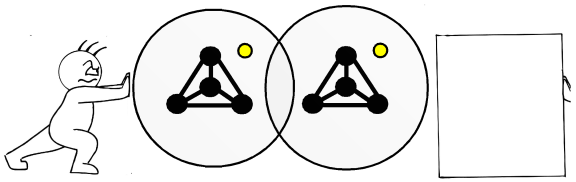
Colossal MagnetoResistance in (n-doped) $Ga_{1-x}Ge_xV_4S_8$

E. Janod *et al.* Submitted 2012

Mott insulators and microelectronic applications : towards "Mottronics" ?

Breaking the Mott Insulating State of AM_4X_8

Pressure



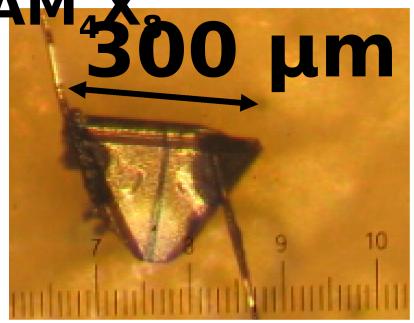
?

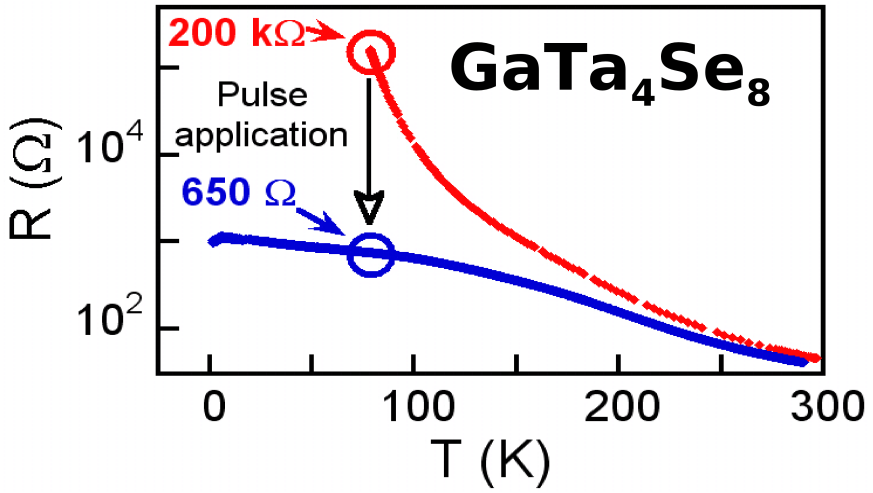
Doping

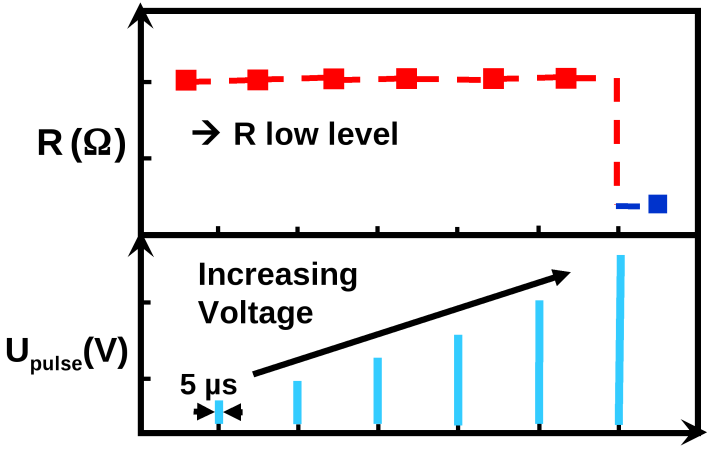
I-M transition under electric Field

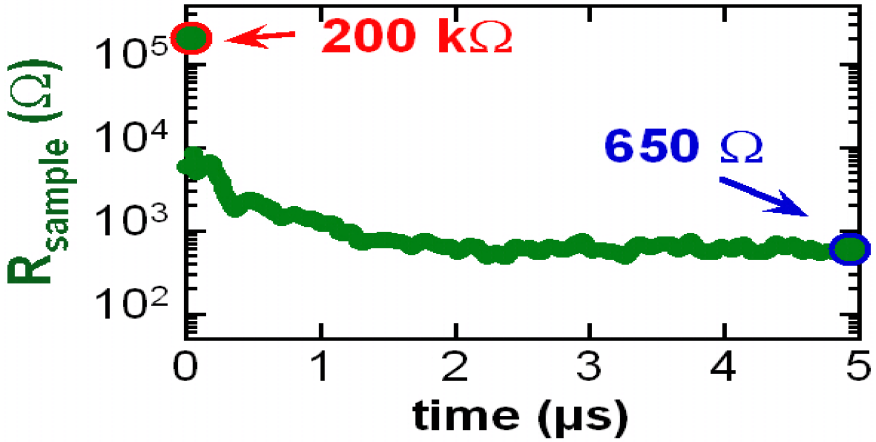
Resistive Switching in the AM_4X_8

Single crystal AM_4X_8





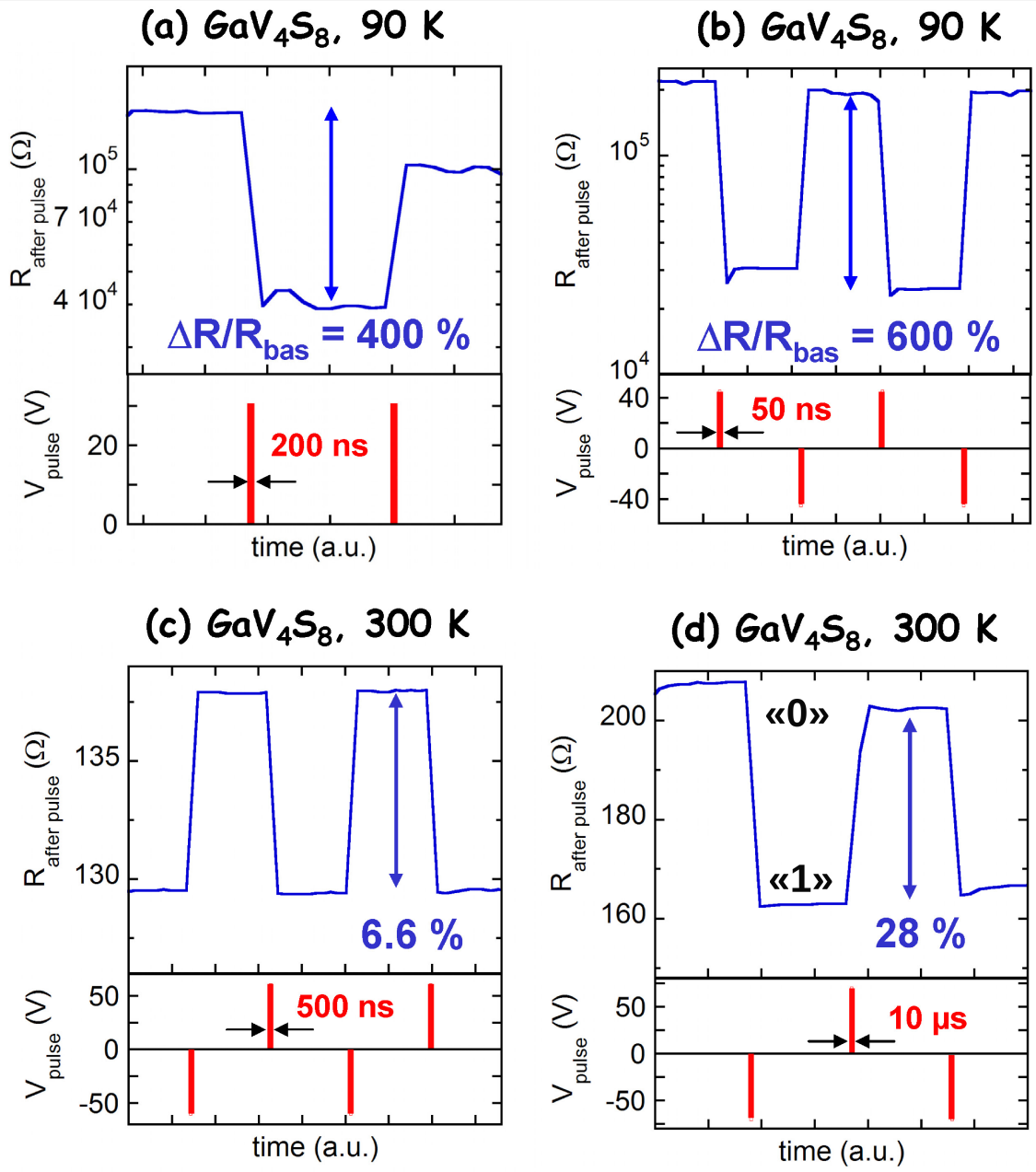




Non Volatile Resistive Switching, t <100 ns

C. Vaju et al., Advanced Materials **20**, 2760

Resistive Switching in the AM_4X_8



➡ **Resistive Switching REVERSIBLE**

➡ **Cycle at Room Temp.**

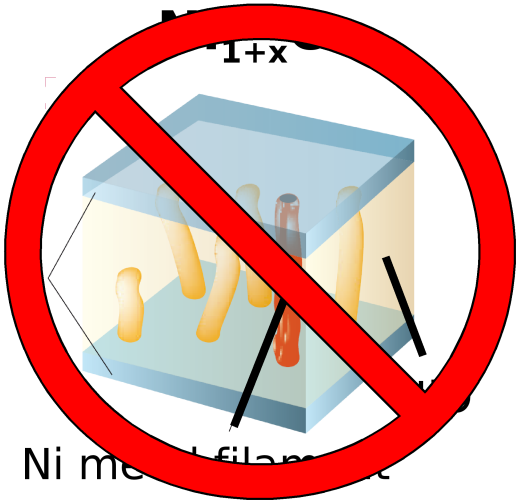
AM_4X_8 = Good candidate for RRAM memories

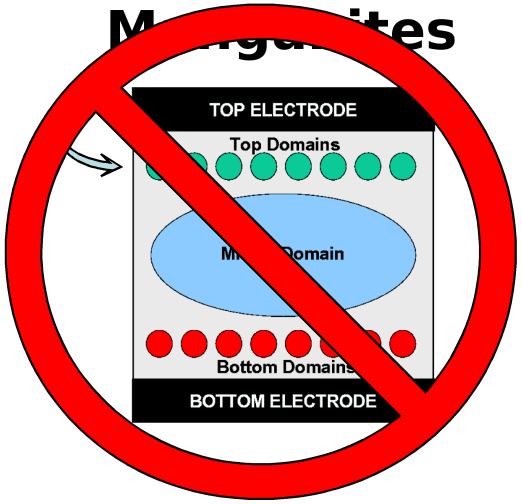
L. Cario *et al.*, Adv. Mater. **22**, 5193 (2010)

L. Cario et al. - Patent CNRS - Université de Nantes

AM_4X_8 : already known mechanism ?

