

# **Magnetism**

## **in diluted magnetic oxides**

František Máca

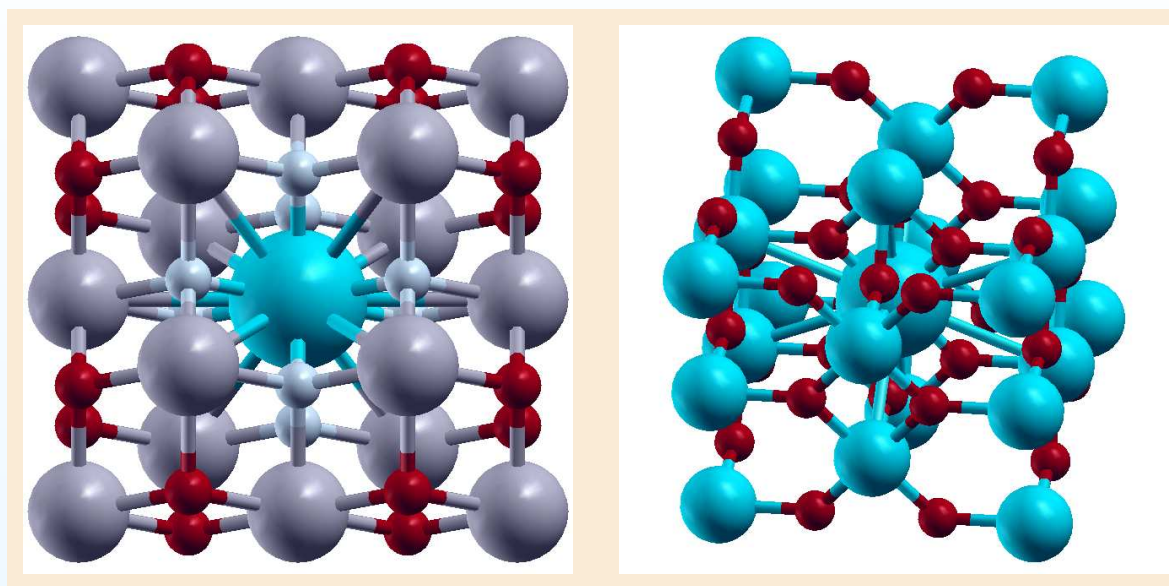
Institute of Physics ASCR, Praha, Czech Republic

in collaboration with

Josef Kudrnovský, Georges Bouzerar and Timothy Ziman

Laboratoire Louis Néel and Institut Laue Langevin, Grenoble, France

## Layout



- ✓ *Magnetism in  $ZrO_2$  and in rutile  $TiO_2$*
- ✓ *Cation vacancies and substitution of cation by alkalic metal atom*
- ✓ *Density functional calculations for oxide compounds*
- ✓ *Magnetic moments on O atoms*
- ✓ *Conclusions*

GA ČR: 202/04/0583

## *Magnetism in oxide compounds*

### **Nonmagnetic oxides + a nonmagnetic impurity element**

*In diluted magnetic semiconductors magnetic dopants introduce magnetism in the mixed system.*

*In some oxide compounds specific nonmagnetic host doping can induce local magnetic moments on neighbor atoms. Making them ferromagnetic can open the possible application in the field of spintronics.*

