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Stacking-Fault Based Microscopic Model for Platelets in Diamond

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We propose a new model for {001} platelets in diamond based on the formation of a metastable stacking-fault. The core of the defect is a double layer of threefold coordinated sp^2 carbon atoms embedded in the sp^3 diamond matrix. The properties of the model were determined using *ab initio* calculations. All significant experimental signatures attributed to the platelets are fully accounted for. The model is also very appealing from the point of view of kinetics, since naturally occurring shearing processes will lead to the formation of the metastable fault.

Perhaps one of the oldest unanswered questions in diamond physics concerns the nature and atomic structure of the extended defects known as platelets. These {001} planar defects were first discovered more than 60 years ago [1] by x-ray diffraction experiments, which observed anomalous peaks corresponding to {00h} reflections. These were immediately associated with lattice defects, since they are forbidden by symmetry in a perfect diamond lattice. From then on, a plethora of experimental data on this planar defect has been gathered, but a complete understanding of its origin and microscopic structure is still lacking. The current knowledge on this defect can be summarized as follows: (i) platelets have been detected only in type Ia diamonds, which contain small aggregates of N impurities; (ii) transmission electron microscopy (TEM) experiments have shown that there is an asymmetry between the [110] and [1$\bar{1}$0] directions [2]; (iii) x-ray and TEM experiments have determined that platelets displace the crystalline lattice by a distance between $0.33a_0$ and $0.4a_0$ [3–7], along the [001] direction, where a_0 is the lattice parameter of diamond. What is observed in these experiments is the existence of two bulk regions separated by a planar defective region, which is perpendicular to the [001] direction and has a width in the above range; (iv) electron energy loss spectroscopy (EELS) experiments indicate that the nitrogen content in platelets can vary from 6% to 61% of a monolayer [8–10]; (v) an infrared absorption line around 1370 cm^{-1} is always present in samples containing platelets [11]; (vi) platelets have been associated with broad luminescence bands, one centered at 1.25 eV [12], which reduces the efficiency of optical windows made of natural diamond, and another at 2.14 eV [13], and possibly with high energy absorption and luminescence bands around 4.6 and 4.4 eV, respectively [14].

In the microscopic model first proposed for platelets in diamond, Frank [5] considered that the defect should be formed by Si impurities replacing part of the carbon atoms in a (001) plane. However, it was later shown that Si is an uncommon impurity in diamond. Subsequently, it was demonstrated that diamonds type Ia contain N impurities in the required concentration [15]. Following that, Lang [16] proposed that the defect would be constituted by a double layer of N atoms (one layer of substitutional N atoms and one layer of interstitial N atoms). However, as mentioned above, the N content in the platelets can vary substantially [8–10], ruling out N impurities as the main constituent of the defect. Since foreign impurities could not account for the existence of platelets, Evans [17] proposed that platelets could be formed by interstitial carbon atoms. Based on Evans' idea, Humble [6] suggested that the double layer of nitrogen atoms in Lang's model should be replaced by a double layer of carbon atoms, thus establishing a so-called interstitial-aggregate model that has since become the most accepted microscopic model for platelets in diamond. More recently, Baker [18] proposed another model for platelets based on the aggregation of the R1 centers.

Very recently, several interstitial models, based on Humble's proposal, have been extensively studied by Goss and co-workers [19], using *ab initio* calculations. Their results indicate that some of the experimental signatures of the platelets can be explained by the interstitial model. However, the aggregate of interstitials does not introduce states in the electronic band gap, and hence it alone cannot account for the optical activity experimentally observed. Goss *et al.* propose that the observed levels in the gap are due to vacancies and nitrogen impurities segregated at the platelets. Therefore, one could expect these properties to be somehow sample dependent. In fact, the main difficulty with the interstitial-aggregate model concerns the energetics and the atomistic mechanism of its formation. The formation energy of interstitial defects in the bulk is quite high (~ 12 eV). Goss *et al.* [19] have proposed that forming a Frenkel pair (a complex of an interstitial and a vacancy) at the platelet would result in a substantial reduction in the interstitial formation energy.

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Here we propose a new model for the microscopic structure of platelets in diamond based on a entirely different mechanism. The model does not require the creation of point defects, instead, the defect is created by a shearing process of the crystal. It sprung from the study of the γ surface [20] or the generalized stacking-fault energy landscape for the (001) slip plane in diamond. In particular, we studied the behavior of the γ surface along the [110] and [1̄10] directions using *ab initio* calculations. The model, aside from accounting for all the known experimental signatures of platelets in diamond, requires a much smaller activation energy for the formation of the planar defect than the interstitial-aggregate model.