Proposed mechanisms for RRAM



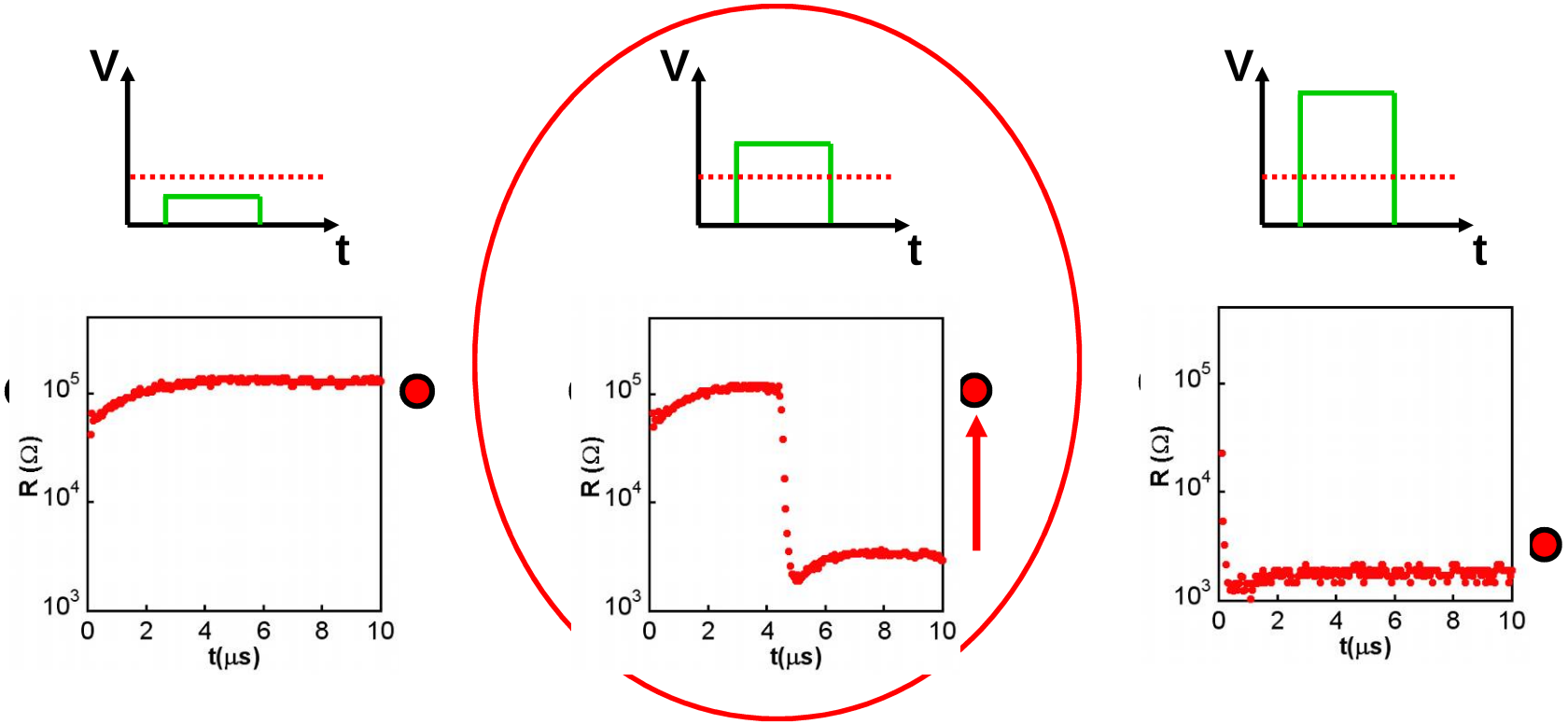


New mecanism of resistive switching ≠ other RRAM

2011, Emerging Research Devices

Resistive switching in the AM_4X_8 compounds

$GaTa_4Se_8$ 77 K

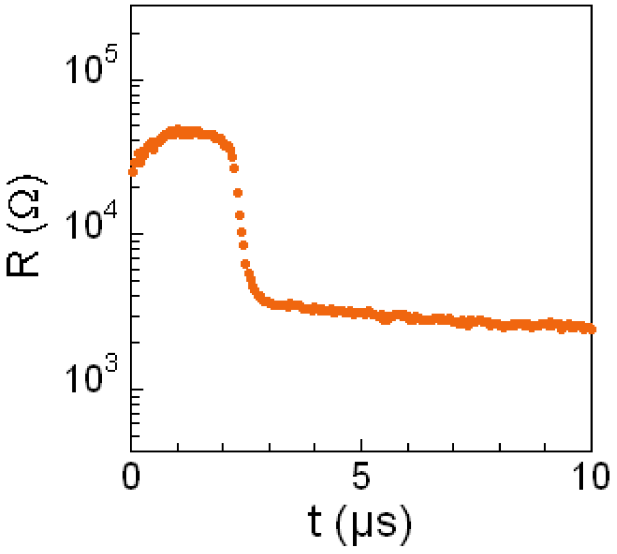


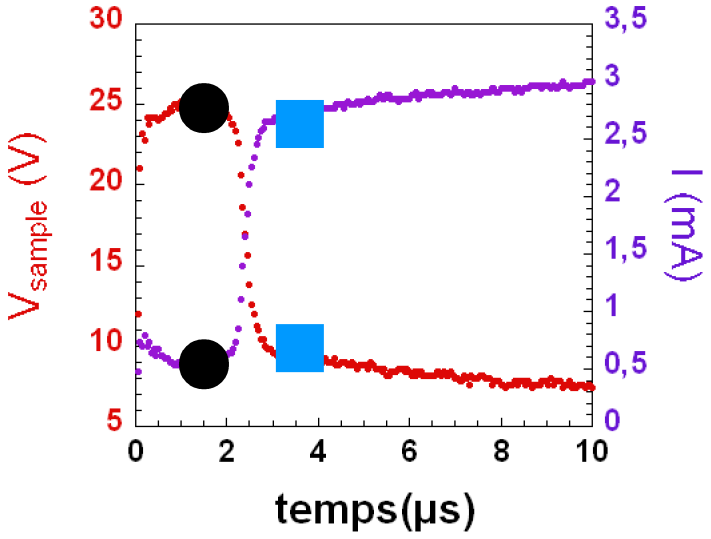
✓ no transition

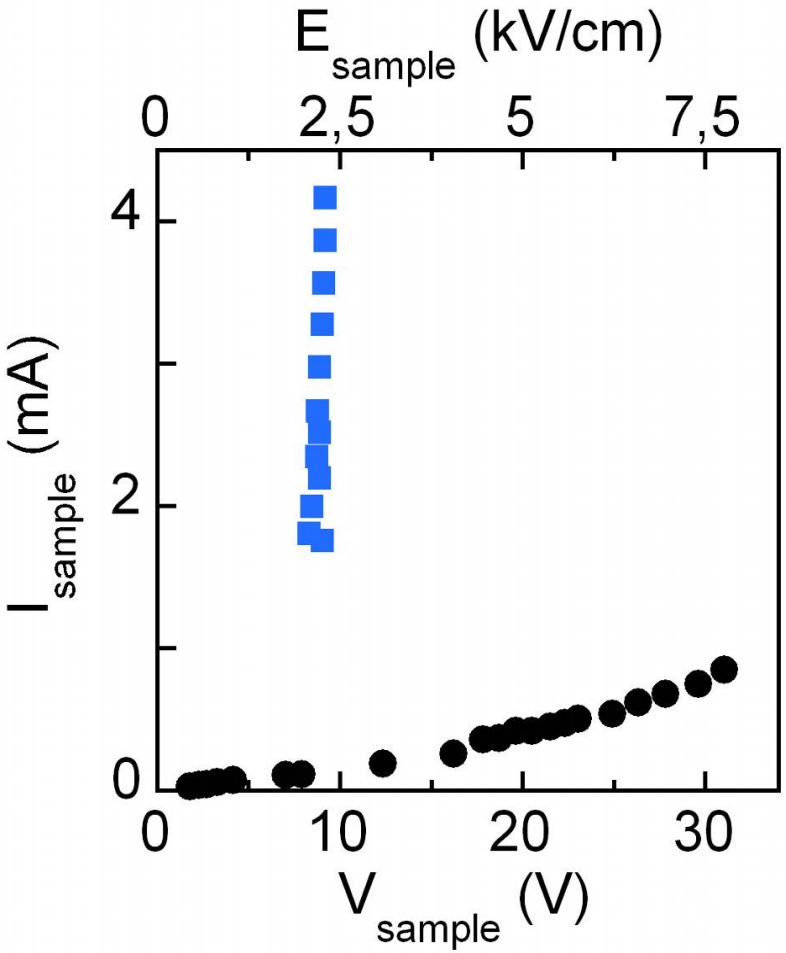
✓ volatile Resistive switching

✓ non-volatile Resistive switching

Electric field controlled electronic phenomena







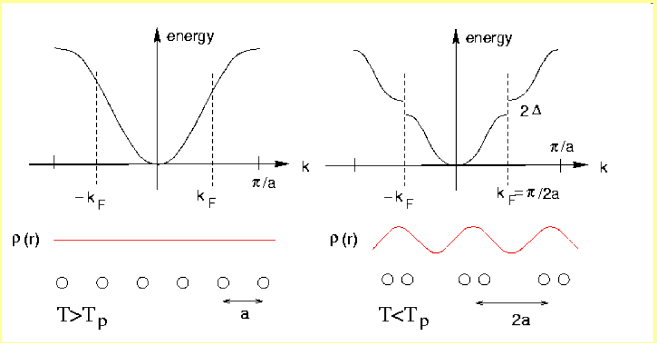
Electric field effect !

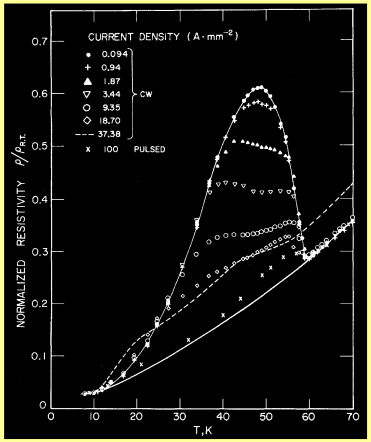
L. Cario, C. Vaju, B. Corraze, V. Guiot, E. Janod, Advanced Materials 22, 5193-5197 (2010)

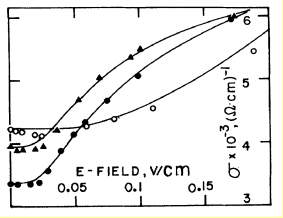
Non linéarités électriques avec champ seuil

existants

Décrochage d'une Onde de Densité de Charge (ODC)







champ seuil E_{th} < 1 V/cm

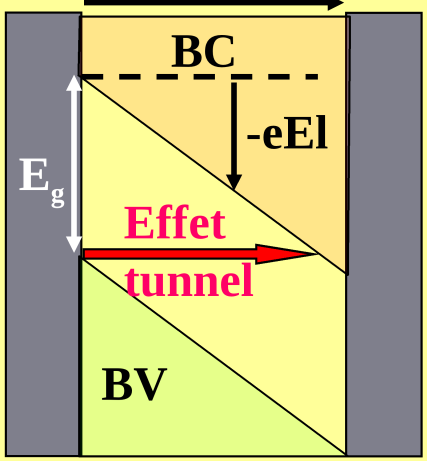
Monceau *et al.*,
PRL 37, 602 (1976)

Claquage diélectrique

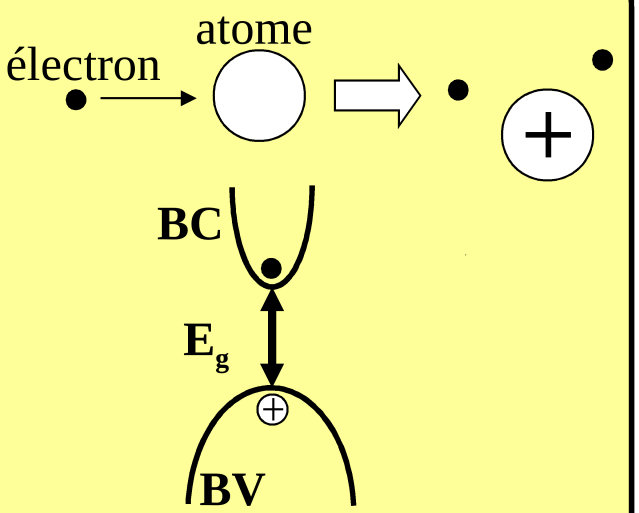
Effet Zener

$E_{th}=E_g/el$ avec l≈1nm

champ seuil E_{th} > MV/cm



Avalanche



champ seuil E_{th} pour Si 100 kV/cm pour InSb 1 kV/cm

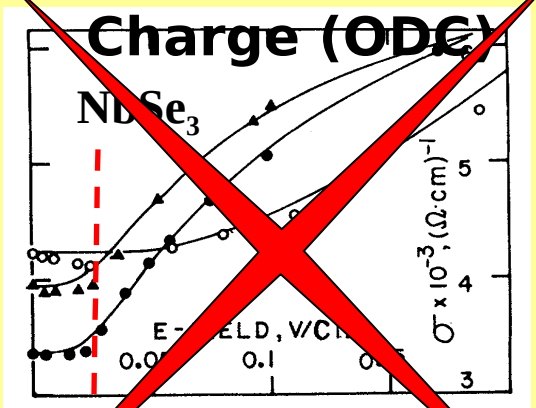
Levinshtein et al.
Breakdown phenomena in semiconductors and semiconductor devices
Selected Volume in electronics and systems Vol 36 World Scientific (2005

