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ABSTRACT

Recent suggestions that hydrogen incorporation at the Ga(1) vacancy in β-Ga_2O_3 may have an impact on its electronic properties have led us to extend our earlier work on these defects. While our previous work provides strong evidence for one, two, and perhaps three or four H trapped into the shifted vacancy configurations introduced by Varley and Kyrtsos, the apparent experimental absence of several H trapped in the unshifted configuration is puzzling. While a structure of two hydrogen atoms trapped in the unshifted configuration is not favored energetically, structures of three or four hydrogens in the unshifted configuration are favored. We suggest that these structures are absent because there are no available pathways for the system to reach them by sequentially trapped H and, therefore, that three- or four-hydrogen defects will occur only in the shifted vacancy configurations.

Islam *et al.*[1] have reported the generation of novel electronic properties of β-Ga_2O_3 associated with hydrogen incorporation by particular chemical and heat treatments of the material. Their results have led them to conclude that trapping of two H atoms at a Ga(1) vacancy leads to p-type behavior, while subsequent n-type behavior is the result of the trapping of four H atoms at the Ga(1) vacancy. They support these conclusions by using density functional theory (DFT) to calculate the binding energies of one, two, three, and four H atoms at the Ga(1) vacancy. These processes, if supported by subsequent results, could play significant roles in the understanding[2] and applications[3,4] of β-Ga_2O_3, as noted by Polyakov *et al.*[5]

However, the models of these defects and of the Ga(1) vacancy suggested by Islam *et al.*[1] and earlier by Wei *et al.*[6] involve an *unshifted* configuration of this defect and have not taken account of the remarkable spontaneous restructuring of the Ga(1) defect that has been found to take place, both with and without trapped H. Specifically, the Ga(1) vacancy is metastable against lower-energy shifts into two inequivalent configurations (Fig. 1) in which a neighboring Ga(1) moves to an interstitial position halfway between its original site and the site of the vacancy.[7–9] These shifted configurations have also been described as interstitial Ga(1) plus two Ga(1) vacancies. This restructuring involves large relaxation energies, as large as 1 eV, so must be taken into account in calculating the binding energies of hydrogens trapped at the Ga(1) vacancy. One of these sites[7,9] [Fig. 1(b)] is favored for the −3 charged vacancy, while the other[8] [Fig. 1(c)] has been suggested to exist after trapping a hole.[10–13] [A third shifted configuration, referred to as "$V_{Ga}^{(a)}$" in Refs. 8 and 14, is less favored energetically both with and without trapped H. Furthermore, the related O–H centers would yield a plethora of IR transitions with [010] projections that have not been observed. Therefore, defects based on configuration $V_{Ga}^{(a)}$ are not considered further. We note as well that the "Kyrtsos" and "Varley" configurations shown in Fig. 1 have been referred to elsewhere[8,14] as "$V_{Ga}^{(b)}$" and "$V_{Ga}^{(c)}$" or[15] $Ga(1)_{23}$ and $Ga(1)_{21}$, respectively.]

Given the different symmetries and the different nature and number of oxygen neighbors of the Ga(1) vacancy in its various configurations, it is clear that understanding the nature and structure of trapped H defects is non-trivial. In fact, a great deal is already understood about these defects from research that has combined infrared spectroscopy, analysis, and DFT calculations.[15–18] While a number of O–H defects may be introduced and transformed by different means,[19,20] several facts stand out from this research. First, no "stretching" O–H vibrations have been detected which have transition moments with projections in the [010], or b, direction; all the observed transition moments lie in the a–c plane of Ga_2O_3. Second, the primary

