Supplementary material for: Defect induced site-selective self-trapped holes and their optical fingerprints in β-Ga_2O_3

F. Bermúdez-Mendoza,[1] E. Nogales,[1] B. Méndez,[1] F. Domínguez-Adame,[1] E. Díaz,[1] and R. Martínez-Casado[1]

Departamento de Física de Materiales, Universidad Complutense, E-28040 Madrid, Spain

(Dated: 6 March 2026)

I. ELECTRONIC STRUCTURE OF β-GA_2O_3 IN PRESENCE OF OXYGEN VACANCIES

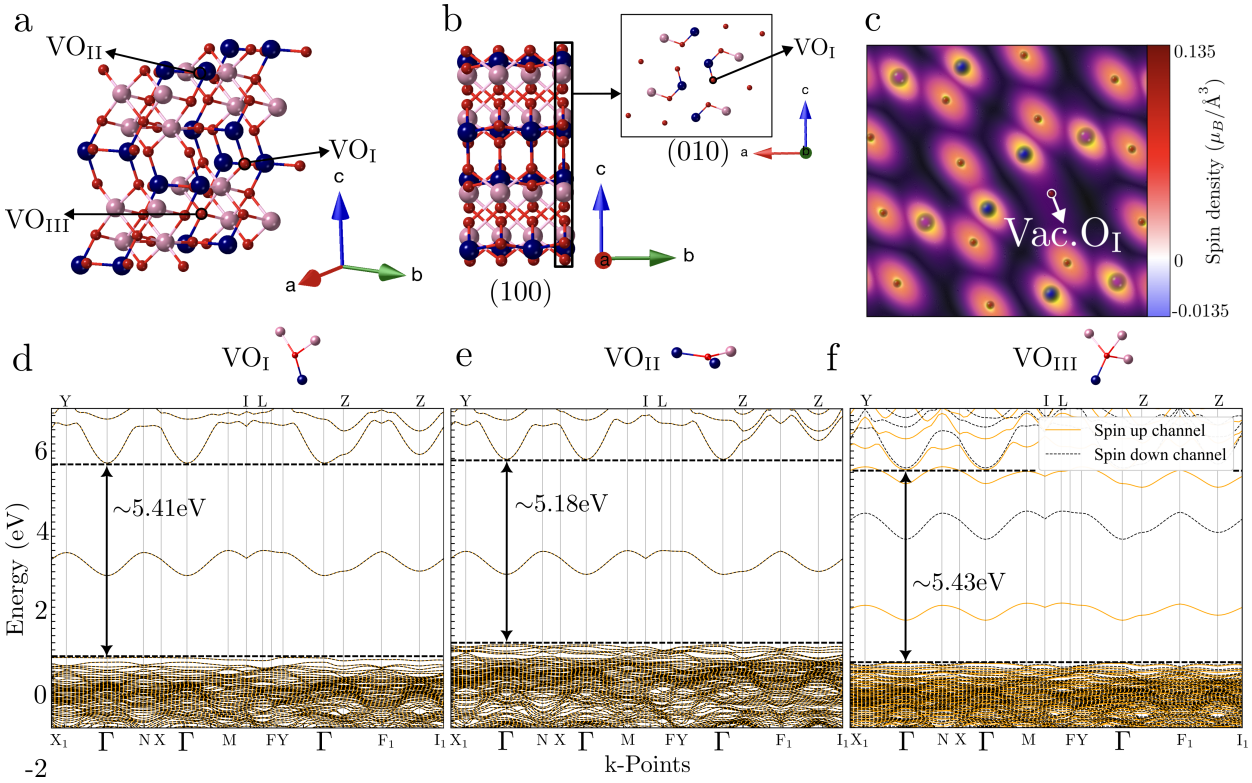

FIG. S1. Oxygen vacancies and associated in-gap states in β-Ga_2O_3. (a) Crystal structure where the three inequivalent oxygen sites considered for vacancy formation are highlighted, VO_I, VO_{II} and VO_{III}. (b) Projection indicating the plane used for the real-space analysis; inset shows the local environment around VO_I (c) Spin-density distribution on the (010) plane in presence of the non-magnetic VO_I, showing no localized spin polarization. (d-f) Spin-resolved (up-yellow and down-black) band structures for cells with VO_I, VO_{II} or VO_{III} where vacancy-induced in-gap states arise.