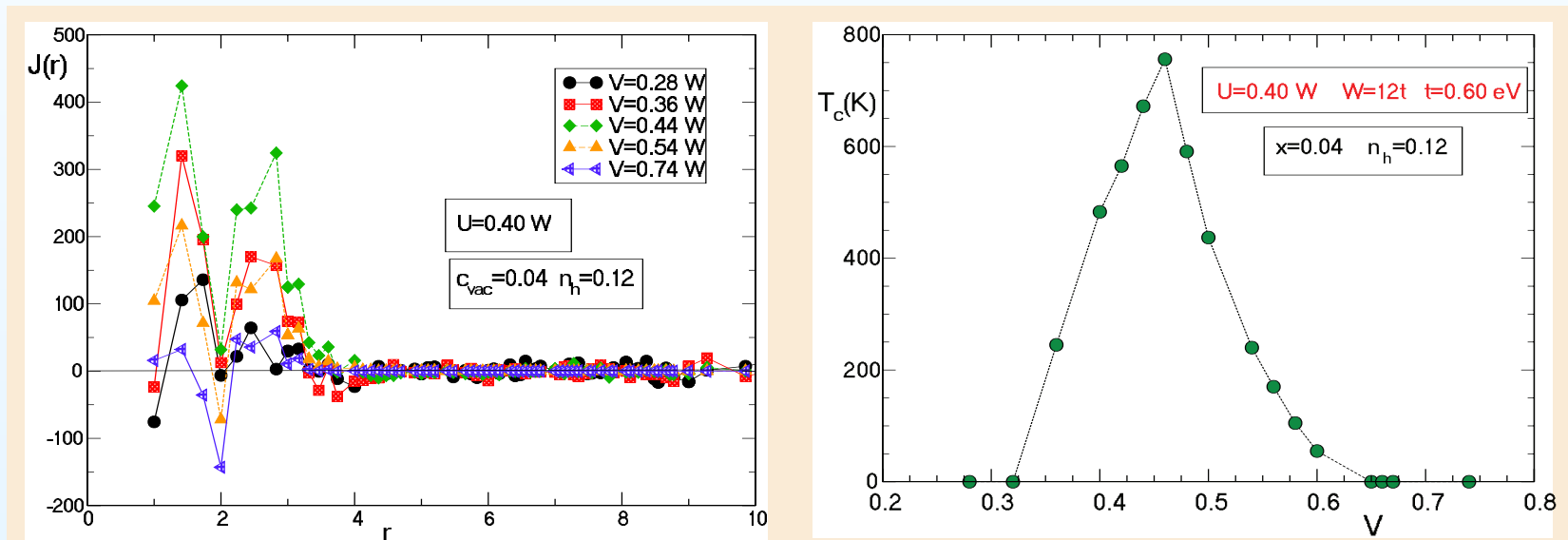
*⇒ Prototype: vacancy-induced ferromagnetism in **ZrO<sub>2</sub>***

*New types of devices: the electric field changes the charge and the spin of electrons*

# Motivation

Vacancy-induced  $d^0$  ferromagnetism in oxide compounds [1].

Model Hamiltonian with effective parameters ( $U, W, V, t, n_h$ )  
+ Heisenberg model for magnetic exchange coupling analysis.



Left: Magnetic couplings (in Kelvin) as a function of separation of vacancies, in units of the cubic lattice spacing. Right: Curie temperature as a function of the potential  $V$  (in units of  $W$ ).

[1] G. Bouzerar and T. Ziman, PRL **96** (2006) 207602.

## *Magnetism without magnetic ions*

---

### **Questions to be answered:**

- *Does the stable charge state of the isolated defect carry a magnetic moment?*
- *What is the **range** of magnetic exchange interactions between a pair of defects in stable charge states?*
- *What is the **minimum concentration** of defects which will establish a continuous percolation in the lattice?*
- *Can be a minimum defect concentration needed for magnetic percolation granted **thermodynamically**?*  
*?? Formation energy of the defect ??*

## Magnetic moment

- *It is difficult to control the concentration of vacancies in oxide in the vacancy-induced  $d^0$  ferromagnetism in oxide compounds.*

## *Magnetic moment*

---

- *It is difficult to control the concentration of vacancies in oxide in the vacancy-induced  $d^0$  ferromagnetism in oxide compounds.*
- *The vacancy on oxygen site is the natural defect in many oxides. A cation vacancy is a very strong defect with high formation energy.*

## *Magnetic moment*

---

- *It is difficult to control the concentration of vacancies in oxide in the vacancy-induced  $d^0$  ferromagnetism in oxide compounds.*
- *The vacancy on oxygen site is the natural defect in many oxides. A cation vacancy is a very strong defect with high formation energy.*
- *Alkalic metal atom substituting the cation can also create magnetism in oxide. The concentration of alkalic metal dopants can be well controlled.*