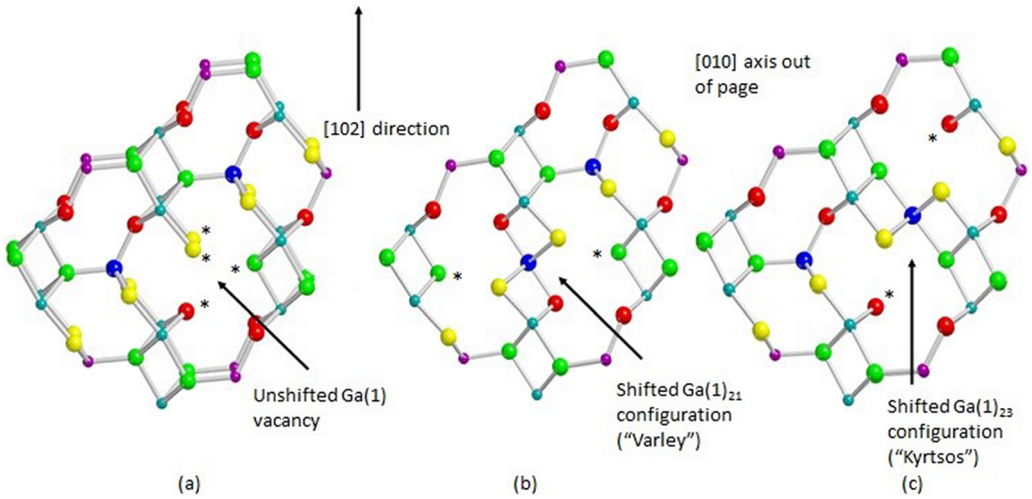

FIG. 1. (a) Unshifted Ga(1) vacancy. (b) Shifted Varley configuration, more stable than the unshifted configuration by ≈ 1 eV (Varley *et al.*[7]). (c) Shifted Kyrtsos configuration, more stable than the unshifted configuration by ≈ 0.7 eV (Kyrtsos *et al.*[8]). The inequivalent atomic sites are color coded as follows: Ga(1), purple; Ga(2), dark green; O(1), red; O(2), yellow; and O(3), light green. The two Ga(1) atoms involved in the shifting are dark blue. Undercoordinated oxygens are denoted by "∗." These figures were constructed using MOLDRAW[23] and POV-Ray.[24]

defect involves two H atoms in the shifted configuration shown in Fig. 3(c).[15–17] This defect has an antisymmetric mode with its transition moment near the [102] direction and a symmetric mode that is forbidden. Discussion of this structure along with a more detailed figure may be found in Ref. 16. Third, a number of these lines have transition moments perpendicular to the (−201) plane.[15] (In unpublished work[18] on the O–D defects produced by the implantation of deuterons into Ga_2O_3, several additional defects have been discovered with transition moments perpendicular to the (−201) plane. Furthermore, no additional defects with transition moments along [010] directions are found in these recent experiments.)

The hybrid DFT calculations[21] cited in Refs. 15–17 and shown in Table I support the relative energies[7,8] of the two shifted Ga(1) vacancy configurations shown in Figs. 1(b) and 1(c). Our extensions of these CRYSTAL06 calculations using the same framework as detailed in Ref. 16 suggest that the atomic motions between these configurations need not pass through the unshifted configuration, but rather that the two relevant Ga(1) atoms shown in dark blue in Fig. 1 can move in concert from one to the other shifted configuration. This result may have important implications concerning the formation of hydrogen centers that involve an unshifted Ga(1) vacancy.

When H trapping occurs and heat treatments allow configurations to change, the relative energies of the H-decorated vacancies in their various structures must be examined. The results reported here along with our published calculations[15–17] yield defect structures and relative energies (Table I) for different numbers of trapped H in the configurations of Figs. 2 and 3. (We do not illustrate an additional unshifted configuration, nearly degenerate with that of Fig. 2(a), in which H is trapped on O(2). This configuration would yield a transition moment with a projection in the [010] direction, which is not observed experimentally.) For a single H, the Kyrtsos configuration of Fig. 2(c) is found to be most stable, but only by ≈ 0.1 eV with respect to the other two.[22] Thus, any of the three configurations shown in Fig. 2 could be contributing to the single O–H spectra, and in fact, the lines seen by experiment whose transition moments are perpendicular to the (−201) plane almost certainly arise from versions of the Varley configuration of Fig. 2(b). For two H atoms, the Kyrtsos configuration of Fig. 3(c) is found to be most stable by 0.2 eV with respect to the lowest-energy unshifted case [Fig. 3(a)] and by 0.6 eV with respect to that of the Varley configuration of Fig. 3(b). The O–H sites of Fig. 3(a) are symmetry-inequivalent and so would yield distinct O–H lines; furthermore, the line arising from O(2)-H would have a substantial [010] component. As noted in Refs. 15–17, the two sites of Figs. 3(b) and 3(c) are symmetry-equivalent, and so in each case, one mode would be observed and a second mode with even symmetry would be forbidden. Dynamically decoupled lines would be seen only for an H-D pair. These lines would have no [010] component.

There is compelling experimental evidence[15–17] that supports the existence, under appropriate conditions, of one- and two- O–H defects

TABLE I. Energies in eV, relative to the unshifted configuration, from CRYSTAL06 calculations.