Non linéarités électriques dans les AM_4X_8 : comparaison avec les modèles existants

Effet Zener

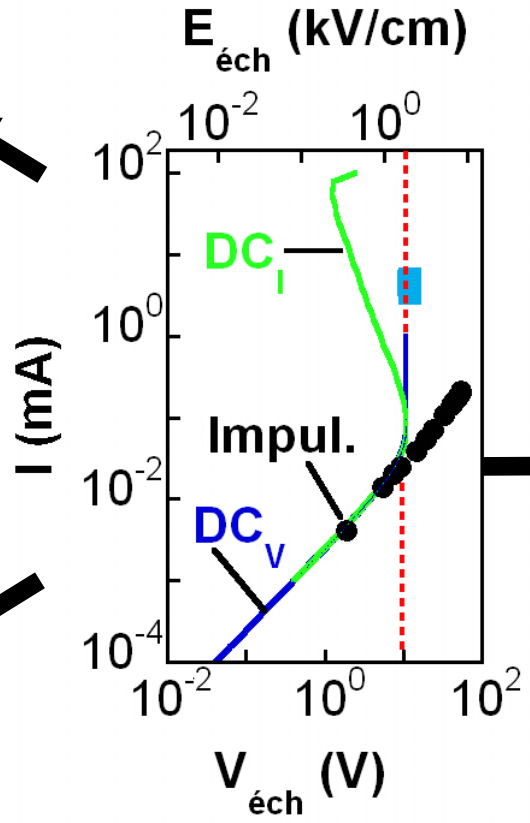
champ seuil E_{th} > MV/cm

Décrochage d'une Onde de Densité de Charge (ODC)



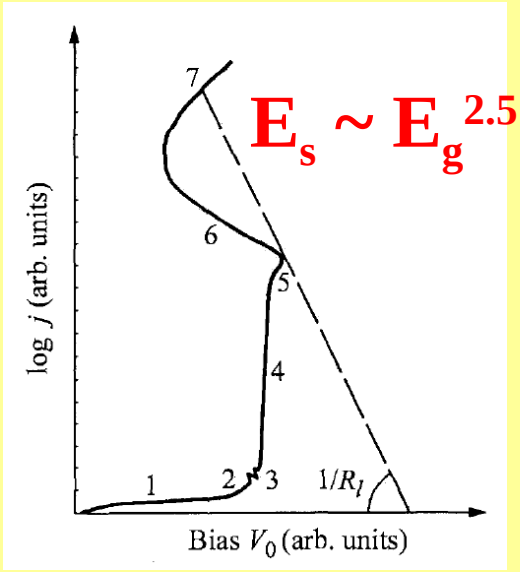
Monceau *et al.*, PRL 37, 602 (1976)

Champ seuil E_{th}< 1 V/cm
I(V) différent



E_{seuil} ≈ 1-10 kV/cm
Gap ~ 0.2 eV

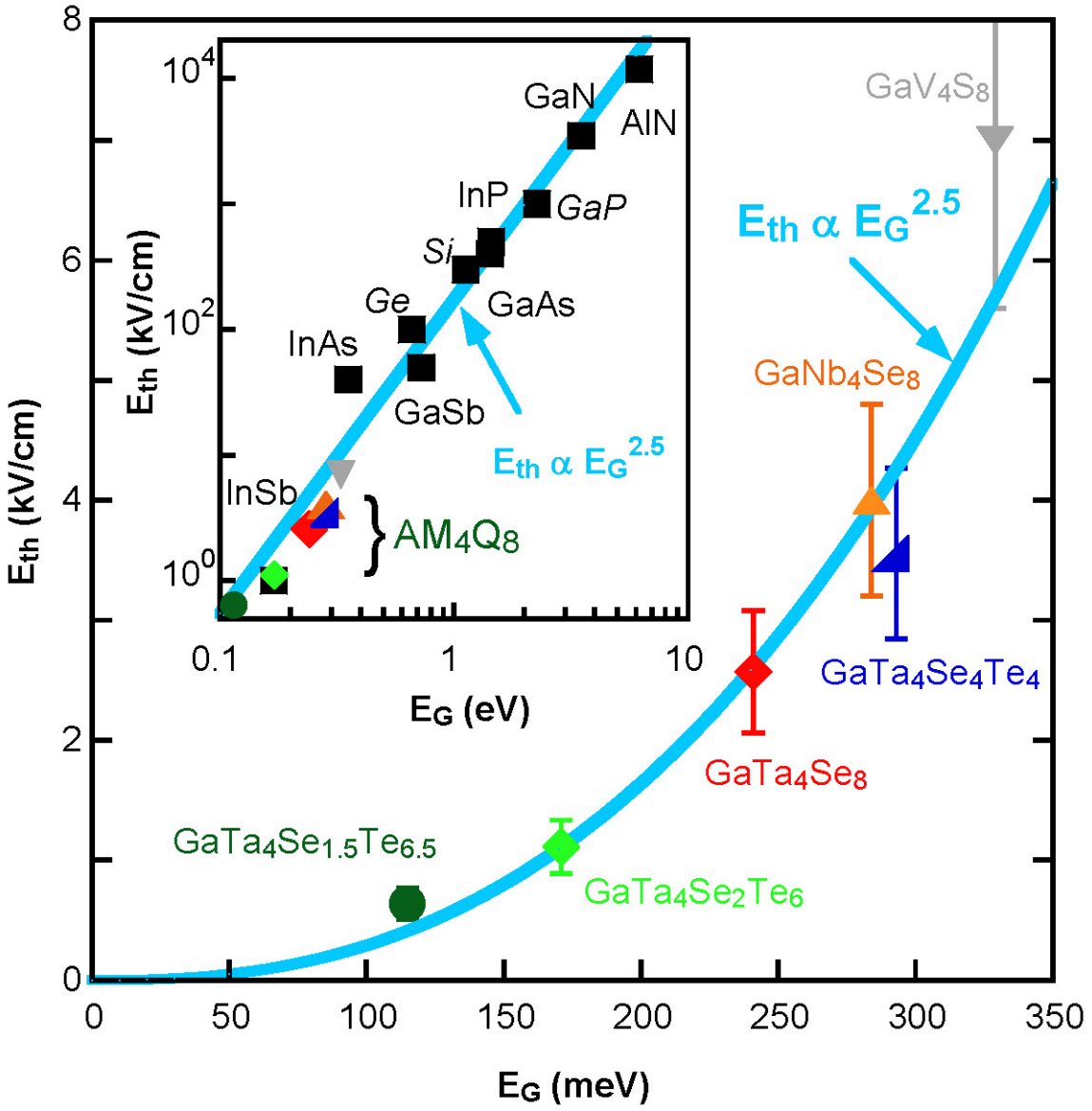
Avalanche



champ seuil compatible
E_{th} ≈ 1-100 kV/cm

Mécanisme Possible !!!

Transition résistive dans les isolants de Mott



Avalanche validée

L. Cario *et al., accepted*
Nature Communication

MAIS

t délai ?

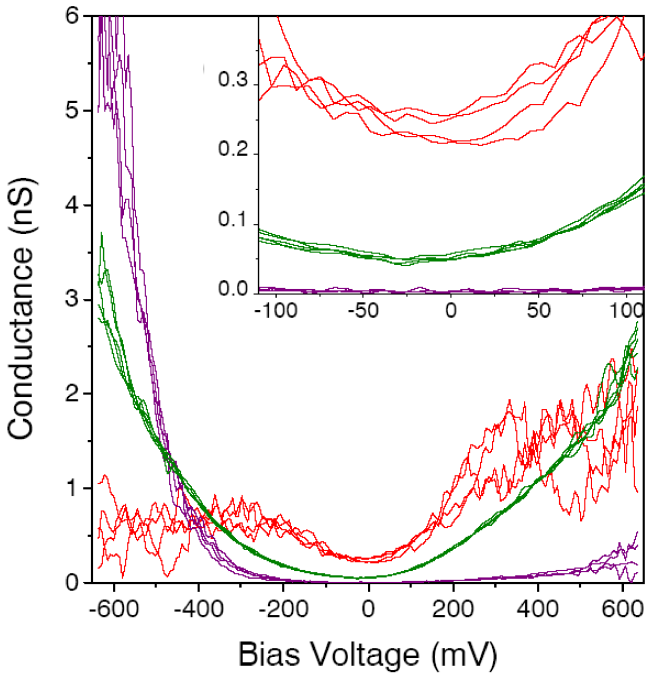
Transition non volatile ?

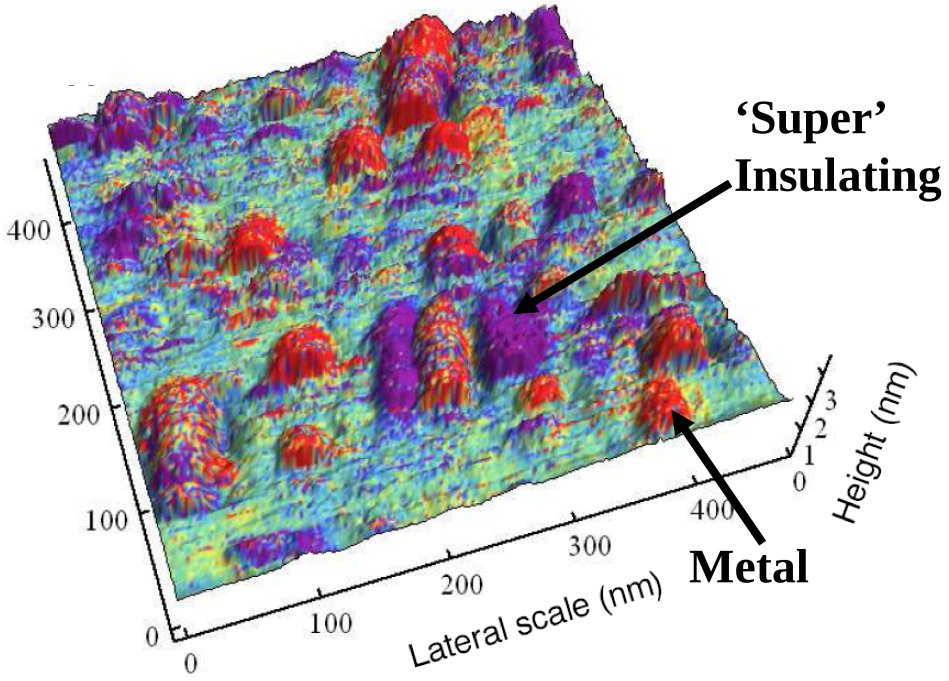
Non-volatile resistive switching

STS study

Institut des NanoSciences de Paris

V. Dubost, F. Debrontrider, T. Cren, D. Roditchev





electronic phase separation

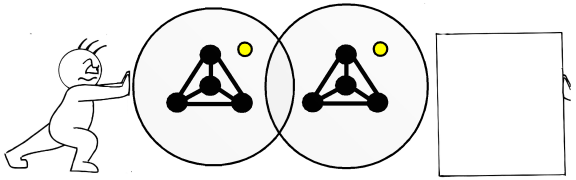
electromechanical coupling

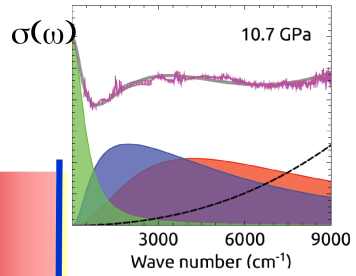
non-volatile Resistive switching

Conclusion

IM transition in the AM_4X_8 Mott Insulator

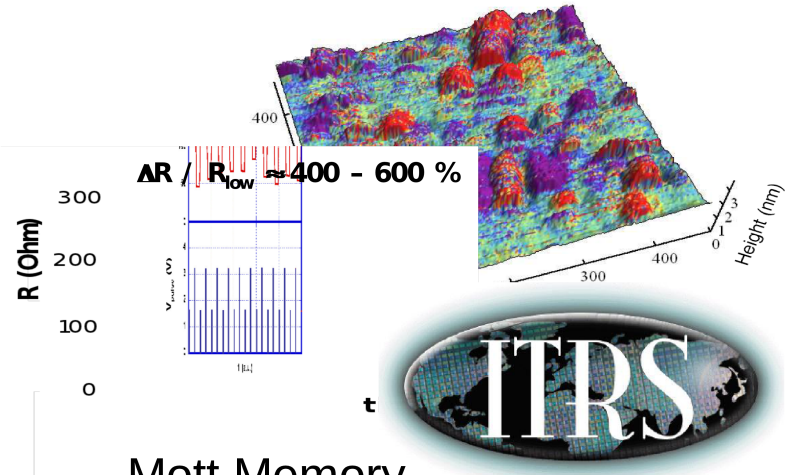
Pressure



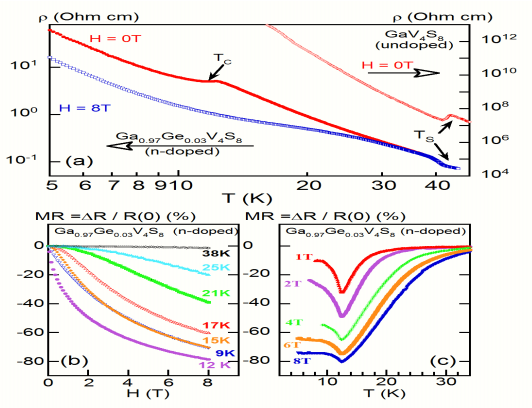


Electric Field

Avalanche effect



Doping



Mott Memory

2011, Emerging Research Devices

Acknowledgments

SCR & IPR Rennes
S. Cordier, M. Potel, M. Guilloux-Viry, E. Collet, M. Lorenc

INSP Institut des NanoSciences de Paris
V. Dubost, F. Debontridder, T. Cren, D.