## *Magnetic moment*

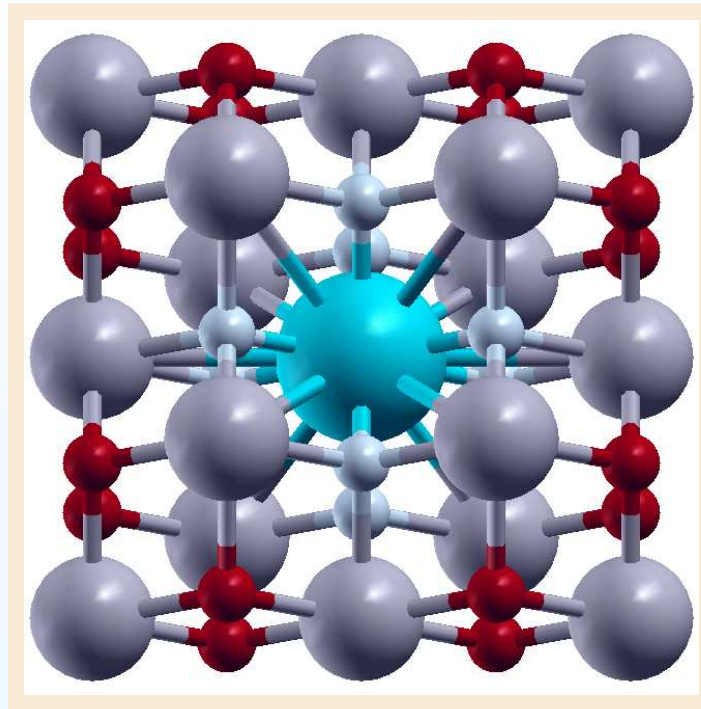
- *It is difficult to control the concentration of vacancies in oxide in the vacancy-induced  $d^0$  ferromagnetism in oxide compounds.*
- *The vacancy on oxygen site is the natural defect in many oxides. A cation vacancy is a very strong defect with high formation energy.*
- *Alkalic metal atom substituting the cation can also create magnetism in oxide. The concentration of alkalic metal dopants can be well controlled.*

*What alkalic metal impurities create the magnetism in the  $ZrO_2$  and in the rutile  $TiO_2$ ?*

## *Theoretical tools*

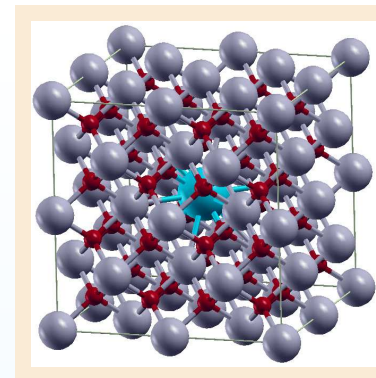
- ✓ *Real-space spin-density-functional method  $\implies$  reliable ground-state total energy and charge- and spin-densities.*
- ✓ *Implementation: full-potential linearized augmented plane wave method (FP LAPW, **WIEN2k** package).*
- ✓ *impurity incorporated into the  $\text{ZrO}_2$  or into the rutile  $\text{TiO}_2$  **supercells** containing 24, 48, and 96 atoms with either cubic or tetragonal symmetry.*
- ✓ *Embedded cluster*  
 $\implies$  *limit of single impurity in host.*  
*Implementation: **TB-LMTO***

# NaZrO<sub>2</sub>



*The cubic supercell NaZr<sub>7</sub>O<sub>16</sub>,  $a = 5.256 \text{ \AA}$ . There are two types of oxygens: the Na neighbors and others. No relaxation of geometry is included. The local magnetic moments are obtained by integration over the muffin-tin sphere ( $R_{Zr} = R_{imp} = 2.35 \text{ a.u.}$ ,  $R_O = 1.70 \text{ a.u.}$ ).  
The unit cell including 24 atoms has magnetic moment  $\mu_{cell} = 2.42 \mu_B$ .*