Configuration	Ga(1) vacancy (−3 charge)	Ga(1) vacancy plus 1 H (−2 charge)	Ga(1) vacancy plus 2 H (−1 charge)	Ga(1) vacancy plus 3 H (0 charge)
Kyrtsos	−0.7	−0.1	−0.2	+0.9
Varley	−1.0	+0.03	+0.4	+0.9

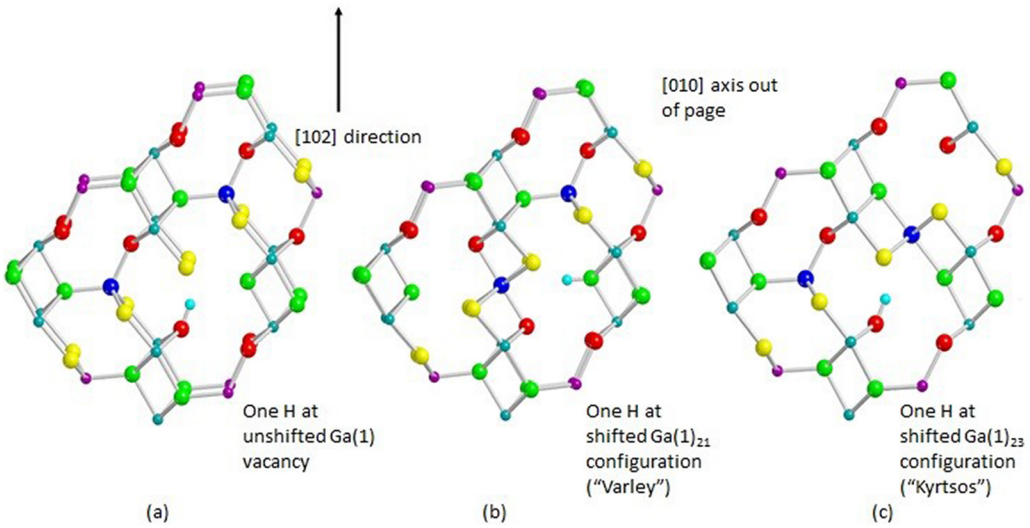

FIG. 2. (a) One H trapped at an unshifted Ga(1) vacancy. (b) One H trapped in a shifted Varley configuration. (c) One H trapped in a shifted Kyrtsos configuration. Color coding as in Fig. 1, with H light blue. These figures were constructed using MOLDRAW[23] and POV-Ray.[24].

of both Kyrtsos [Figs. 2(c) and 3(c)] and Varley [Figs. 2(b) and 3(b)] types. Furthermore, the absence of O–H lines with projections in the [010] direction means that the unshifted configuration with two H atoms shown in Fig. 3(a) is absent, even though this unshifted configuration is lower in energy than the Varley configuration [Fig. 3(b)], which gives rise to O–H lines with transition moments perpendicular to the (−201) plane.

Our results suggest that the experimental absence of two H atoms at the unshifted vacancy arises from details of the H trapping and relaxation processes. A single H trapped on O(3) in the lowest-energy Varley vacancy configuration [Fig. 2(b)] may remain in this metastable configuration under appropriate conditions and may contribute to the IR spectrum. Alternatively, the system may relax from Fig. 2(b) to the unshifted configuration [Fig. 2(a)] in which H has transferred to an adjacent O(1), while the shifted Varley Ga(1) has returned to its normal site. Subsequent relaxation into the lower-energy Kyrtsos configuration [Fig. 2(c)], which requires only the further motion of a single Ga(1), would then be expected to follow. This suggests that a single H trapped in the unshifted configuration [Fig. 2(a)] will not be observed.

If a second H is trapped at an existing Varley site [Fig. 3(b)], the distance of the second H from its location in either of the other two configurations [Figs. 3(a) and 3(c)] means that this configuration

