

# First-principles investigation of paramagnetic centers in $v\text{-SiO}_2$ , Ge-doped $\text{SiO}_2$ and $v\text{-GeO}_2$ .

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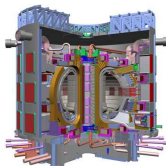
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# Motivation: Developing radiation tolerant optical fibers

- ITER plasma diagnostic system



- Space applications

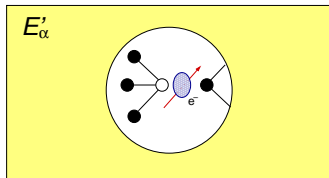
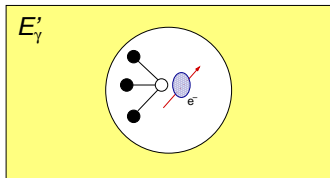


- monitoring systems for nuclear power plants and waste storage

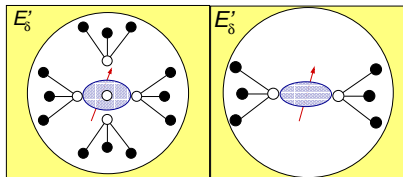


# $E'$ centers in $\alpha$ -SiO<sub>2</sub>: $E'_\gamma$ , $E'_\alpha$ , and $E'_\delta$

Proposed models:



?



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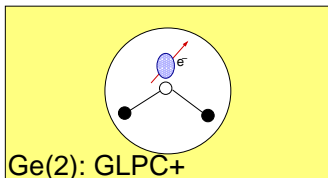
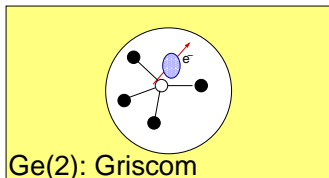
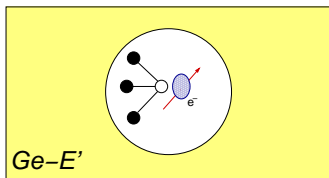
Griscom, Nucl. Inst. & Methods B1, 481 (1984).

Buscarino et al. Phys. Rev. Lett **97**, 135502 (2006).

Jivanescu et al. Phys. Rev. B **83**, 094118 (2011).

# Ge paramagnetic centers in $\nu$ -SiO<sub>2</sub>: Ge- $E'$ , Ge(2)

Proposed models:



?

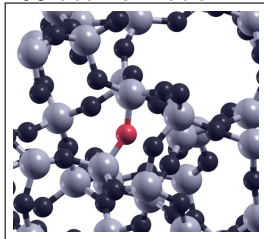
Griscom, Opt. Mater. Express **1**, 400 (2011).

Fujimaki et al. Phys. Rev. B **57**, 3920 (1998).

- GGA exchange-correlation functionals (80 ryd cutoff)
- QE and QE-GIPAW (from [www.qe-forge.org/](http://www.qe-forge.org/)):  
g-tensor GIPAW, Pickard and Mauri, PRL **88**, 086403 (2002).

## Positively charged oxygen vacancies in $\alpha$ -SiO<sub>2</sub>:

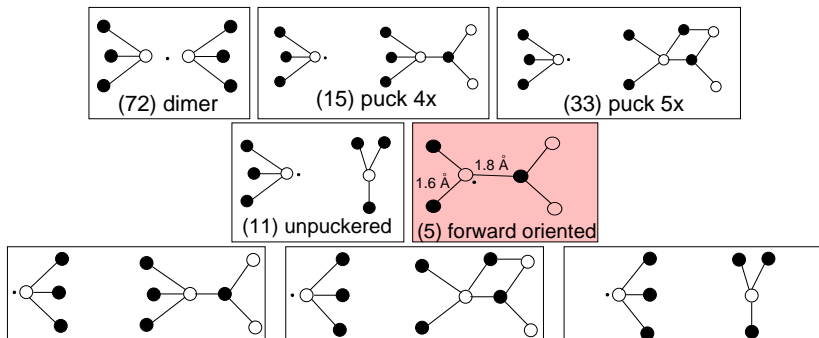
108 atoms model:



- remove a bridging oxygen from a chosen site and relax in the  $q = +1$  charged state.
- 72 SiODC models are obtained (Si<sub>2</sub> dimers)
- relax in the  $q = +2$  and again in the  $q = +1$  (non-dimers)

# EPR parameters of $E'$ centers: configurations

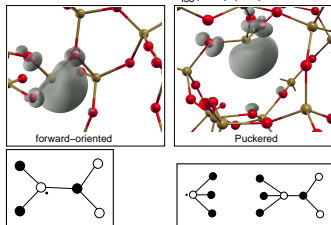
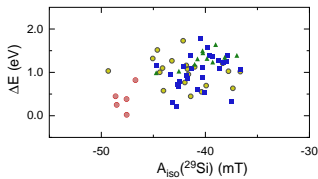
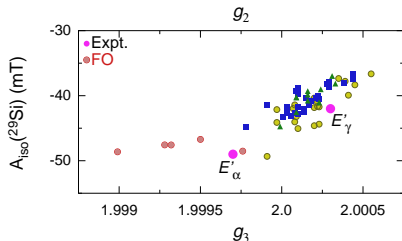
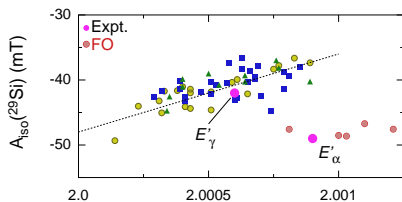
Configurations obtained after ab initio relaxation of SiODC models:



L. Giacomazzi, L. Martin-Samos, A. Boukenter, Y. Ouerdane, S. Girard, N. Richard, PRB 90, 014108 (2014).

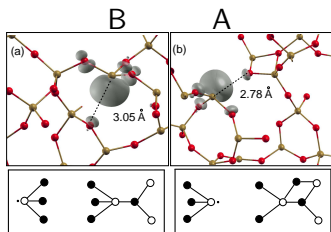
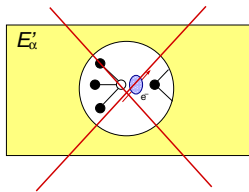
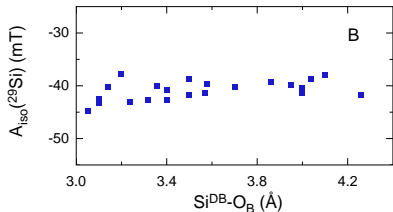
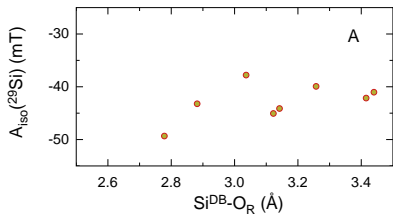
Uchino et al PRB 74, 125203 (2006); PRL 84, 1475 (2000).

# Results: Si DB puckered, unpuckered, and forward-oriented (FO) configurations



No way to find puckered configurations with  $A \sim -49$  mT and  $g_2 \sim 2.0010$  as shown by the  $E'_\alpha$ .