# Impurity in ZrO<sub>2</sub>



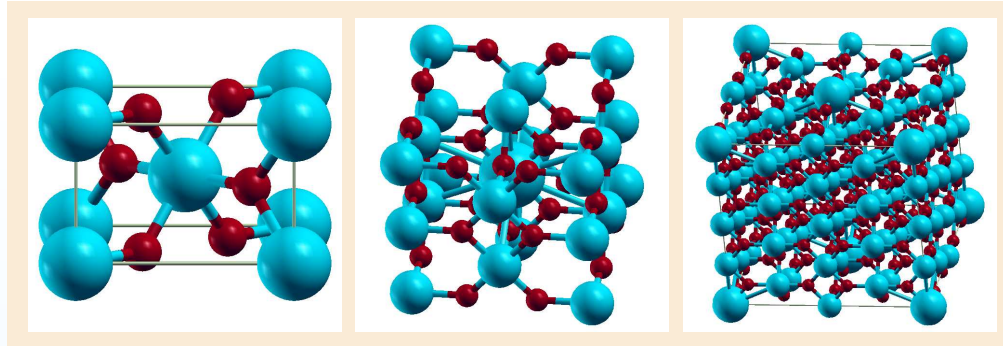
47/48 atoms in the unit cell - 6.25%

Impurity	$\mu_{\text{imp}}$	$\mu_{\text{O}_1}$	$\mu_{\text{O}_2}$	$\mu_{\text{Zr}_1}$	$\mu_{\text{cell}}$
<b>vac</b>	-	<b>0.41</b>	0.05	-0.02	<b>4.00</b>
<b>Na</b>	0.00	<b>0.17</b>	0.03	0.00	<b>1.70</b>
<b>K</b>	0.07	<b>0.25</b>	0.05	-0.01	<b>2.81</b>
<b>Rb</b>	0.37	<b>0.25</b>	0.02	0.00	<b>3.00</b>
<b>Cs</b>	0.66	<b>0.19</b>	0.02	0.01	<b>3.00</b>

95/96 atoms in the unit cell - 3.125%

<b>vac</b>	-	<b>0.41</b>	0.03	0.00	<b>4.00</b>
<b>Na</b>	0.00	<b>0.12</b>	0.01	0.00	<b>1.30</b>
<b>K</b>	0.07	<b>0.22</b>	0.03	-0.01	<b>2.63</b>
<b>Rb</b>	0.37	<b>0.25</b>	0.02	0.00	<b>3.00</b>
<b>Cs</b>	0.65	<b>0.19</b>	0.01	0.01	<b>3.00</b>

