Paramagnetic centers in a-GeO_2

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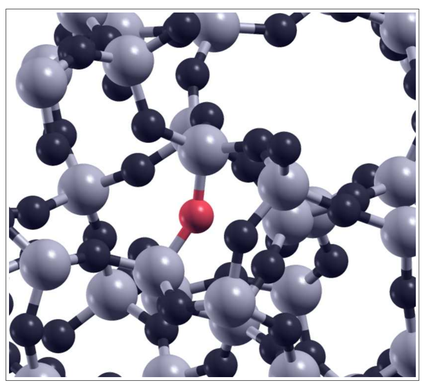
Abstract

- In this work we investigate paramagnetic centers in amorphous germania (a-GeO_2) by means of theoretical electron paramagnetic resonance (EPR). We provide an analysis of the Fermi contacts and of the g-tensors calculated by first-principles for the E'-Ge, Ge-Ge and Ge forward-oriented (GeFO) configurations.
- The EPR parameters calculated for the Ge-Ge configurations, where the unpaired electron is shared between two Ge nearest neighbors, do not support such a model of the E'-Ge*, nor the latter can be simply regard ed as an E'-Ge center with a distorted geometry.
- A fair agreement with the experimental EPR parameters support the assignment of the Ge(2) center in a-GeO_2 to GeFO configurations. Furthermore we show that electronic levels induced in the bandgap by GeFO configurations are considerably deeper ($\sim$ 1 eV) with respect to those related to the E'-Ge centers.

1 EPR parameters of E'-Ge centers: Methods & Models

- GGA exchange-correlation functionals
- Calculations performed with the QuantumEspresso and QE-GIPAW codes. (from *www.qe-forge.org/*).
- $\mathrm{g}, \mathbf{A}$ by First-Principles Theory of EPR [Pickard and Mauri, PRL **88**, 086403 (2002)].

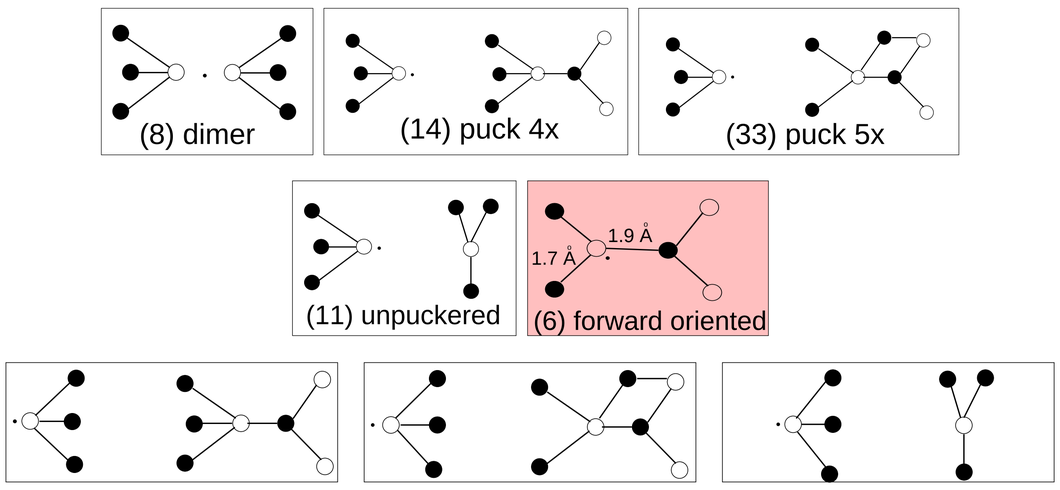
2 Positively charged oxygen vacancies in a-GeO_2:



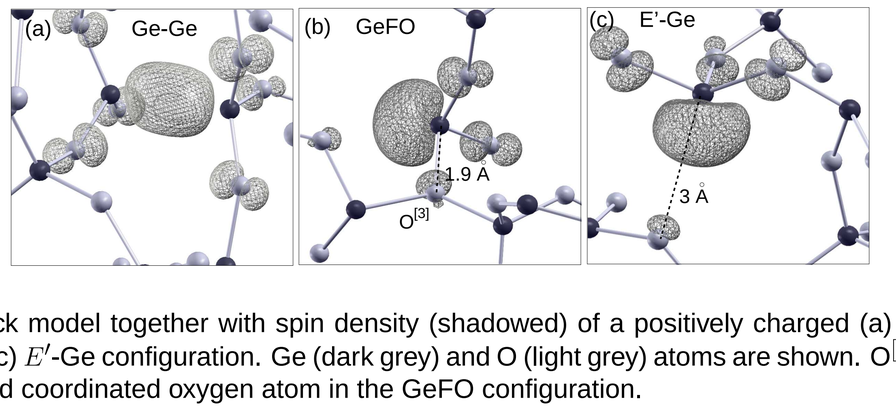
- 108 atoms model [L. Martin-Samos *et al.* PRB 71(1) 014116 (2005).]
- remove a bridging oxygen from a chosen site and relax in the $q = +1$ charged state.
- 72 silicon-oxygen deficient centers (SiODC) models are obtained $\Rightarrow$ Si_2 dimers
- relax in the $q = +2$ and again in the $q = +1$ $\Rightarrow$ non-dimer configurations: puckered, unpuckered, and forward-oriented (FO)
- For each SiODC configuration we replace Si with Ge and perform a first-principles relaxation (vc-relax) of the structure.

L. Giacomazzi, L. Martin-Samos, A. Boukenter, Y. Ouerdane, S. Girard, N. Richard, Phys. Rev. B **90**, 014108 (2014); Opt. Mater. Express **5**, 1054 (2015).

2.1 GeODC configurations



2.2 Spin-density



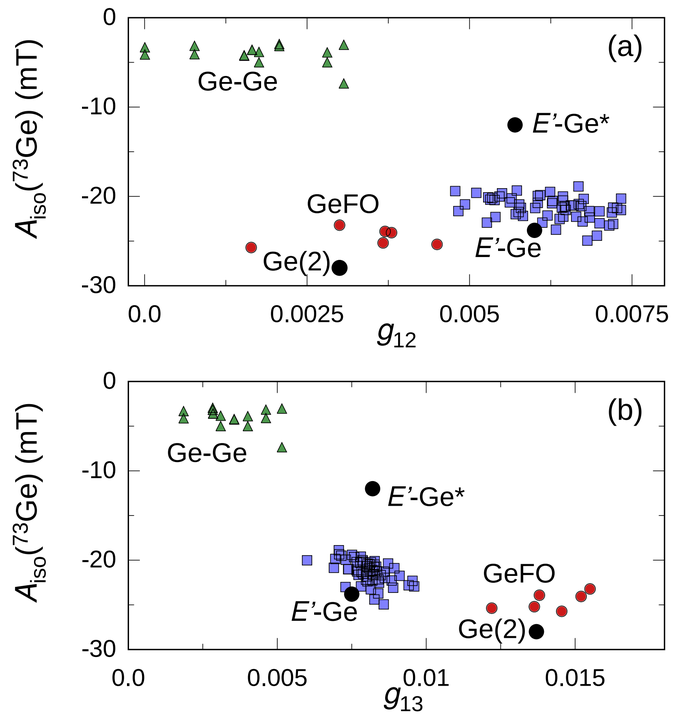
Ball and stick model together with spin density (shadowed) of a positively charged (a) Ge-Ge (b) GeFO and (c) E'-Ge configuration. Ge (dark grey) and O (light grey) atoms are shown. $O^{[3]}$ indicates the three-fold coordinated oxygen atom in the GeFO configuration.

2.3 Positively charged oxygen vacancy in in GeO_2 quartz

g principal values of a positively charged oxygen vacancy (puckered configuration) in GeO_2 quartz as calculated in this work (TW) at Γ point and using $2 \times 2 \times 1$ and $2 \times 2 \times 2$ k-points meshes. Experimental values $g_{//}$ and $g_{\perp}$ from Garlick *et al.* J. Phys. C Solid St. Phys. 4, 2230 (1971) are also given for comparison:

	k-points	g_1	g_2	g_3	g_{12}	g_{13}
TW	Γ	2.0043	1.9976	1.9958	0.0068	0.0085
TW	221	2.0020	1.9950	1.9931	0.0070	0.0089
TW	222	2.0015	1.9946	1.9932	0.0069	0.0083
Expt.		2.0015		1.9940		

