Comment on "*Ab Initio* Calculations to Model Anomalous Fluorine Behavior"

Ab initio calculations on the behavior of fluorine (F) in Si were reported recently [1]. In Table I of Ref. [1], the incremental binding energy of a F atom to a F_3V complex to form a F_4V complex is reported to be 0.1 eV, with an abrupt decrease (in absolute value) from about 2 eV for the other F_nV complexes. We [2] have found instead that, in the same conditions as in Ref. [1], the incremental binding energy of the last F to F_4V is 2.0 eV, close to that found for the other F_nV. Otherwise stated, we predict F_4V in Si to have a formation energy roughly 2 eV lower than in Ref. [1]. While there is no guarantee of it being a global configurational minimum, our structure is evidently a much improved guess at the ground state of the F_4V complex in Si compared to that of Ref. [1].

The reason for this is easily understood. Si first neighbors are at 2.35 Å from a vacant site, and the sum of a typical Si-F bond length plus the F covalent radius is 2.4 Å. Therefore, there is no room at the vacancy for more than one strictly dangling-bond-oriented Si-F bond, and a mutual avoidance of the F's decorating a vacancy is expected. In F_4V, indeed, F-Si bonds rotate away from the original dangling-bond direction so as to avoid F contacts within the vacancy. In Fig. 1(a), we show the relaxed structure of F_4V. The F-Si bond lengths are about 1.68 Å, a typical value for these complexes. The approximate symmetry is C_{2h} [the view in Fig. 1(a) is along the twofold axis], but no symmetry was imposed in the calculation.

If the relaxation is started from 4 F's attached to dangling bonds along (111)-like directions, even if the symmetry is formally removed, the system remains trapped in a nearly tetrahedral configurational local minimum, whereby F's avoid each other relaxing radially away from the vacant site. The resulting structure, depicted in Fig. 1(b), has a F incremental binding energy of 0.1 eV, exhibits large outward relaxations, and has Si-F bond lengths $\simeq 1.55$ Å [-10% compared to Fig. 1(a)]; i.e., it has the same energetics and geometry as, it visually resembles, and, therefore, it most probably *is* the structure reported in Ref. [1].

The improved ground-state structure of F_4V just reported has some implications for the results reported in Ref. [1]. Several entries involving or concerning F_4V in Tables I and II need revision; all the concentrations of F-V complexes in Fig. 3 should also be revised, because F_4V is coupled to all other F-involving complexes; the energies for transforming divacancy-F complexes into F_4V plus emitted F (Table II) should also be reconsidered: In particular, the claim that F_6V_2 is stable against V-I (I: self-interstitial) recombination and ensuing transformation into F_4V plus emitted F is not valid any more.

We note that the present results, along with those on other clusters [1,2], suggest that F saturates all available dangling bonds in a vacancy cluster with a nearly constant energy gain per added F, a general rule of thumb which should be of use in the modeling of large-size vacancy-F clusters at large F doses. We also note that the present F_4V (and none other of the F-V complexes investigated in either Refs. [1] or [2]) is stable against V-I recombination with emission of interstitial F (in fact, marginally stable, $\sim$0.4 eV for neutral native defects), but it is unstable if the final state for F is a F-I or F-F complex in Si ($\sim$1 eV binding [2]), and even more so for emitted F being bound at a Si surface dangling bond. In general, the formation energy and, hence, the stability properties and the concentration of F-V complexes depend on the F chemical potential characterizing the reservoir with which F is assumed to be in equilibrium. F-V complexes can be produced in high concentrations in Si only for high nonequilibrium F doses (e.g., in ion implantation), whereas their concentration would be negligible if F were in equilibrium with a standard thermodynamical solubility-limiting reservoir such as SiF_4 or a Si surface.

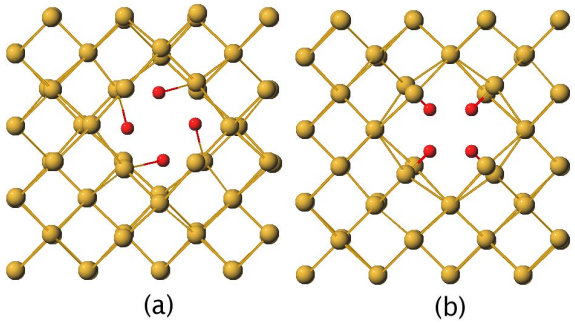

FIG. 1 (color online). Top view of the fully relaxed (a) C_{2h}-like and (b) T_d-like structures of the F_4V complex in Si. Structure (a) is 2.0 eV lower in energy. F-Si bond lengths are 1.68 Å in (a) and 1.55 Å in (b).

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[2] G. M. Lopez, V. Fiorentini, G. Impellizzeri, S. Mirabella, and E. Napolitani, Phys. Rev. B **72**, 045219 (2005); and unpublished results. Same code and supercell as in Ref. [1]; F all-electron projector augmented wave data set with cutoff 270 eV; $4 \times 4 \times 4$ k mesh.