Our results were obtained through *ab initio* density functional theory calculations, within the generalized gradient approximation, using the SIESTA code [21]. A double-zeta localized basis set with polarization orbitals was used. The interaction between the valence electrons and the ionic cores was modeled using *ab initio* norm-conserving pseudopotentials. A 216-atom supercell (with a Γ-point sampling of the Brillouin zone) was used in all calculations, except for the vibrational density of states calculations, where a 64-atom supercell (sampled with 8 k points) was employed. Conjugate-gradient atomic relaxations were performed until the residual forces on each atom were smaller than 0.01 eV/Å. To check for accuracy, we calculated the intrinsic stacking-fault energy in the (111) slip plane, obtaining 0.279 J/m^2, in excellent agreement with the experimental value 0.285 ± 0.040 J/m^2 [22].

The γ surface for a given crystalline plane is obtained by cutting the infinite crystal in half along the plane and shearing the upper part with respect to the lower part by a displacement (slip) vector, which belongs to the plane. Our results for the cut of the γ surface along the [1̄10] direction are shown in Fig. 1. One of the curves displays the unrelaxed γ surface, which exhibits a maximum corresponding to a displacement of $(a_0/4)[1\bar{1}0]$. For this displacement, the atoms in both sides of the cut approach each other very closely and are aligned along the [001] direction. Figure 1 shows a quite large release of energy that results from allowing the atoms to relax along the [001] direction only. This results from the fact that, in the unrelaxed configuration, the distance between carbon atoms in the plane of the cut is only 0.89 Å (35% smaller than the relaxed value of 1.35 Å), which leads to a large overlap repulsion between the ionic cores. A similar large energy release (of several eV) upon relaxation was also obtained in calculations of the same shear process in Si [23]. In fact, we found that the slip at $(a_0/4)[1\bar{1}0]$ corresponds to a local minimum of the γ surface along this direction, in contrast with the case of Si and Ge, where this configuration corresponds to the so-called unstable stacking fault. On the other hand, shearing along the [110] direction does not bring the system to any intermediate stable configuration, and our calculations confirm that the γ surface does not exhibit any local minimum, a behavior in this case similar to what is found in Si [23]. Our calculations were performed at constant volume. We checked for possible cell-volume effects and found them to be negligible. Since at first we allowed relaxation of the $(a_0/4)[1\bar{1}0]$ configurations along the [001] direction only, we verified that this is a local minimum of the γ surface by allowing all the atoms to move freely. That such configuration is stable in diamond and not in silicon and germanium, stems from the stability of the sp^2 bonding in diamond.

Figure 2(a) depicts the relaxed atomic structure corresponding to the metastable stacking fault at $(a_0/4)[1\bar{1}0]$. The blue colored carbon atoms are threefold coordinated, whereas the gold colored ones are the usual fourfold coordinated carbon atoms in diamond. The core of the defect is formed by a double layer of threefold coordinated carbon atoms. In Fig. 2(b), we display the structure of one unit of the core of the defect (with a few neighboring atoms), when viewed along the [110] direction. This unit is formed by the repetition of a hexagonal ring consisting of four threefold coordinated atoms and two fourfold coordinated atoms. The length of the bonds between threefold coordinated atoms is 1.35 Å, which is even shorter than the carbon bonds in graphite (1.42 Å), while the bonds between threefold coordinated and fourfold coordinated atoms are about 1.52 Å long, very close to the value of 1.57 Å we obtained for the bond length in bulk diamond. Note that, in Fig. 2(b), the length of the bonds between the fourfold coordinated atoms just outside the defect core is already the bond length in bulk diamond. Therefore, this structure can be seen as two semi-infinite pieces of bulk diamond "glued" together by chemical bonds that are 1.35 Å long, which is equal to $0.38a_0$, and is in the range of the lattice displacement experimentally observed in the platelets. Moreover, it is also easy to see that the atomic
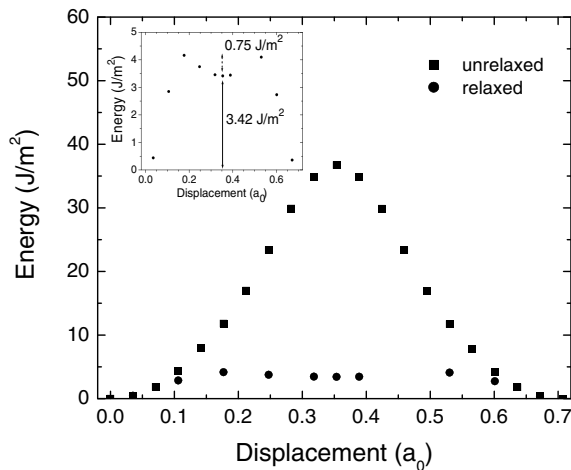