We performed spin-polarized calculations for neutral oxygen vacancies at the three inequivalent oxygen sites in β-Ga_2O_3. The real-space magnetization $m(\vec{r}) = \rho_\alpha(\vec{r}) - \rho_\beta(\vec{r})$ remains negligible, i.e. no exchange splitting develops. Therefore, oxygen vacancies do not stabilize oxygen-centered self-trapped holes (STHs) under the conditions considered here, in agreement with the well-established closed-shell and deep-donor character of the oxygen vacancy (VO) in β-Ga_2O_3[1–4]. At the same time, VO introduce occupied, weakly dispersive in-gap bands [Fig. S1(d-f)]. These account for deep donor states, whose energies

depend on the oxygen sublattice and therefore imply a particular defect-dependent sub-gap optical response[1,2,5,6]. Additionally these VO donor levels do not create a non-zero spin-density so they don't support the localized spin fingerprint characteristic of self-trapped holes or Ga-vacancy STH complexes[3,7,8]. Instead, their dominant role is to act as an electron reservoir that can feed donor-acceptor recombination with hole-like acceptors (including self-trapped holes and gallium-vacancy STH complexes), which is commonly invoked to rationalize sample-dependent visible luminescence in β-Ga_2O_3[6,9–12]. This donor-like picture is also consistent with electron spin resonance (ESR) observations of electron-like centers associated with oxygen deficiency in conductive samples[13].

II. ELECTRONIC STRUCTURE OF β-GA_2O_3 IN PRESENCE OF GALLIUM VACANCIES: $1 \times 2 \times 2$ CELL

Within periodic boundary conditions, the introduction of one VGa per supercell represents an ordered vacancy array. By increasing the supercell size the artificial vacancy concentration and the interactions between periodic images are reduced, thereby approaching the dilute-defect limit relevant for isolated point defects. This is particularly important in ionic ultrawide-band-gap oxides, where defect-induced lattice polarization and local relaxations can extend over several Å, making finite-size convergence comparatively slow[3,14]. To assess finite-size effects, we repeated the VGa calculations in a smaller $1 \times 2 \times 2$ supercell (80 atoms), shown in Fig. S2. A single VGa in this cell corresponds to a higher nominal defect concentration (1/32 Ga sites, $\simeq 3.1\%$) and a shorter periodic defect–defect separation than in the $2 \times 2 \times 2$ supercell used in the main text (1/64 Ga sites, $\simeq 1.6\%$). At this higher concentration, defect-derived levels show enhanced splitting and dispersion, and the relative stability of competing trapping geometries can be affected. This matters especially for STHs defects where there exists an overlap between the localized O-2p hole (and its accompanying local distortion) and its periodic images. Thus, the in-gap STH leads to a broader shifted band. Consistent with this picture, Fig. S2(a,b) shows that system with both VGa_I and VGa_{II} still bind an oxygen-centred STH with a localized spin density, while Fig. S2(c,d) shows the corresponding spin-polarized in-gap states. For this reason, the $1 \times 2 \times 2$ results are used as a finite-size/high-concentration robustness check, whereas the $2 \times 2 \times 2$ cell is taken as our best compromise toward the dilute limit for the main analysis. Importantly, the