# Impurity in $TiO_2$



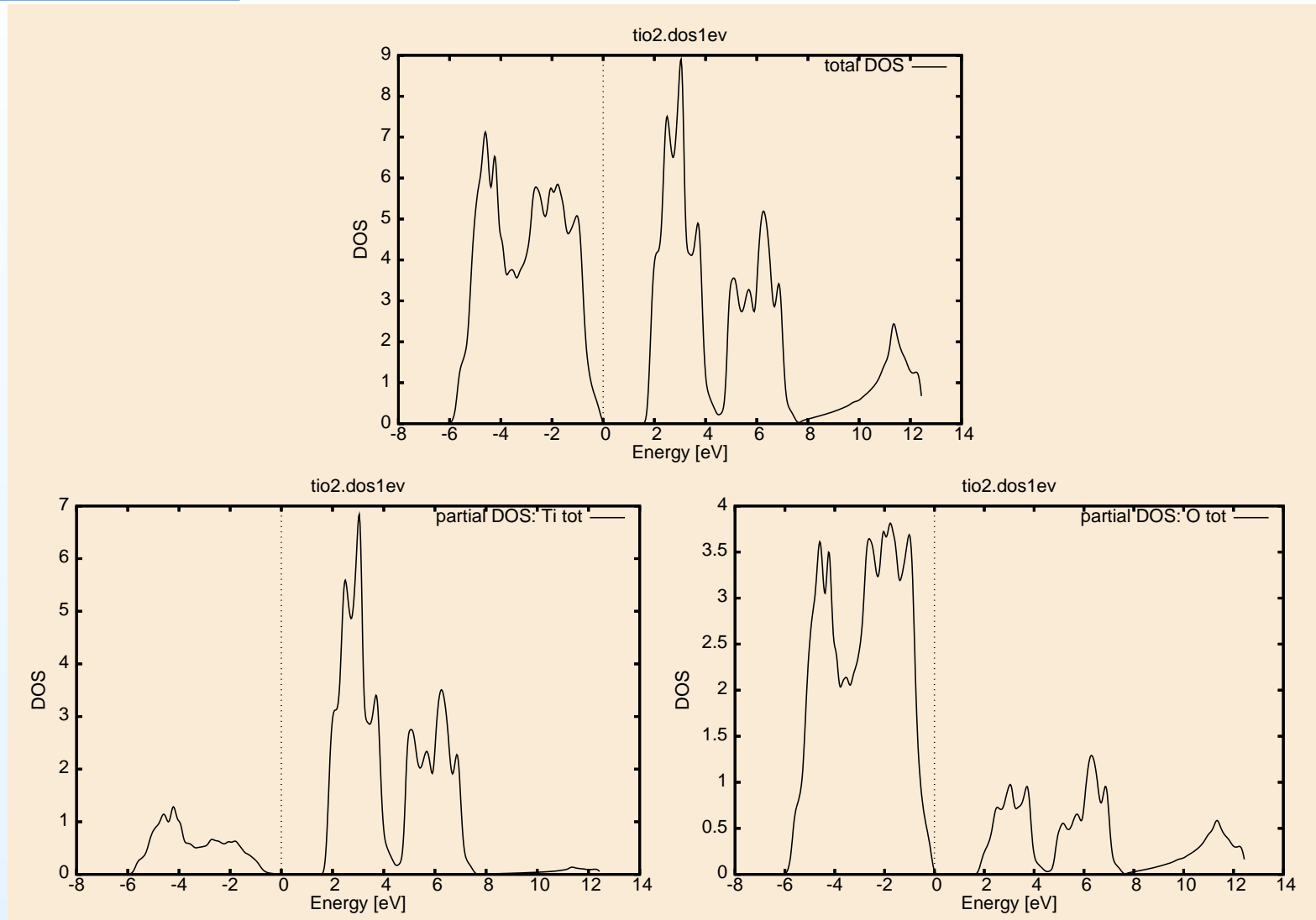
23/24 atoms in the unit cell - 12.5%

Impurity	$\mu_{\text{imp}}$	$\mu_{O_1}$	$\mu_{O_2}$	$\mu_{Ti_1}$	$\mu_{\text{cell}}$
<b>vac</b>	-	<b>0.51</b>	0.42	-0.08	<b>3.94</b>
<b>Na</b>	0.02	<b>0.32</b>	0.25	-0.05	<b>2.58</b>
<b>K</b>	0.21	<b>0.28</b>	-0.05	-0.01	<b>1.60</b>
<b>Rb</b>	0.27	<b>0.17</b>	0.03	0.02	<b>1.30</b>
<b>Cs</b>	0.16	<b>0.06</b>	0.01	0.04	<b>0.70</b>