FIG. 1.   Profile of the γ surface of the (011) plane along the [1̄10]. The inset shows the details of the energy minimum for the displacement $(a_0/4)\langle 1\bar{1}0\rangle$ after atomic relaxation.
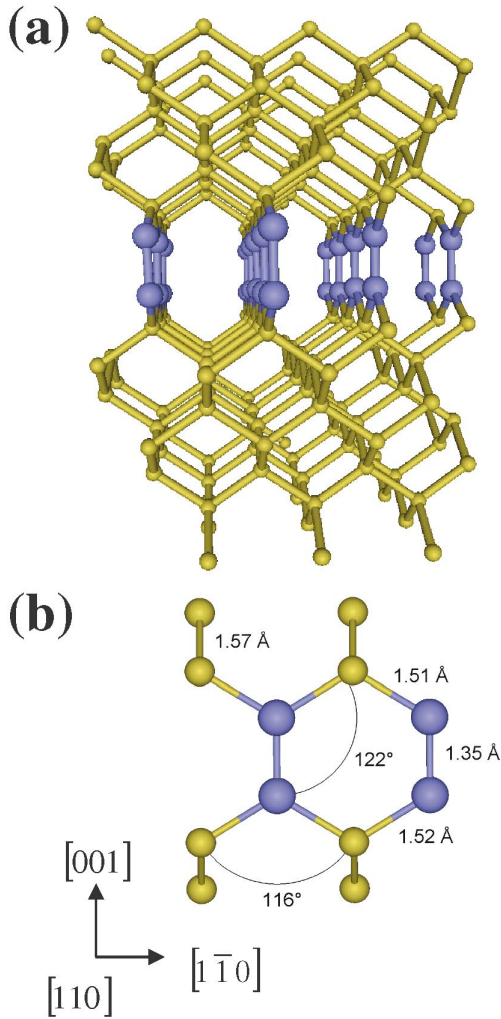
FIG. 2 (color). (a) Atomic structure of the planar defect. The blue colored atoms are threefold coordinated carbon atoms and the gold colored atoms are fourfold coordinated carbon atoms, (b) Detail of the core of the planar defect indicating bond lengths and angles.

structure of the core along the $[1\bar{1}0]$ direction is different from that along $[110]$ direction, reflecting the asymmetry of the γ surface between the two directions. This extended defect has been discussed before [24], however, within a completely different context, related to grain boundaries in artificially grown diamonds.

In Fig. 3, we show our *ab initio* results for the vibrational density of states (VDOS) for the planar defect and for bulk diamond. First, we remark that our calculations can reproduce quite well the bulk VDOS. Moreover, our results show clearly the appearance of three peaks above the highest allowed frequency in the bulk. Two of these peaks lie just above the bulk band edge, at 1373 and 1441 cm^{-1}, values which are in very good correspondence with the frequencies (1372 and 1426 cm^{-1}) of the experimental bands usually associated with platelets [11]. The first peak at 1373 cm^{-1} is more intense and can be associated with the B' band. By computing the vibration frequency of
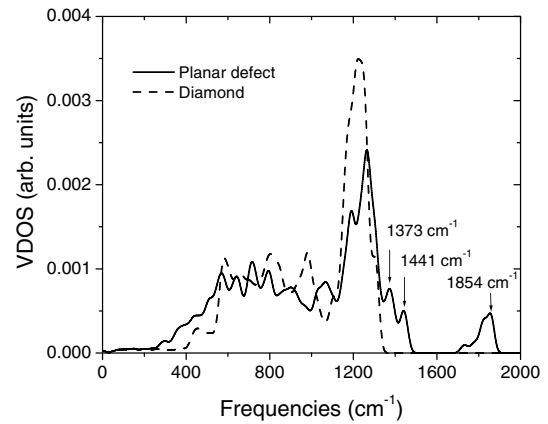

FIG. 3. Vibrational density of states in bulk diamond and in diamond containing a planar defect.

the stretch mode of the compressed bonds in the core of the defect, we determined that the third peak in Fig. 3, at 1854 cm^{-1}, is a localized mode associated with these compressed sp^2 bonds in the core [25]. As far as we know this frequency is out of the range usually investigated in infrared absorption studies of platelets, 900 to 1650 cm^{-1} [26]. Possibly, one-phonon absorption frequencies above 1650 cm^{-1} have not been investigated because of the onset of the two-phonon absorption band in the bulk, around this frequency. This phonon peak at 1854 cm^{-1} is quite interesting, because it opens the possibility that the validity of our model could be experimentally investigated.