# Si DB "interacting" model of the $E'_\alpha$ ?

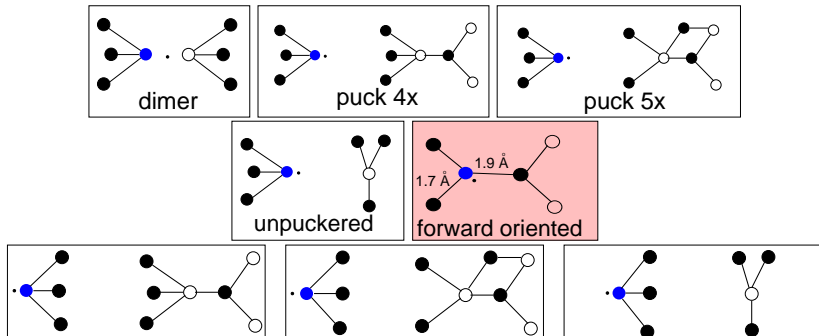


- trends could exist but local environment strongly affect  $A_{\text{iso}}(\text{Si})$
- distance  $\text{Si}^{\text{DB}}\text{-O}^{\text{B,R}} \sim 3 \text{ \AA}$  does not seem a criterion supporting the existence of an  $E'$  center at 49 mT.

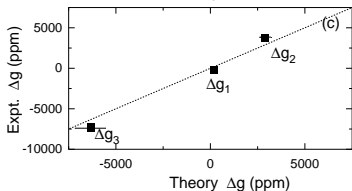
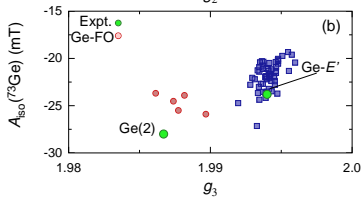
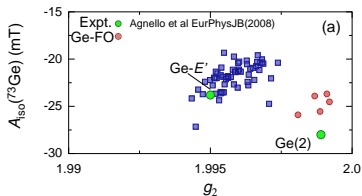


# EPR parameters of Ge centers: configurations

Configurations obtained after ab initio relaxation of GeODC models:



# EPR parameters of Ge- $E'$ and Ge-FO: distributions



- Ge puckered  $\rightarrow$  Ge- $E'$
- Ge-FO  $\rightarrow$  Ge(2)

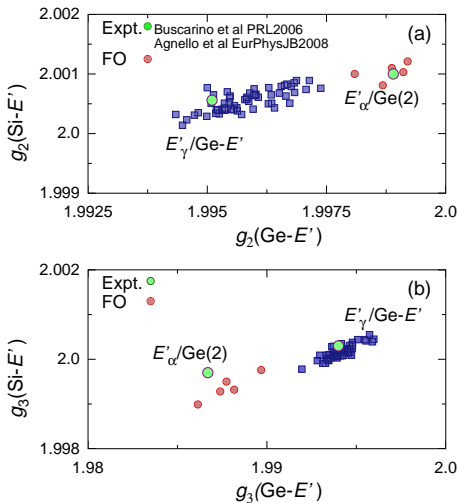
Expt.:

$$\Delta g_i = g_i(\text{Ge}(2)) - g_i(\text{Ge} - E')$$

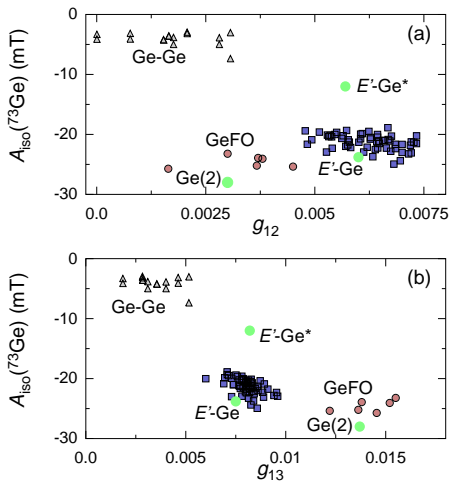
Theory:

$$\Delta g_i = g_i(\text{GeFO}) - g_i(\text{Ge} - E'_c)$$

# Ge(2) i.e. the Ge analogue of the $E'_\alpha$

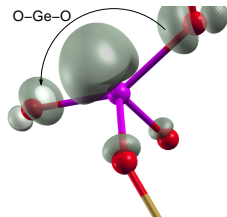
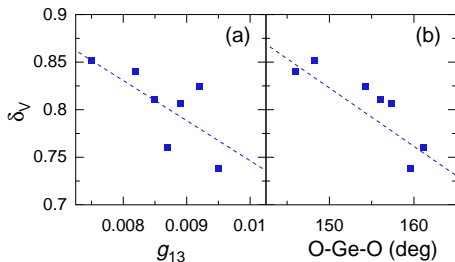


# The Ge(2) center in pure $\nu$ -GeO<sub>2</sub>



Giacomazzi, Martin-Samos, Richard, Microel Eng. **147**, 130 (2015).