96 atoms in the unit cell - 3.125%

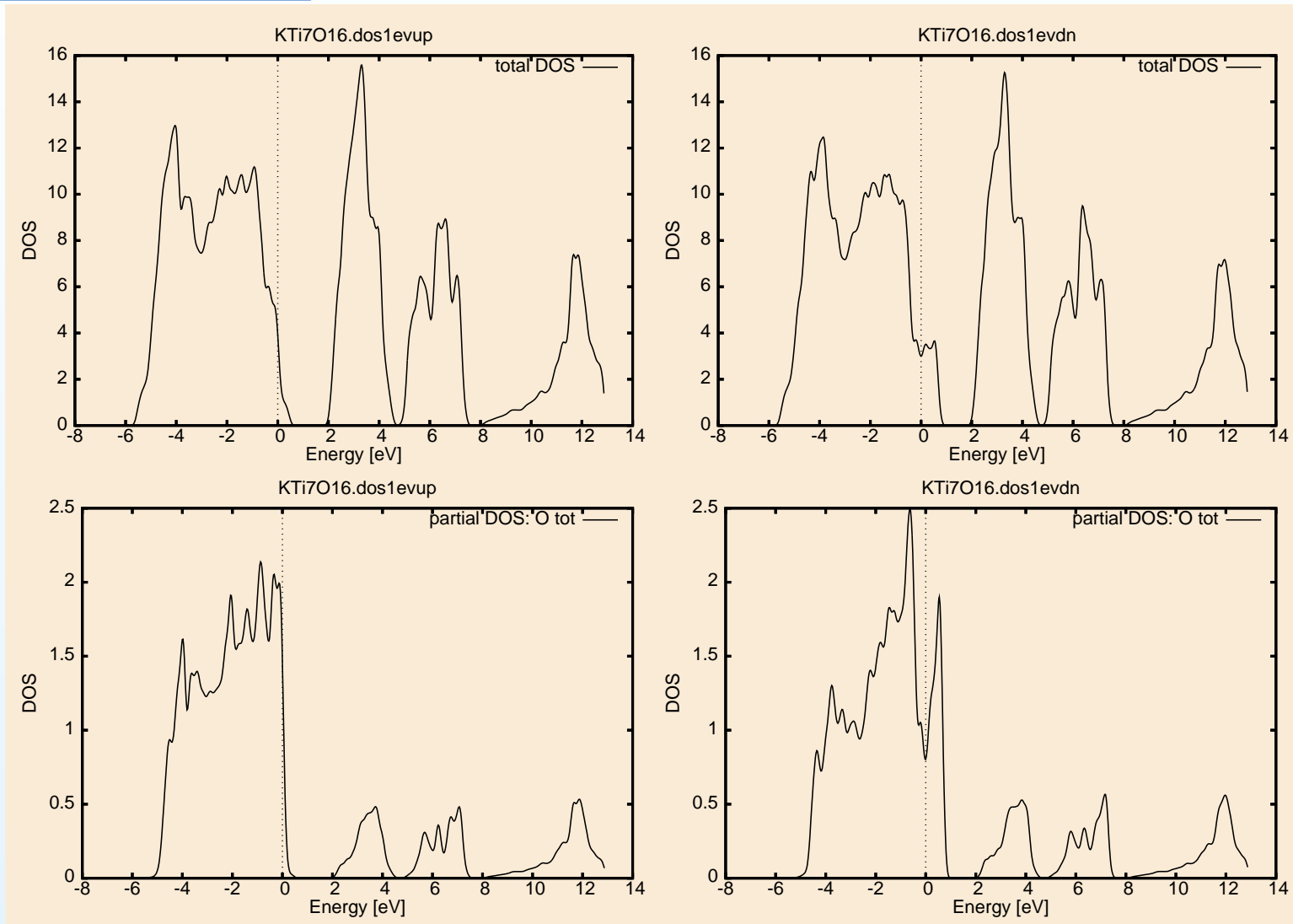
<b>Na</b>	0.00	<b>0.09</b>	0.05	-0.01	<b>0.83</b>
<b>K</b>	0.36	<b>0.31</b>	0.19	0.01	<b>2.92</b>
<b>Rb</b>	0.58	<b>0.27</b>	0.23	0.04	<b>3.00</b>
<b>Cs</b>	0.23	<b>0.09</b>	0.05	0.07	<b>1.50</b>