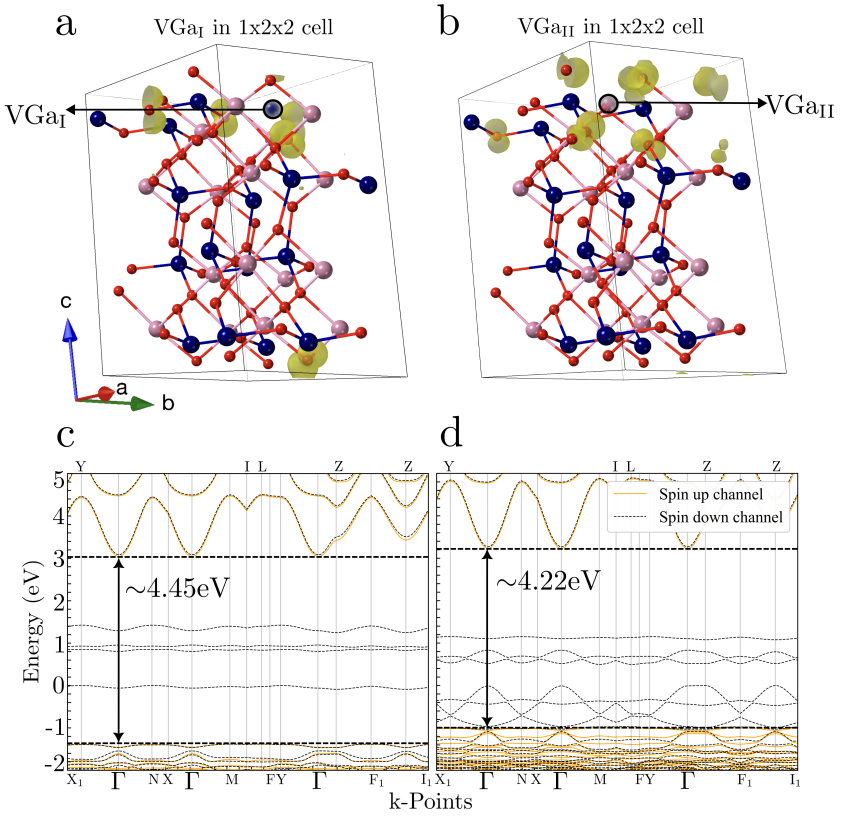

FIG. S2. Gallium-vacancy in-gap states in a $1\times2\times2$ β-Ga_2O_3 supercell. (a,b) Spin-density distribution for systems in presence of VGa_I and VGa_{II}, showing strong state localization on neighbouring O sites. (c,d) Spin-resolved band structures (up-yellow and down-black) with nearly dispersionless, spin-polarized mid-gap states inside the apparent bandgap (4.45 eV for VGa_I and 4.22 eV for VGa_{II}).

qualitative conclusion is unchanged and remains consistent with hybrid-DFT and electron paramagnetic resonance (EPR) assignments of VGa related centers in β-Ga_2O_3[3,15,16].

REFERENCES

[1]J. B. Varley, J. R. Weber, A. Janotti, and C. G. Van de Walle, Appl. Phys. Lett. **97**, 142106 (2010).

[2]T. Zacherle, P. C. Schmidt, and M. Martin, Phys. Rev. B **87**, 235206 (2013).

[3]P. Deák, Q. D. Ho, F. Seemann, B. Aradi, M. Lorke, and T. Frauenheim, Phys. Rev. B **95**, 075208 (2017).

[4]A. Usseinov, Z. Koishybayeva, A. Platonenko, V. Pankratov, Y. Suchikova, A. Akilbekov, M. Zdorovets, J. Purans, and A. I. Popov, Materials **14**, 7384 (2021).

[5]L. Y. Hao, J. L. Du, and E. G. Fu, J. Appl. Phys. **134**, 085101 (2023).

[6]M. D. McCluskey, J. Appl. Phys. **127**, 101101 (2020).

[7]B. E. Kananen, N. C. Giles, L. E. Halliburton, G. K. Foundos, K. B. Chang, and K. T. Stevens, J. Appl. Phys. **122**, 215703 (2017).

[8]Y. K. Frodason, K. M. Johansen, L. Vines, and J. B. Varley, J. Appl. Phys. **127**, 075701 (2020).

[9]L. Binet and D. Gourier, J. Phys. Chem. Solids **59**, 1241 (1998).

[10]Q. D. Ho, T. Frauenheim, and P. Deák, Phys. Rev. B **97**, 115163 (2018).

[11]H. Liu, C. Xu, X. Pan, and Z. Ye, J. Electron. Mater. **49**, 4544 (2020).

[12]V. Patil, B.-T. Lee, and S.-H. Jeong, J. Alloys Compd. **894**, 162551 (2022).

[13]M. Yamaga, H. Tsuzuki, S. Takano, E. G. Villora, and K. Shimamura, J. Non-Cryst. Solids **358**, 2458 (2012).

[14]C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, Rev. Mod. Phys. **86**, 253 (2014).

[15]B. E. Kananen, N. C. Giles, L. E. Halliburton, G. Foundos, K. Chang, and K. T. Stevens, Appl. Phys. Lett. **110**, 202104 (2017).

[16]C. Kaewmeechai, J. Strand, and A. L. Shluger, Phys. Rev. B **111**, 035203 (2025).