3 Results: distributions of EPR parameters of E'-Ge and Ge-FO in a-GeO_2

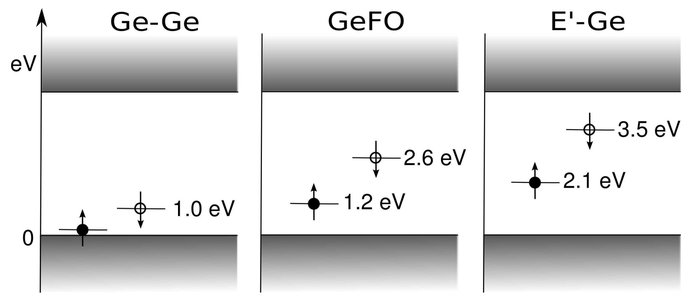


Ge puckered and unpuckered distributions (blue square) give rise to the E'-Ge center while Ge(2) center arises from Ge forward-oriented configurations (red discs).

(averages)	$A_{iso}(^{73}Ge)$ (mT)	g_1	g_2	g_3	g_{12}	g_{13}
Ge-Ge	-4.0	2.0077	2.0060	2.0042	0.0017	0.0035
E'-Ge (puck.)	-21.8	2.0027	1.9965	1.9947	0.0062	0.0080
GeFO	-24.6	2.0030	1.9996	1.9989	0.0034	0.0141
E'-Ge Expt.[a]	23.8	2.0012	1.9952	1.9937	0.0060	0.0075
E'-Ge* Expt.[a]	12	2.001	1.9955	1.9930	0.0055	0.0080
Ge(2) Expt.[a,b]	28			1.9885	0.0030[b]	0.0137[b]

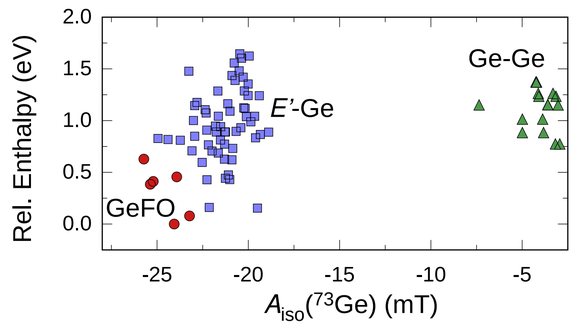
[a] Tsai *et al.* J. Appl. Phys. 62, 2264 (1987); [b] Alessi *et al.* J.Non-Cryst Solids 357, 1900 (2011).

3.1 Electronic levels



The DFT calculated band gap ($\sim$4.4 eV) largely underestimates the experimental value in a-GeO_2 (about 5.6-5.8 eV, Ravindra *et al.* PRB36, 6132 (1987)) as typical in DFT calculations (Tamura *et al.* PRB69, 195204 (2004)). Ge-Ge configurations give rise to defect levels just above the top of the valence band, while in GeFO and E'-Ge the corresponding levels are moved up of about 1 and 2 eV respectively. We remark that, despite the spin densities of GeFO and E'-Ge configurations look quite similar [see Sec. 2], the defect states induced by GeFO are about 1 eV deeper in the band gap than defect states induced by E'-Ge configurations.

3.2 Relative stability



Relative enthalpy (with respect to the lowest enthalpy configuration) vs ^{73}Ge Fermi contact as calculated for E'-Ge (squares) and GeFO (discs) and, Ge-Ge dimer (triangles) configurations.

Conclusions and perspectives

- In this work we presented a first-principles investigation of paramagnetic centers in a-GeO_2. We show that the Ge(2) center in a-GeO_2 arises from low relative enthalpy configurations i.e the GeFO configurations. Furthermore the electronic levels of our GeFO are about 1 eV deeper in the band gap than defect states induced by E'-Ge configurations.
- Concerning the E'-Ge* center we could not find a suitable structural model. Yet our calculations show that this center should not be originated from a positively charged Ge-Ge configuration or from a variant of the E'-Ge involving just a local structural distortion.
- NEB and GW/BSE calculations are in progress in order to have a better understanding of the properties of the above discussed Ge defects.

L. Giacomazzi, L. Martin-Samos, N. Richard, "Paramagnetic centers in amorphous GeO_2", Microelectronic Engineering 147, 130 (2015); L. Giacomazzi, L. Martin-Samos, A. Boukenter, Y. Ouerdane, S. Girard, N. Richard, Opt. Mater. Express **5**, 1054 (2015).

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