# LDOS for $TiO_2$



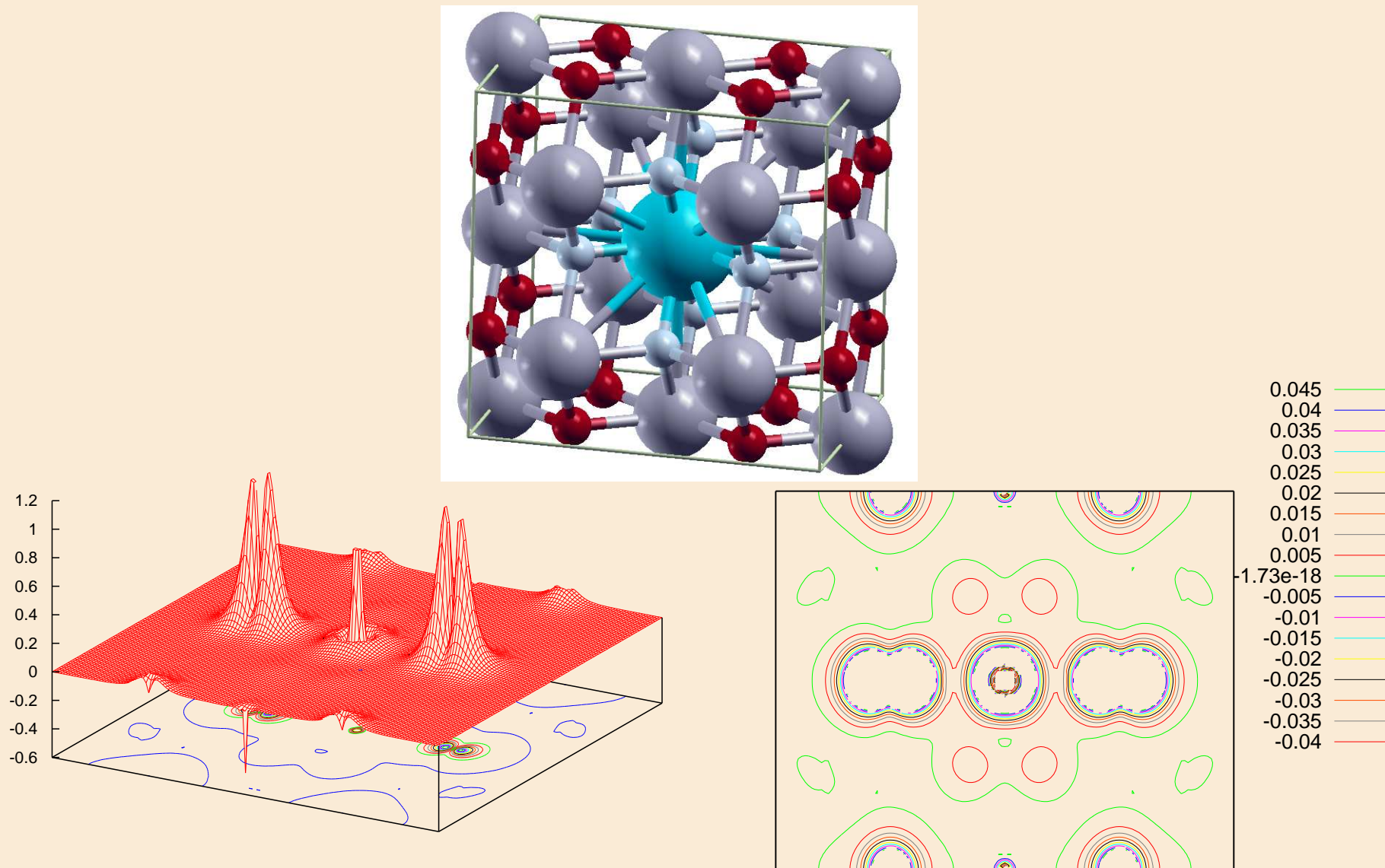
*Spin resolved LDOS for the rutile supercell  $Ti_2O_4$ : total DOS, then LDOS for Ti and O are presented.*

# LDOS for $KTi_7O_{16}$



*Spin resolved LDOS for the rutile supercell  $KTi_7O_{16}$ : up (left panel) and down (right panel), first row is total DOS, then LDOS for O is presented.*