LPS ORSAY
M. Rozenberg, P. Stoliar

INSTITUT des MATÉRIAUX JEAN ROUXEL iMN Physique Chimie et Génie des Matériaux
V. Guiot, C.Vaju, E. Souchier, J. Martial, S. Salmon, J. Tranchant, P. Moreau, L. Lajaunie, M.P. Besland, B. Corraze, E. Janod, L. Cario

Cluj University
E. Dorolti, V. Pop

GREMAN Tours
V. TaPhuoc, M. Chligui

NC St. Univ.
H. Koo, E. Kan, M. Whangbo

Financial support:

CNRS CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE
UNIVERSITÉ DE NANTES
Agence Nationale de la Recherche ANR

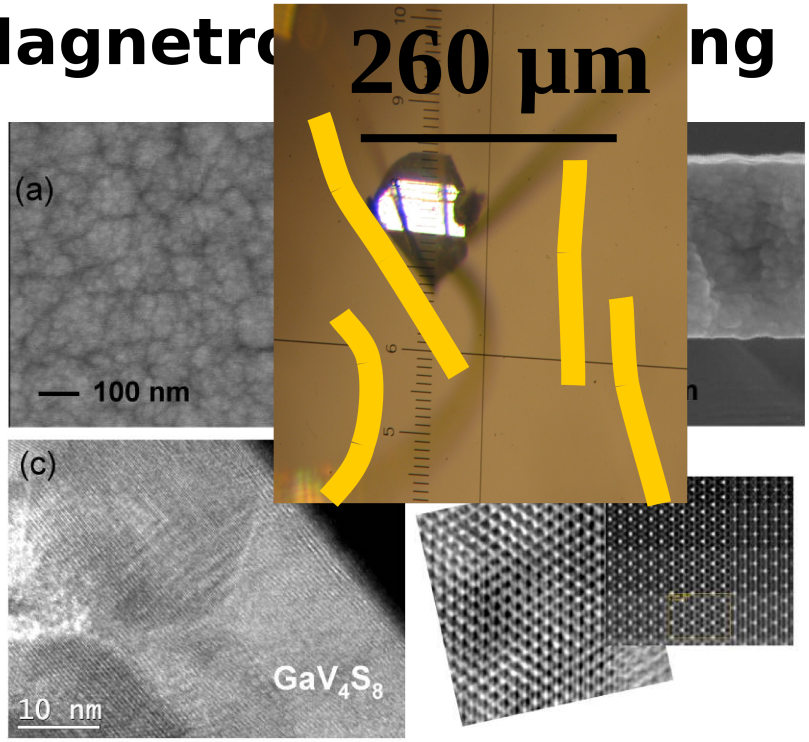
ANR NV-CER (2005-08)
ANR NanoMott (2009-12)
ANR Mott-RRAM (2012-14)

Région PAYS DE LA LOIRE
NanoSciences NORD-OUEST
ST

From the functionality to the device : GaV_4S_8 thin films

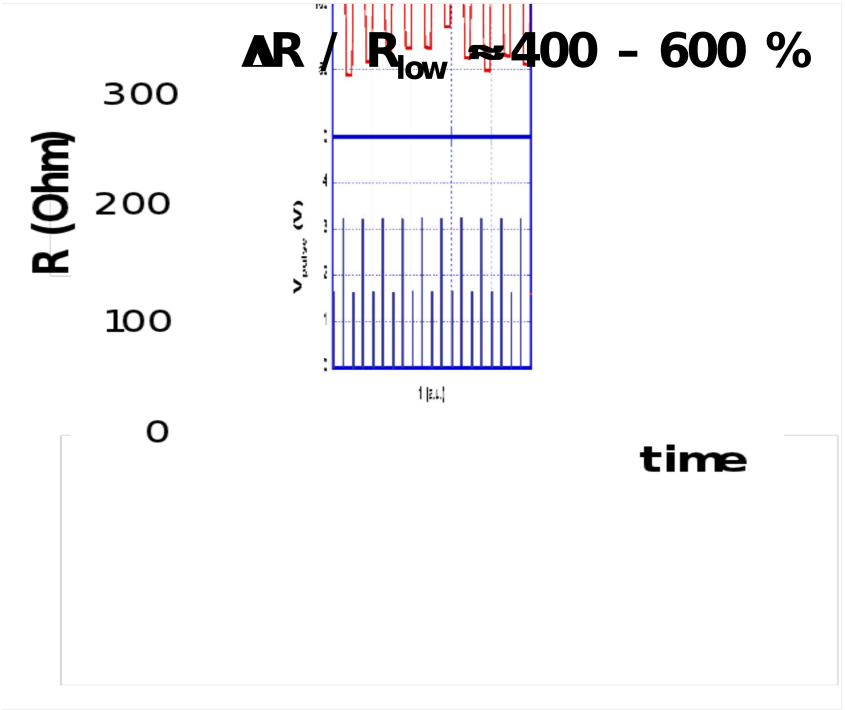
From RS on single crysta ➡ RS on thin films

lagnetro ng



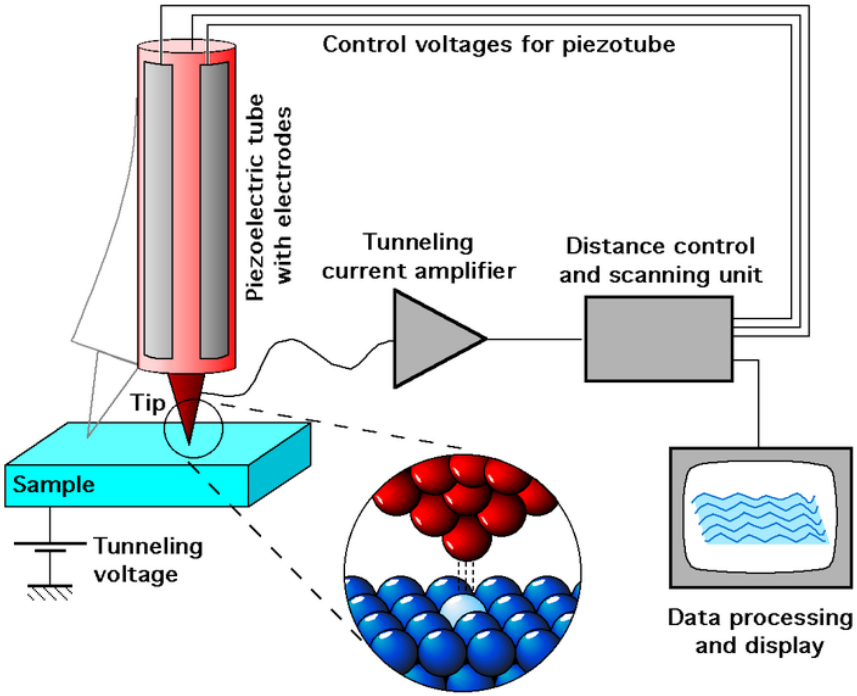
E. Souchier *et al.*, PSS-RRL 5, 53 (2011)

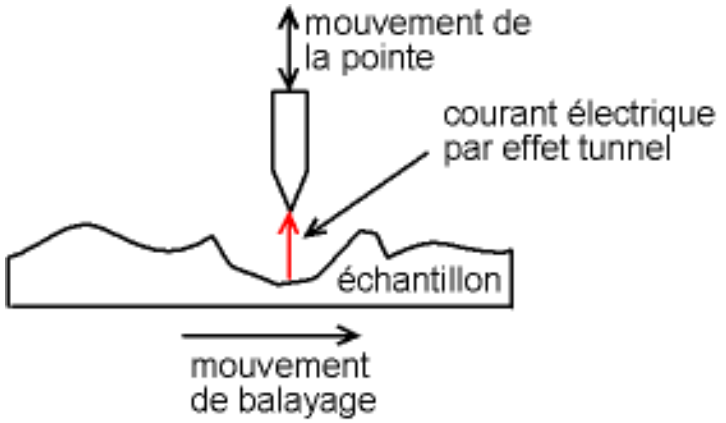
MIM, pad size 2×2 µm²



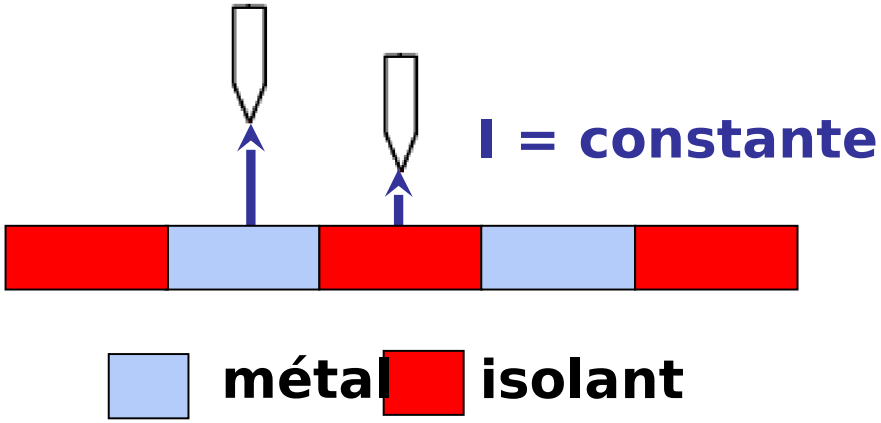
Towards the non-volatile “Mott memories”

Etude des AM4X8 par microscope à effet tunnel
Scanning tunnelling microscopy (STM)





Différente hauteur pour le même courant tunnel !!

