Paramagnetic centers in $\alpha$-GeO$_2$

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Abstract

- In this work we investigate paramagnetic centers in amorphous germania ($\alpha$-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 regarded as an $E'$-Ge with a distorted geometry.
- A fair agreement with the experimental EPR parameters support the assignment of the Ge(2) center as 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.

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/.

2 Positively charged oxygen vacancies in $\alpha$-GeO$_2$:

- 108 atoms model [L. Martin-Samos et al. PRB 71(1) 014116 (2005)].
- 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 Results: distributions of EPR parameters of $E'$-Ge and Ge-FO in $\alpha$-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).

3.1 Electronic levels

The DFT calculated band gap (about 4.4 eV) largely underestimates the experimental value in $\alpha$-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 $\alpha$-GeO$_2$. We show that the Ge(2) center in $\alpha$-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.