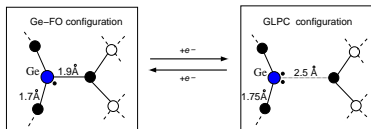
# The Ge(2) is not a trapped elect. center as Ge(1)!



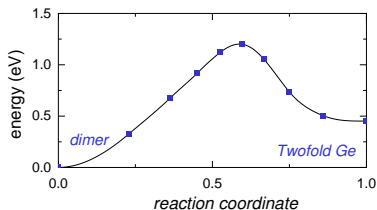
In Ge(2)  $g_{13} = 0.0140$ : for Griscom's model to be true it implies a highly deformed  $\text{GeO}_4^-$  tetrahedron with  $\delta_V \sim 0.5$  as for  $\text{O-Ge-O} \sim 180^\circ$ .

L. Giacomazzi *et al.* Opt. Mater. Express **5**, 1054 (2015).

# Twofold Si and Ge (GLPC): *in progress*

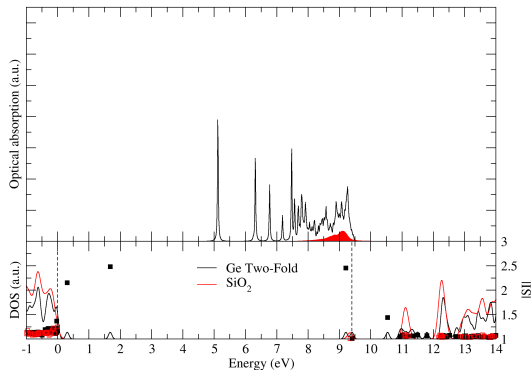


By first principles relaxation of the neutral Ge-FO a two-fold Ge is obtained. This is consistent with the observed Ge(2) generation from GLPC [Agnello et al Eur. Phys. J. B 61, 25 (2008)].



A neutral Ge-Si (Si-Si) dimer can transform into a twofold Ge (Si) configuration by overcoming  $\sim 1$  eV ( $\sim 2$ ) barrier.

# Twofold Si and Ge (GLPC): *in progress*



Just in case you doubt it is really a GeODC(II): calculations of the optical absorption spectrum gives a peak at 5.1 eV !


Giacomazzi, Martin-Samos, Richard et al *in progress* (2015).

- $E'_\alpha$  arises from "forward-oriented" configurations, while no clear evidence is found for the Si DB "interacting model".
- Ge(2) originates from Ge-FO and thus is the Ge analogue of the  $E'_\alpha$  center.
- As shown by this work, first-principles calculations of EPR parameters are a powerful tool for studying paramagnetic defects, not only for  $E'$  centers in vitreous silica but also in doped silica (e.g. Ge(2) and Ge- $E'$  in Ge-doped SiO<sub>2</sub>).
- Calculations of the optical absorption spectra are in progress for the twofold Si and Ge configurations derived from the Si-FO and Ge-FO.

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L. Giacomazzi, L. Martin-Samos, A. Boukenter, Y. Ouerdane, S. Girard, N. Richard, *Opt. Mater Express* **5**, 1054 (2015).

L. Giacomazzi, Martin-Samos, N. Richard, *Microel. Eng.* **147**, 130 (2015).

L. Giacomazzi *et al* *Phys. Rev. B* **90**, 014108 (2014). 



Thank you for your attention