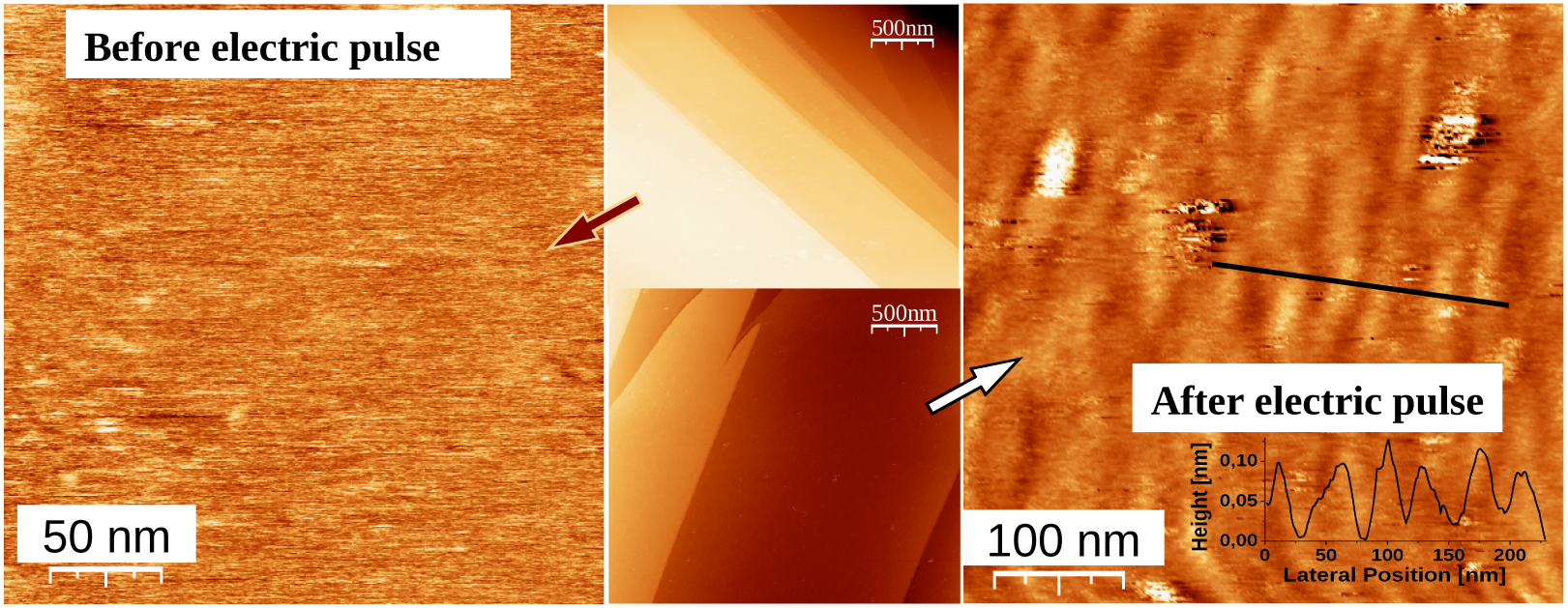


Non-volatile resistive switching : electronic phase separation

STM study of $GaTa_4Se_8$

Institut des NanoSciences de Paris

V. Dubost, F. Debrontrider,
T. Cren, D. Roditchev



electronic phase separation

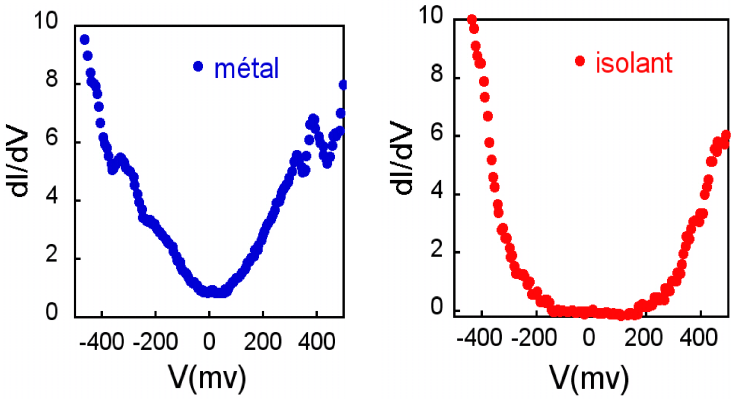
C. Vaju, *et al.* advanced Materials 20, 2760 (2008)

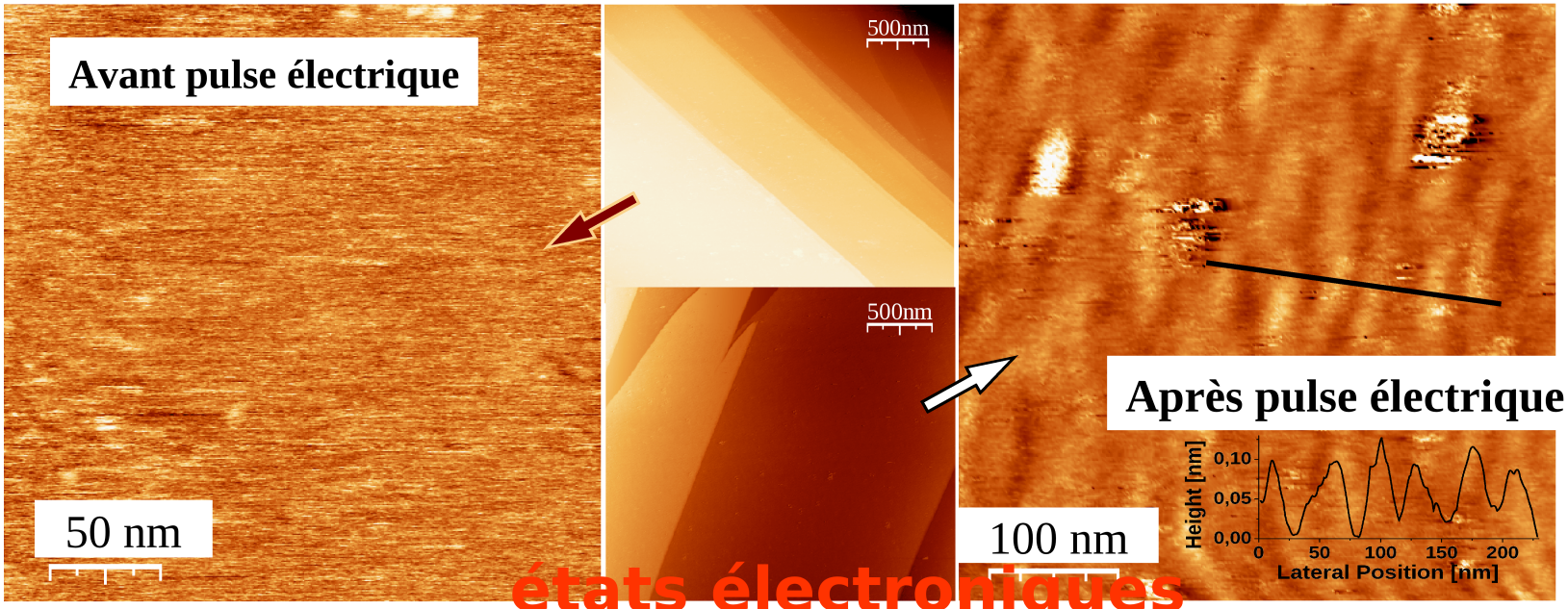
Séparation de phase électronique, STM*

$GaTa_4Se_8$

INSP
Institut des NanoSciences de Paris

* D. Roditchev, T. Cren, V. Dubost INSP-Paris

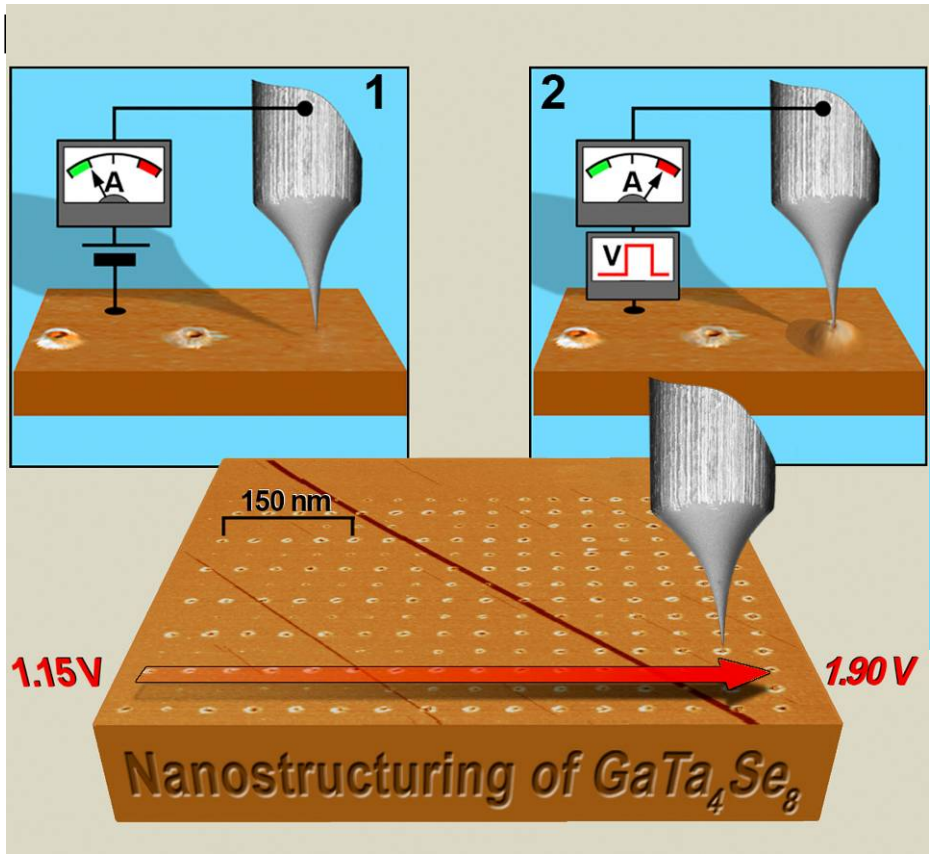




C. Vaju, et al.
Advanced Materials 2008

états électroniques inhomogènes
zones métalliques et isolantes

Pulse application through the STM tip: electro-mechanical coupling

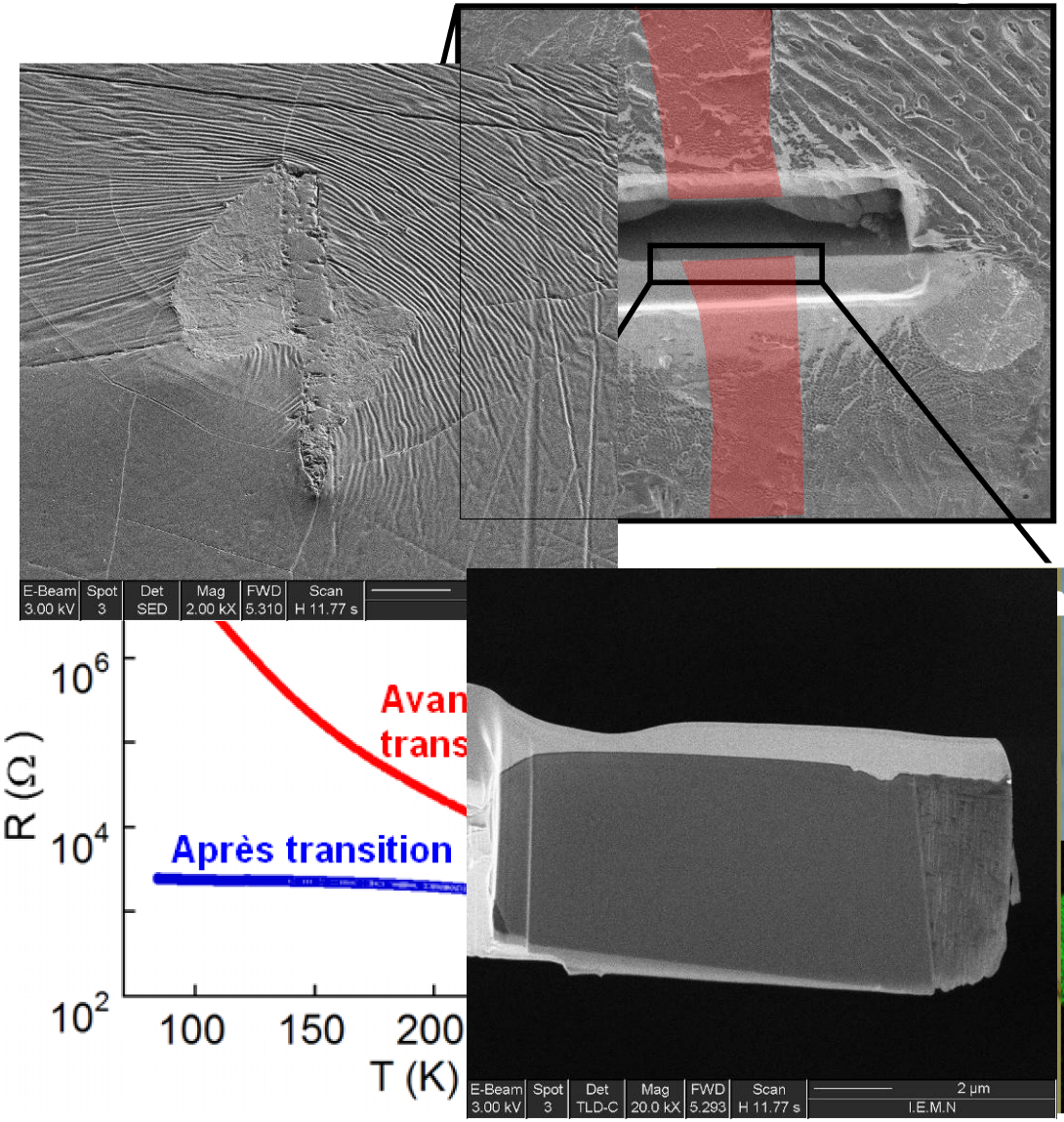


Nano-writing : 1 Tdots / cm² !

