The V+I defects in diamond: An *ab initio* investigation of the electronic structure, of the Raman and IR spectra, and of their possible recombination

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The double defect in diamond, vacancy (V) plus $\langle 100 \rangle$ self-split-interstitial (V+I), is investigated at the *ab initio* quantum mechanical level, by considering the vicinal case VI_1 (V is one of the first neighbors of one of the two C atoms constituting the I defect) and the two possible "second neighbors" cases, VI_2^D, VI_2^S, in which a carbon atom is a first neighbor of both V and I. The case in which the two defects are at a larger distance is simulated by considering the two isolated defects separately (VI_∞). A 6-21G local Gaussian-type basis set and the B3LYP hybrid functional are used for most of the calculations; richer basis sets and other functionals (a global hybrid as PBE0, a range-separated hybrid as HSE06, LDA, PBE, and Hartree-Fock) have also been used for comparison. With this computational approach we evaluate the energy difference between the various spin states, the location of the corresponding bands in the energy gap of pristine diamond, as well as the defect formation energy of the four defects. The path for the recombination of V and I is explored for the vicinal case, by using the *distinguished reaction coordinate* strategy. A barrier as high as 0.75 eV is found with B3LYP between VI_1 and the perfect diamond recombined structure; when other hybrids are used, as PBE0 or HSE06, the barrier increases up to 1.01 eV (pure density functional theory produces lower barriers: 0.62 and 0.67 for PBE and LDA, respectively). Such a barrier is lower than the one estimated in a very indirect way through experimental data, ranging from 1.3 to 1.7 eV. It confirms however the evidence of the extremely low recombination rate also at high temperature. The Raman (and IR) spectra of the various defects are generated, which permit one to unambiguously attribute to these defects (thanks also to the graphical animation of the modes) many of the peaks observed in damaged diamond above the dominant peak of perfect bulk. For the residual non-attributed peaks, more complicated aggregations of defects should be explored. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4966635]

I. INTRODUCTION

Since several decades, diamond has represented a material of high technological relevance, thanks to its extreme physical properties which make it attractive for many applications in different fields, ranging from microelectromechanical systems to heatsinks, laser windows, particle detectors, etc.[1,2] In this context, the same properties that make this material technologically appealing also pose hard challenges in the micro/nano-fabrication and structural functionalization. In particular, the high atomic density and strong covalent bonding of the sp^3 diamond crystal determine significant issues in the control of the diffusion and recombination of structural defects.

Defects are typically created in diamond when low-fluence ion implantation is performed to either dope the material for electrical applications[3,4] or (as explored in more recent studies) create optically active centers for applications in quantum optics.[5,6] In this process, the formation of both interstitial and vacancy point defects in lightly damaged

diamond has been widely observed in previous works, thanks to the unequivocal attribution of characteristic optical absorption and photoluminescence features, i.e., the GR1 ($\lambda = 742$ nm) and ND1 ($\lambda = 394$ nm) lines corresponding, respectively, to the neutral and negatively charged vacancy, and the 3H emission ($\lambda = 503$ nm) for the interstitial.[7–9]

While in the case of electrical functionalization the creation of Frenkel pairs in the diamond structure is generally regarded as an undesiderable side-effect of the implantation of doping elements,[10] in quantum-optical applications the creation of vacancies and/or interstitials can play a key role in the creation of the desired optically active complexes.[11,12] In any case, once the desired complexes are activated, it is highly suitable to efficiently remove all residual defects from the material.

To this scope, thermal annealing is typically performed at the highest possible temperature, i.e., close to the Debye temperature of diamond (~1800 K), above which the diamond structure starts graphitizing. Regardless of these efforts, it is

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