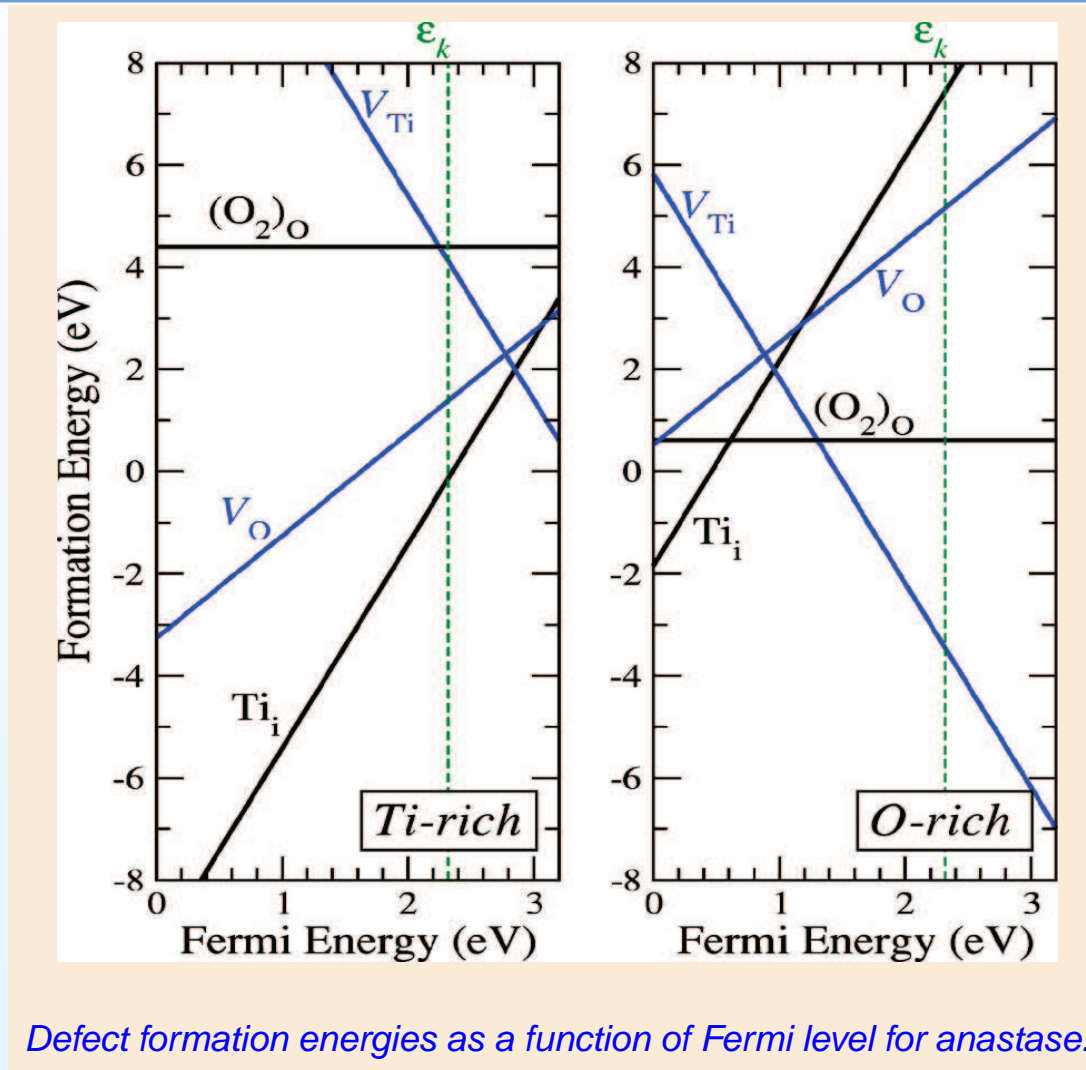
# Magnetization for $KZr_7O_{16}$



Local magnetization for the  $KZr_7O_{16}$  in the plane  $(110)$ .



# Formation energies in *anastase* $\text{TiO}_2$



[1] S. Na-Phattalung et al.,  
PRB 72 (2006) 125205.

$$\Delta H(D^q, E_F, \mu) = [E(D^q) - E(H)] + (\mu_\alpha^{\text{elem}} + \Delta\mu_\alpha) + q(E_v + \Delta E_F)$$

# Conclusions

- ✓ *The substitution of Zr(Ti) by Na, K, Rb and Cs creates magnetic moments localized on neighboring oxygen atoms in ZrO<sub>2</sub> (TiO<sub>2</sub>).*

# Conclusions

- ✓ *The substitution of Zr(Ti) by Na, K, Rb and Cs creates magnetic moments localized on neighboring oxygen atoms in ZrO<sub>2</sub> (TiO<sub>2</sub>).*
- ✓ *This is associated with the development of an impurity band in the vicinity of Fermi level. The impurity band is splitted, majority band is occupied and minority band unoccupied.*

# Conclusions

- ✓ *The substitution of Zr(Ti) by Na, K, Rb and Cs creates magnetic moments localized on neighboring oxygen atoms in  $ZrO_2$  ( $TiO_2$ ).*
- ✓ *This is associated with the development of an impurity band in the vicinity of Fermi level. The impurity band is splitted, majority band is occupied and minority band unoccupied.*
- ✓ *Our preliminary calculations of formation energies for creation of a cation vacancy as well as for substitution of cation by an alkalic metal atom in **rutile**  $TiO_2$  indicate defect concentrations far to achieve magnetic percolation.*