Gigantic electro-mechanical Effect

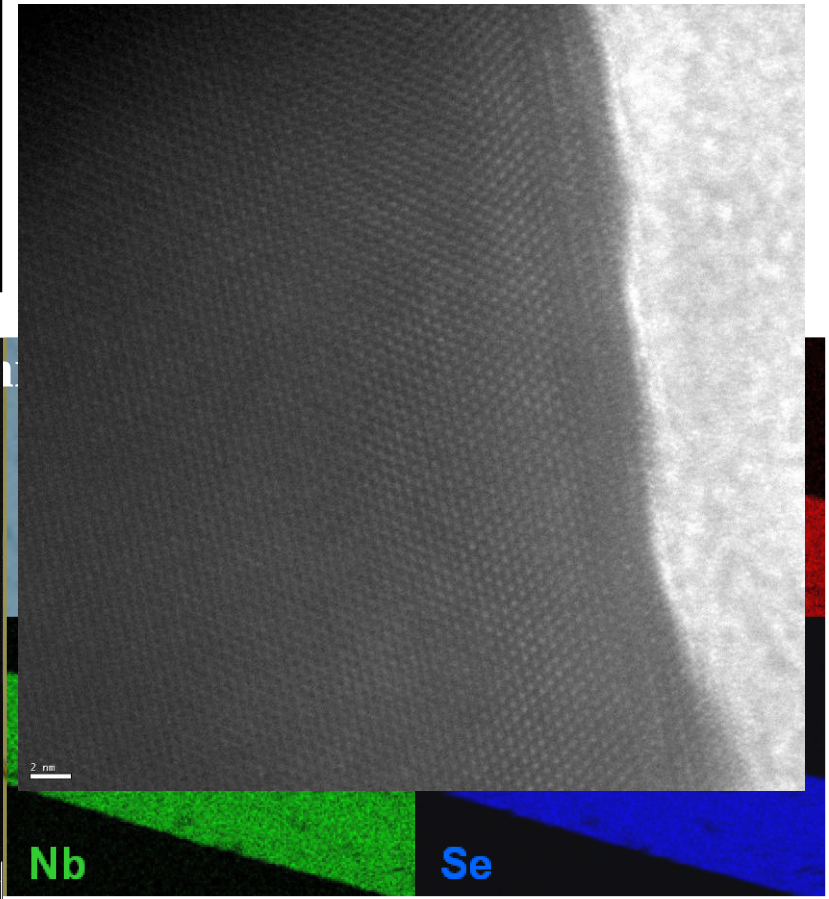
V. Dubost et al. Advanced Functional Materials 19, 2800-2804 (2009)

Thermal effect : chemical or structural change ?



« Transited » crystal GaV_4S_8

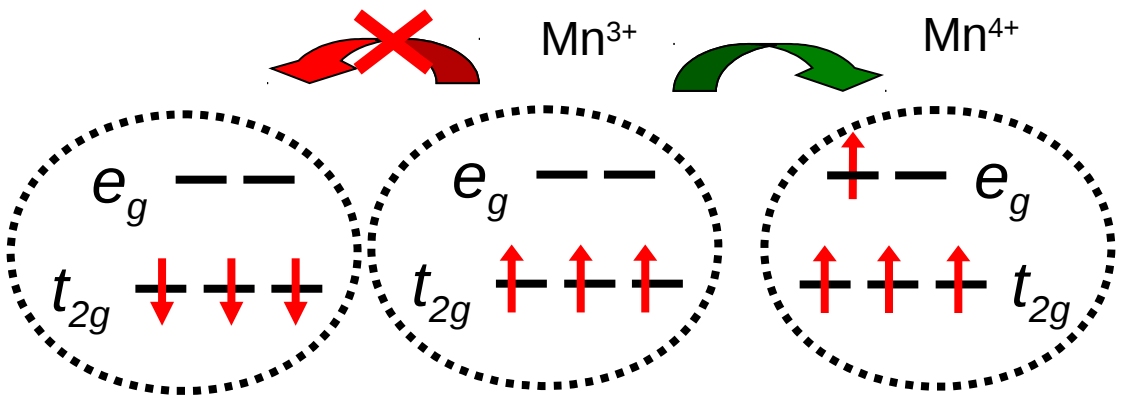
TEM images P. Moreau & L. Lajaunie (IMN)



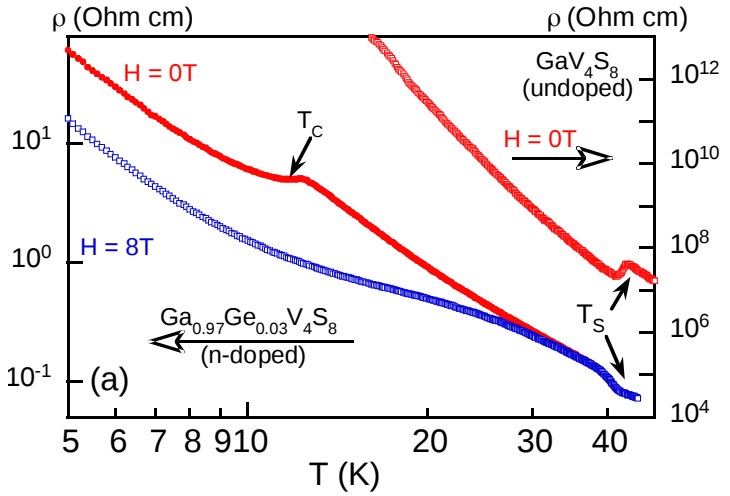
✓ **no chemical or structural change (< 10-1000 nm)**

Mechanism of negative CMR

Manganites

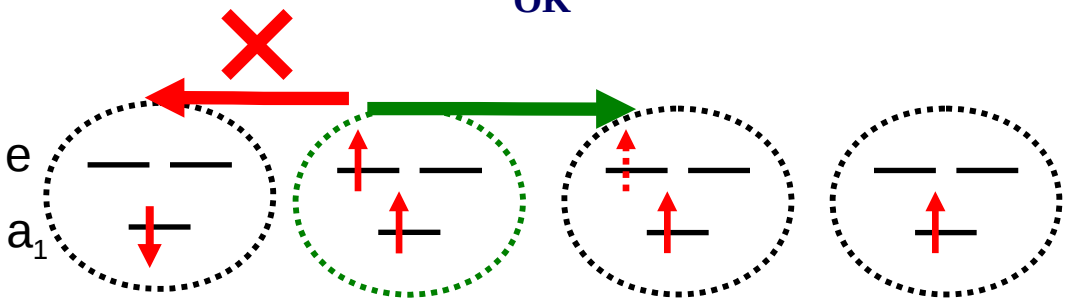


Ge-doped GaV_4S_8

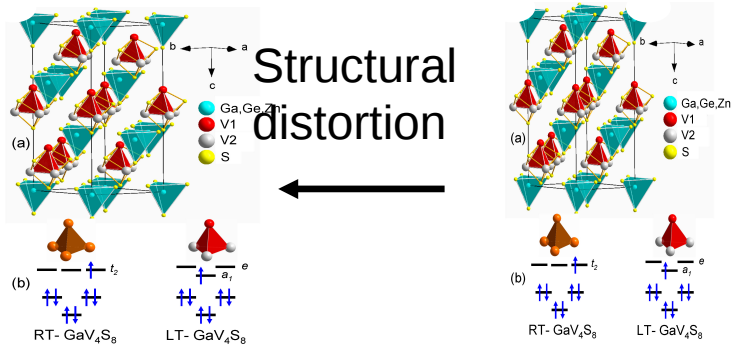


GaV_4S_8 n-doped → negative CMR

OK



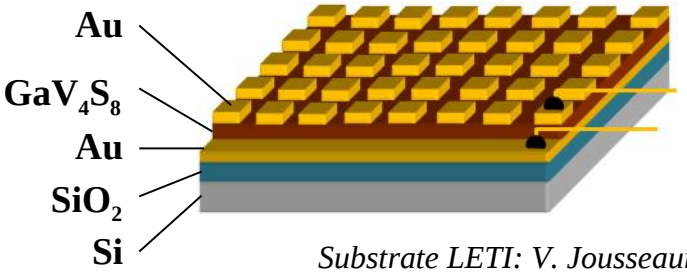
E. Janod *et al.* Submitted 2012



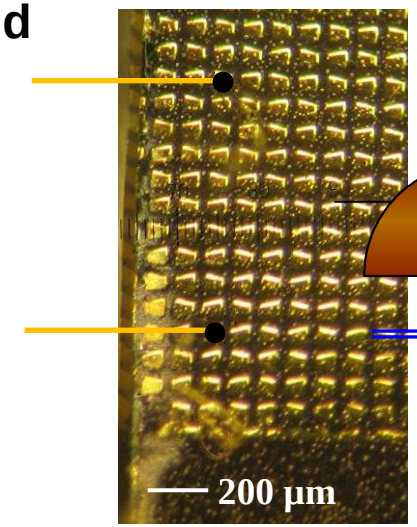
H. Müller, W. Kockelmann and Dirk Johrendt, *Chem. Mater.* **2006**, *18*, 2174.

Metal / Insulator / Metal (MIM) Structure

J. Tranchant, M.-P. Besland

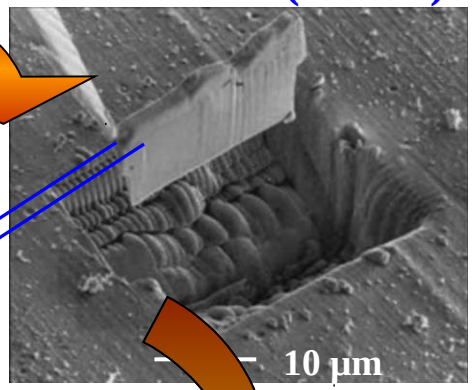


Substrate LETI: V. Jousseaume

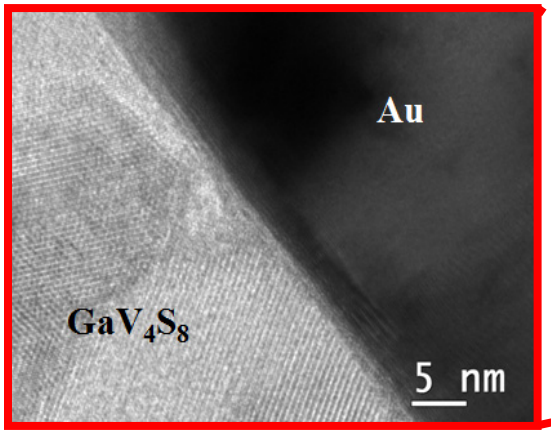


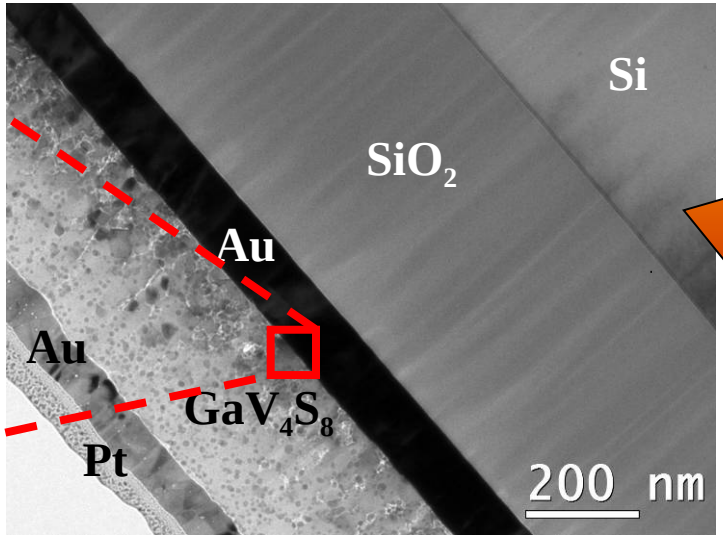
300 nm

FIB
D. Troadec (IEMN)