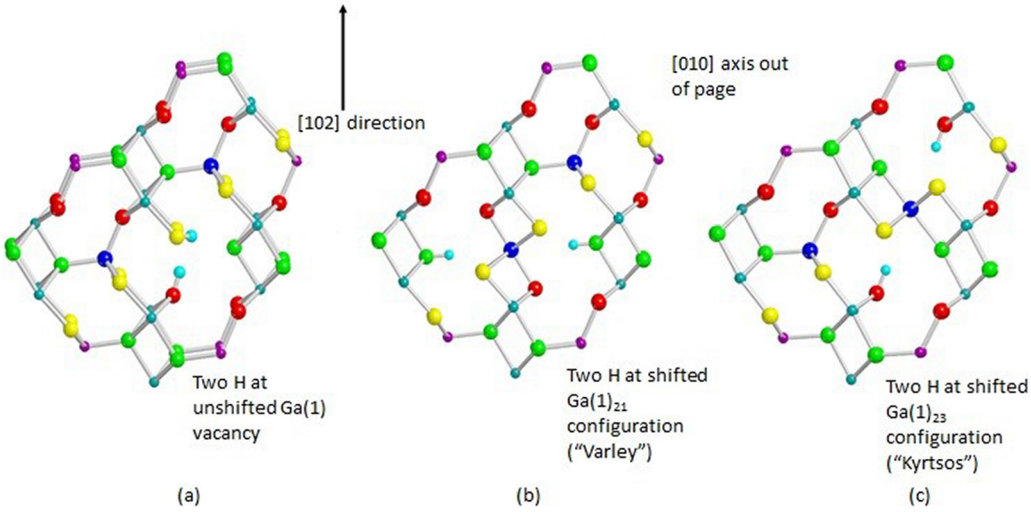

FIG. 3. (a) Two H atoms trapped at an unshifted Ga(1) vacancy. The O–H axis for H trapped at an O(2) lies nearly in the [010] direction. (b) Two H atoms trapped in a shifted Varley configuration. (c) Two H atoms trapped in a shifted Kyrtsos configuration. Color coding as in Fig. 1, with H light blue. These figures were constructed using MOLDRAW[23] and POV-Ray.[24]

should be strongly metastable, contributing to the IR spectrum, even though not favored energetically. While the two-H unshifted configuration of Fig. 3(a) is favored energetically over that of Fig. 3(b), the lack of its one-H precursor will lead to its absence. This then leaves the Kyrtsos configuration [Fig. 3(c)] as the remaining, and the most stable, two-H defect, as observed experimentally.

Because the two shifted configurations [Figs. 1(b) and 1(c)] each have only two undercoordinated oxygen atoms (denoted by "∗"), their attraction for a third or fourth H would be weaker than that of the unshifted vacancy [Fig. 1(a)], which has four such oxygen atoms. Indeed, we find that for three H atoms, the unshifted vacancy is most stable by ≈ 0.9 eV with respect to either shifted case, and the unshifted four-H structure is favored in a similar manner. However, we find that each of these three- and four-H unshifted-vacancy configurations would have at least one vibrational mode with a strong [010] component, and there is no experimental evidence[15–17] for such modes. Thus, the absence of any defects with H atoms trapped at an unshifted Ga(1) vacancy with the structures proposed by Islam *et al.*[1] or Wei *et al.*[6] in spite of their low energy appears to be a puzzle.

The absence of experimental evidence for H centers with multiple H atoms trapped at an unshifted Ga(1) vacancy could mean that in the samples studied in Refs. 15–17, there were no defects with three or four H atoms, although we have presented evidence[15] for their existence in the Varley configuration. Instead, we suggest that despite their energetic favorability, three-and four-H defects simply do not occur in the unshifted configuration. If we accept the experimental evidence for the absence of two-H defects in the unshifted configuration and the corresponding robustness of the Varley and Kyrtsos structures for two-H defects, it follows that subsequent H trapping will continue to decorate these shifted configurations. There simply may be no pathway for subsequent additional H atoms to reach their lowest-energy configurations within an unshifted Ga(1) vacancy.

The absence of experimental evidence for multiple hydrogens trapped at an unshifted Ga(1) vacancy means that physical conclusions[1,6] based on trapped hydrogens must be obtained from the actual, shifted, structures of these defects. While defects with three or four hydrogen atoms trapped at an unshifted Ga(1) vacancy may have lower energy than for defects with a shifted Ga(1) vacancy, the absence of pathways to reach these configurations by the sequential trapping of additional H atoms at temperatures for which these defects have been investigated can explain their absence in recent experiments.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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[22]It is expected that the relative energies of different configurations of the vacancy that has trapped a hole[10–13] will resemble those of the vacancy that has trapped a single H since the hole would be associated with the same O that traps H. In fact, the small energy difference between the unshifted and the Kyrtsos configurations for the trapped hole was noted in Ref. 13. It is possible that the two similar but unique EPR defects reported in Refs. 10–12 (EPR1) and Ref. 13 (IR1) come from these two configurations.
[23]See P. Ugliengo, see http://www.moldraw.unito.it for "MOLDRAW" (2006).
[24]See http://povray.org for information about "POV-Ray."