We now discuss the electronic structure of the metastable fault. Figure 4 depicts both the electronic density of states of a bulk diamond cell and of a supercell containing the planar defect. In the figure, the zero in the energy scale corresponds to the highest occupied level. The first important point to note is that the planar defect gives rise to deep levels in the band gap. The inset in Fig. 4 shows the levels in the diamond band gap without broadening. The lowest empty levels lie about 1.0 eV. Also, in the inset, one can see empty levels about 2.1 eV. Above that, there are empty
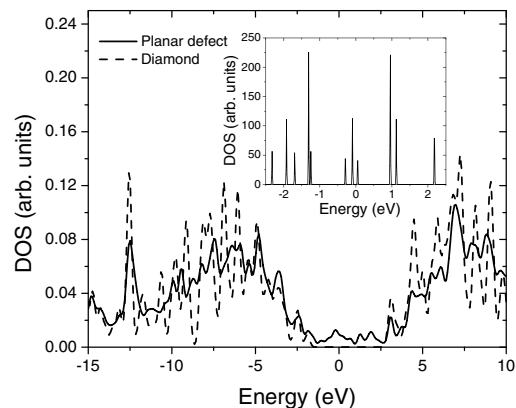

FIG. 4. Electronic density of states of bulk diamond and of diamond containing a planar defect. The inset shows the levels without broadening.

levels that coincide with the bottom of the conduction band of the bulk at about 3.1 eV (not shown in the inset). Our results agree with the luminescence bands at 1.25 and 2.14 eV, usually associated with the platelets. It is important to emphasize that these levels appear in the gap as consequence of the planar defect, without the intervention of either native defects or impurities.

We have also investigated the possibility of the occurrence of a similar intermediate metastable stacking fault in the (111) slip plane. A very similar situation to the (001) plane occurs in this case when the system is sheared along the $[1\bar{2}1]$ direction by a displacement of $(\sqrt{6}/12)a_0$. However, the configuration turned out to be unstable, with the atomic planes adjacent to the cut always slipping to either the perfect crystal or the intrinsic stacking-fault configurations. This indicates that the sp^2 hybridization in this case is not favorable, possibly because the atomic density in the (111) plane is larger than that of the (001) plane. This behavior explains why platelets are not observed in the (111) plane.

We now compare our model with the self-interstitial model. First, according to the results in Fig. 1, the activation energy per unit of area required to form the metastable stacking fault in our model is $(3.42 + 0.75)$ J/m^2 = 0.26 eV/Å^2. This activation energy per unit of area should be compared with the activation energy per unit of area required in the interstitial model. According to Goss *et al.*, the lowest energy to create a Frenkel pair at the platelet, for climb of the jog, and to diffuse the vacancy away from the platelet is about 8.8 eV, which would imply in an energy per unit of area of 1.39 eV/Å^2. Therefore, the activation energy for the formation of the stacking fault in our model is about 5 times smaller than the corresponding activation energy in the model based on interstitials. Furthermore, in order to understand the role played by N aggregates in the formation of platelets, we studied the case of the *A* center (a pair of nearest-neighbors N substitutional impurities), which is the most common N aggregate in diamond. We found that the presence of only one *A* center in the 216-atom supercell, with 1 N atom on each side of the cut (corresponding to a 6% concentration of N in the stacking fault), causes an 8% reduction of the activation energy barrier to 0.24 eV/Å^2. We expect that a larger concentration of these centers should further reduce the activation barrier. The physical reason for this is the fact that since N is a trivalent impurity in diamond, less covalent bonds have to be broken by the shearing process that creates the defect. The formation energy of the stacking fault, i.e., the energy of the local minimum in Fig. 1, was also reduced due to the presence of the *A* center, going from 0.21 to 0.19 eV/Å^2. Aside from a more favorable energetics of formation, we believe that our model accounts for the optical properties of platelets in a more complete and straightforward way. Also, regarding sym-

metry properties, the study by Goss *et al.* indicates that the interstitials can be arranged in a number of different structures, which have similar formation energy, not all of them exhibiting the asymmetry between the $[110]$ and the $[1\bar{1}0]$ directions. In contrast, this asymmetry is essentially built-in in our model. In a nutshell, we propose a new model for platelets in diamond based on the shearing process of {001} planes that explains all experimental data available.

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