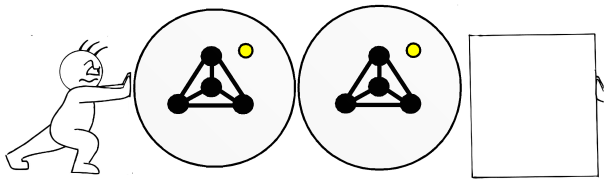


TEM
P. Moreau (IMN)

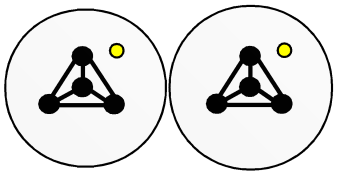




Solution solide $GaTa_4Se_{8-y}Te_y$ (y = 0 à 6.5)
Faire varier le gap par pression chimique

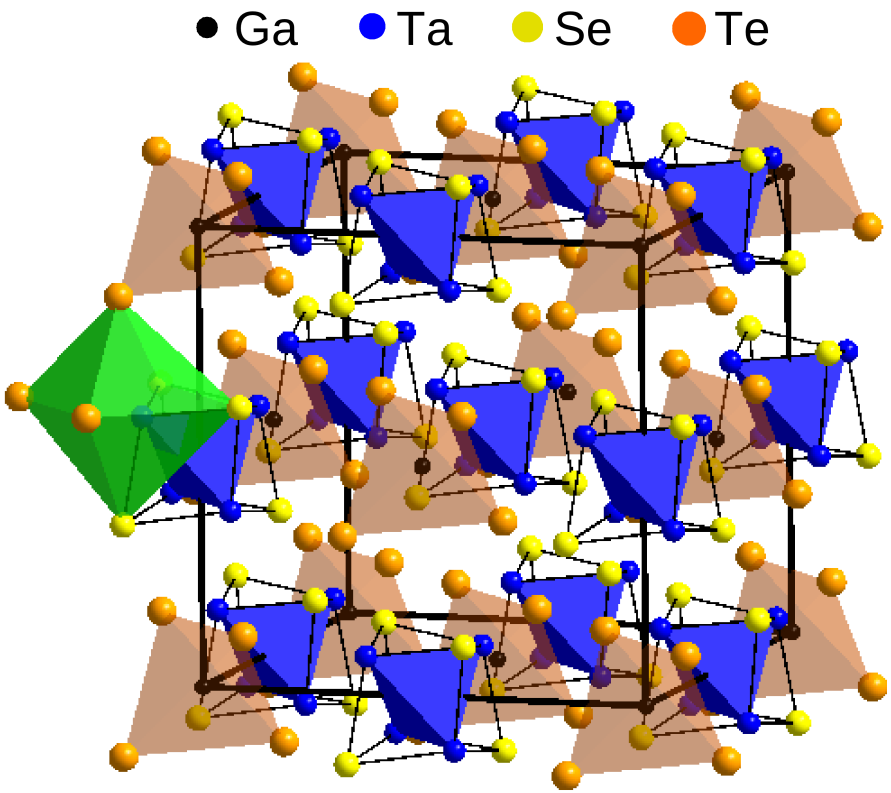


Pression physique

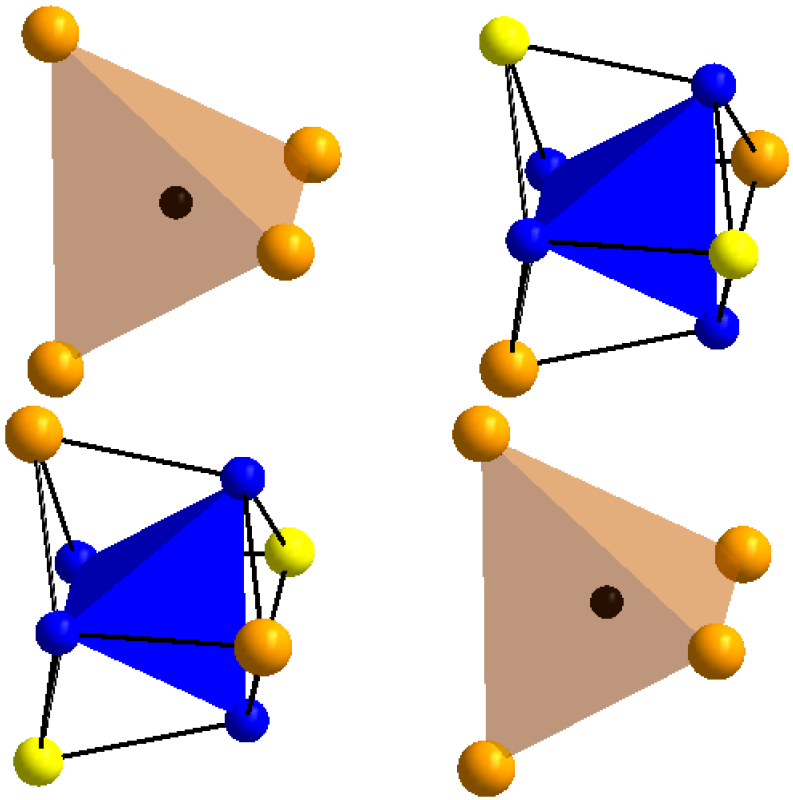


Pression chimique

$GaTa_4Se_8$ ⇒ $GaTa_4Se_{8-y}Te_y$



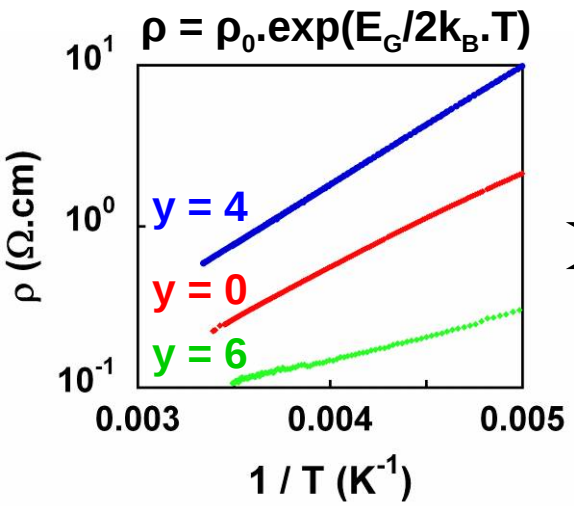
$GaTa_4Se_4Te_4$



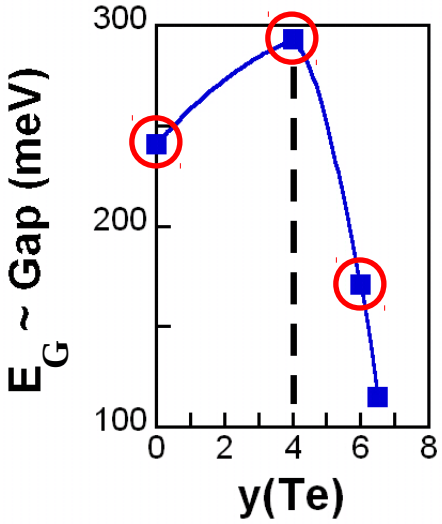
$GaTa_4Se_2Te_6$

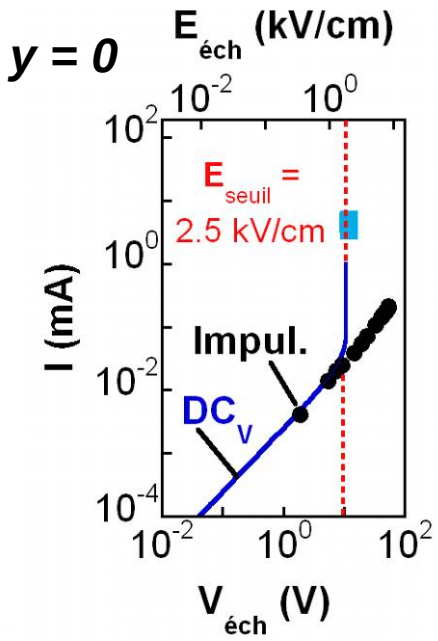
Guiot *et al. Chem. Mat.* **2011** 23(10) 2611

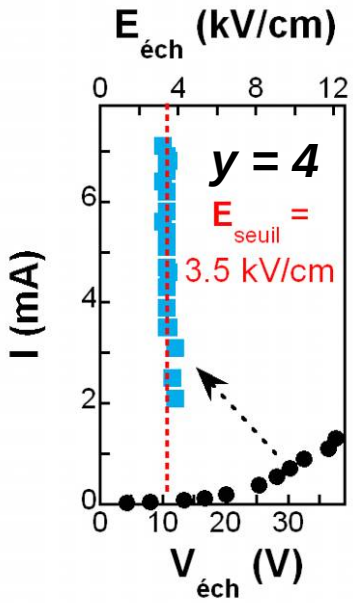
Evolution du champ seuil avec le gap

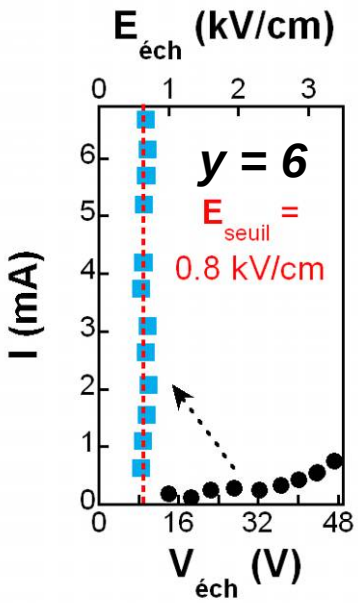


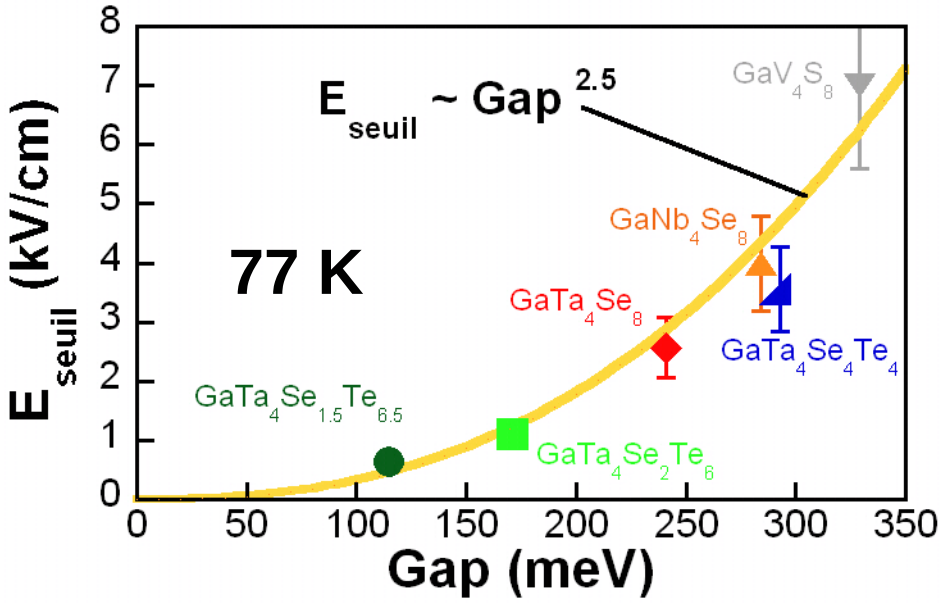
$GaTa_4Se_{8-y}Te_y$



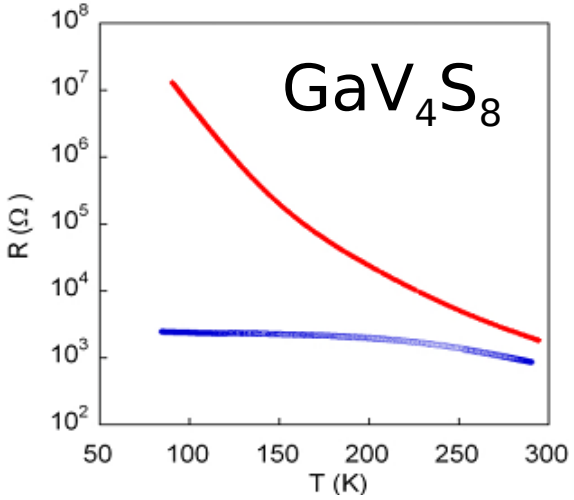


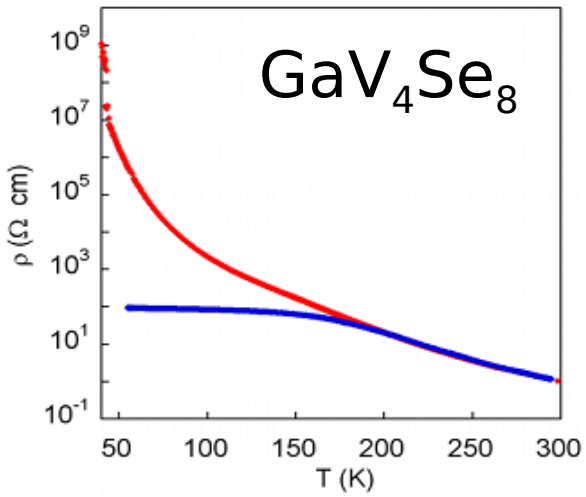


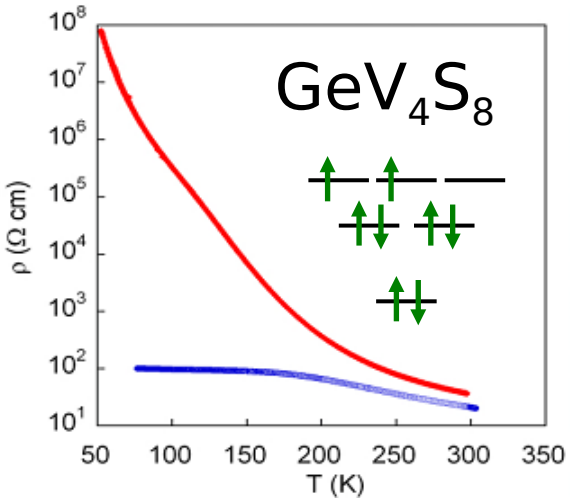


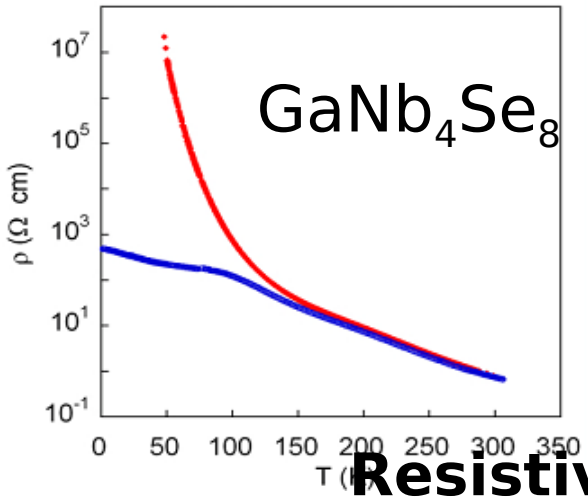


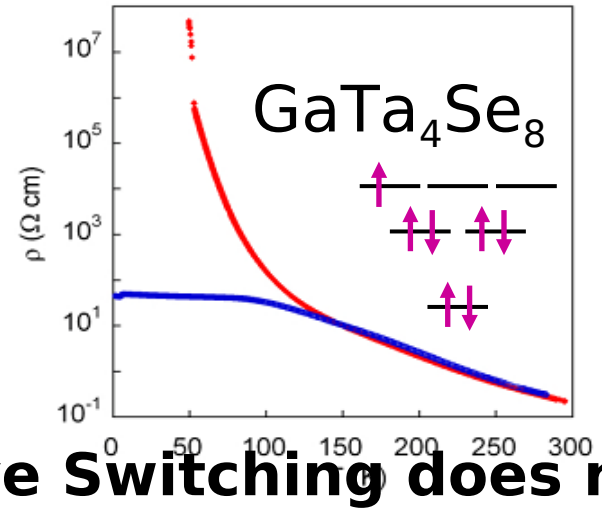
Resistive Switching in the AM_4X_8

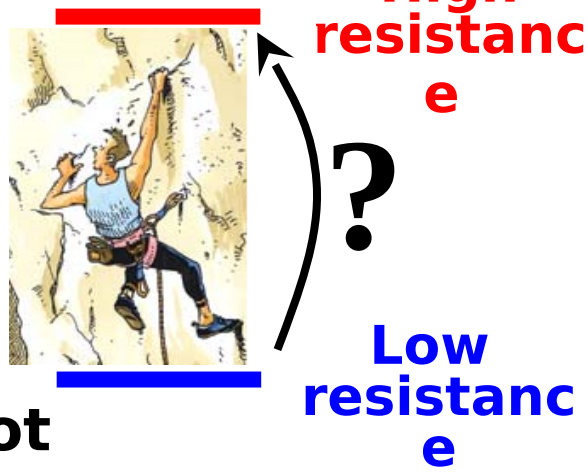








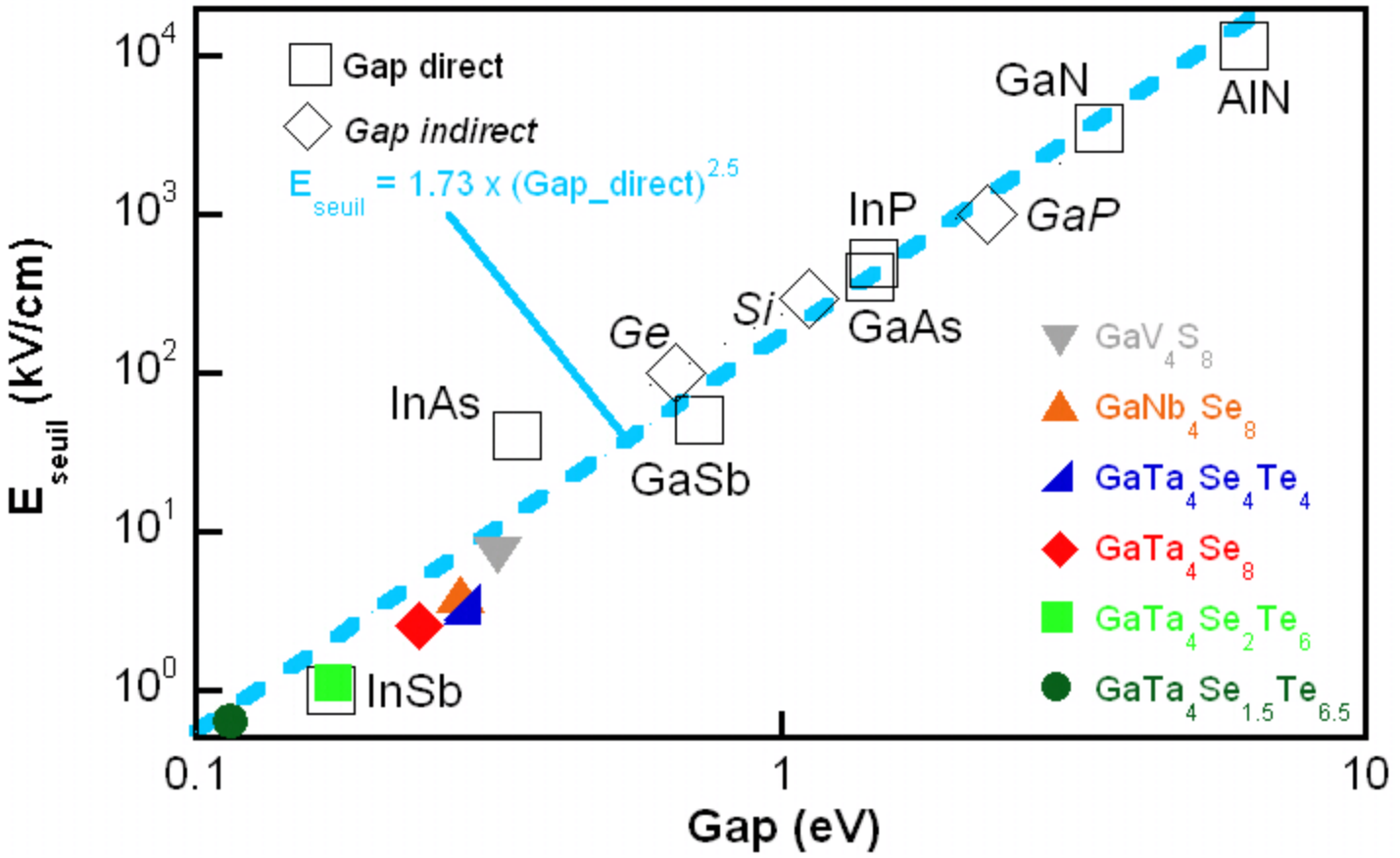




Resistive Switching does not depend on :

- **Chemical elements**
- **Clusters filling**

Lien champ seuil - gap

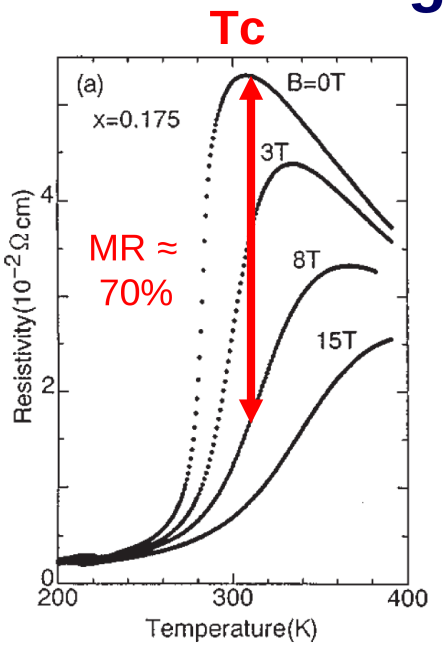


Forte évidence de la validité d'un phénomène d'avalanche dans des isolants de Mott à faible gap !!!

Negative CMR in the ferromagnetic $Ga_{1-x}Ge_xV_4S_8$

Manganites

→ **negative CMR**

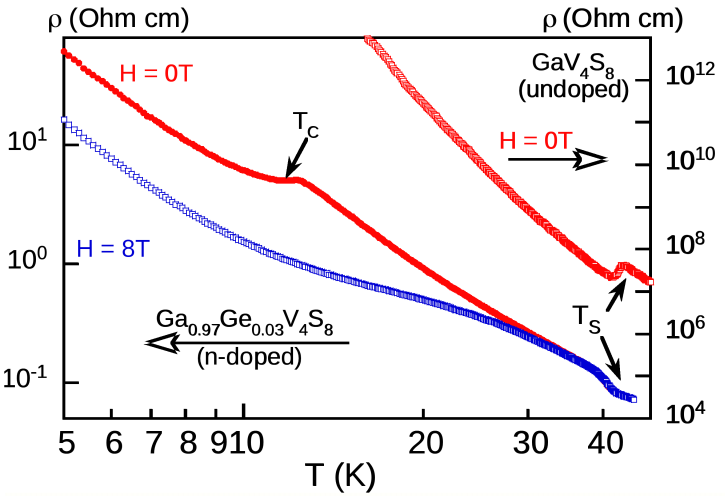


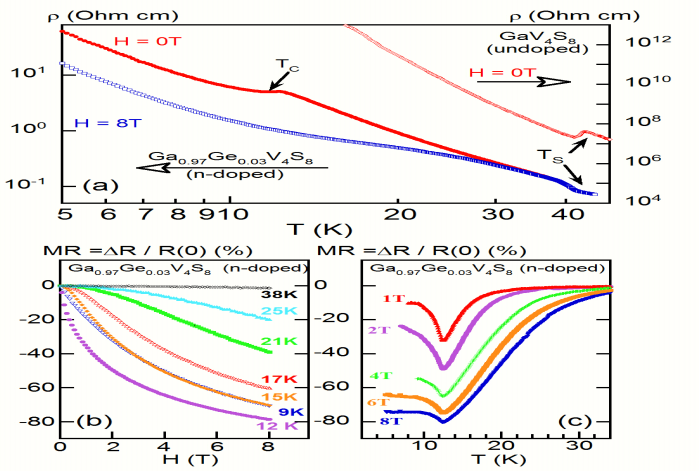
$La_{1-x}Sr_xMnO_3$ (x=0.175) crystal

Tokura *et al.*,

J. Phys. Soc. Jpn. **63**, 3931 (1994)

Ge-doped GaV_4S_8





Colossal MagnetoResistance in (n-doped) $Ga_{1-x}Ge_xV_4S_8$

E. Janod *et al.* Submitted 2012