A stacking-fault based microscopic model for platelets in diamond

C. R. Miranda and A. Antonelli

*Instituto de Física “Gleb Wataghin”, Universidade Estadual de Campinas, CP 6165, CEP 13083-970, Campinas, SP, Brazil*

R. W. Nunes

*Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, CEP 30123-970, Brazil*

(Dated: November 11, 2018)

We propose a new microscopic model for the {001} planar defects in diamond commonly called platelets. This model is based on the formation of a metastable stacking fault, which can occur because of the ability of carbon to stabilize in different bonding configurations. In our model, the core of the planar defect is basically a double layer of three-fold coordinated $sp^3$ carbon atoms embedded in the common $sp^3$ diamond structure. The properties of the model were determined using ab initio total energy calculations. All significant experimental signatures attributed to the platelets, namely, the lattice displacement along the [001] direction, the asymmetry between the [110] and [110] directions, the infrared absorption peak $B'$, and broad luminescence lines that indicate the introduction of levels in the band gap, are naturally accounted for in our model. 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.

PACS numbers: 61.72.Nn, 61.72.Bb, 63.20.Pw, 71.15.Nc, 71.55.Cn

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 sixty 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 [2]; ii) transmission electron microscopy (TEM) experiments have shown that there is an asymmetry between the [110] and [110] directions [3]; iii) TEM experiments have also determined that platelets displace the crystalline lattice by approximately $0.4a_0$ [4], along the [001] direction, where $a_0$ is the lattice parameter of diamond; iv) electron energy loss spectroscopy (EELS) experiments indicate that the nitrogen content in platelets can vary from 6% to 61% [5, 6, 7], ruling out N impurities as the main constituent of the defect. Therefore, one could expect these properties to be somehow sample dependent. In fact, the main difficulty with the interstitial 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 [8]. Following that, Lang [13] 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 [1, 2, 7], ruling out N impurities as the main constituent of the defect. Since foreign impurities could not account for the existence of platelets, Evans [15] proposed that platelets could be formed by interstitial carbon atoms. Based on Evans’ idea, Humble [4] 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 [16] 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 [17], 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.
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. [17] 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.

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 [18] 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 [110] 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.

The results we present here were obtained through ab initio calculations, within the framework of the density functional theory (DFT) and the generalized gradient approximation (GGA), using the SIESTA code [19]. 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 was used in most of the calculations, except for the vibrational density of states calculations, where a 64-atom supercell was employed. The Γ point was used in the Brillouin zone sampling for the 216-atom supercell, whereas for the calculations using the 64-atom supercell, 8 k-points were used. To check the 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 [21].

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 [110] direction are shown in Fig. 1. One of the curves displays a corresponding to the metastable stacking fault at (001) slip plane along the [001] direction. The blue colored carbon atoms are three-fold coordinated, whereas the gold colored ones are the usual four-fold coordinated carbon atoms in diamond. The length of the bonds between the four-fold coordinated atoms is 1.35 Å, while the bonds between three-fold coordinated and four-fold coordinated atoms are about 1.52 Å long, very close to the value of 1.57 Å, which is even shorter than the carbon bonds in graphite (1.42 Å).

Our results for the cut of the γ-surface along the [110] direction, obtained 0.279 J/m^2, in excellent agreement with the experimental value 0.285 ± 0.040 J/m^2 [21].

![Fig. 1: Profile of the γ-surface of the (011) plane along the [110]. The inset shows the details of the energy minimum for the displacement (a_0/4)(110) after atomic relaxation.](image)

The blue colored carbon atoms are three-fold coordinated, whereas the gold colored ones are the usual four-fold coordinated carbon atoms in diamond. The length of the bonds between three-fold coordinated atoms is 1.35 Å, which is even shorter than the carbon bonds in graphite (1.42 Å), while the bonds between three-fold coordinated and four-fold coordinated atoms are about 1.52 Å long, very close to the value of 1.57 Å. The inset shows the details of the energy minimum for the displacement (a_0/4)(110) after atomic relaxation.
FIG. 2: (a) Atomic structure of the planar defect. The blue colored atoms are three-fold coordinated carbon atoms and the gold colored atoms are four-fold coordinated carbon atoms. (b) Detail of the core of the planar defect indicating bond lengths and angles.

platelets. Moreover, it is also easy to see that the atomic structure of the core along the [110] 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 [22], however, within a completely different context, related to grain boundaries in artificially grown diamonds.

In Fig. 3, we show our \textit{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 cm\(^{-1}\) and 1441 cm\(^{-1}\), values which are in very good correspondence with the frequencies (1372 cm\(^{-1}\) and 1426 cm\(^{-1}\)) of the experimental bands usually associated with platelets \[8\]. The first peak at 1373 cm\(^{-1}\) is more intense and can be associated with the \(B'\) band. By computing the vibration frequency of 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 \[24\]. As far as we know this frequency is out of the range usually investigated in infrared absorption studies of platelets, 900 cm\(^{-1}\) to 1650 cm\(^{-1}\) \[23\]. This is quite interesting, because this third peak opens the possibility that the validity of our model could be experimentally investigated.

We now discuss the electronic structure of the metastable fault. Fig. 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 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 eV 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 oc-
currence of a similar intermediate metastable stacking fault in the (111) slip plane. For this plane, a very similar situation, with the atoms adjacent to the cut getting near each other, also happens when the system is sheared along the \([1\bar{1}0]\) direction by a displacement of \((\sqrt{6}/12)\alpha_0\). In the case of Si and Ge, previous calculations \cite{21} indicate that the atomic configuration obtained after relaxation is still a distinct local maximum for the \(\gamma\)-surface of the glide set. In the case of diamond, the \(\gamma\)-surface resembles a plateau, which 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. Since the atomic density in the (111) plane is larger than in the (001) plane, the \(sp^2\) hybridization of the atoms adjacent to the cut should be less favorable than the \(sp^3\), which would explain 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 \((3.42+0.75)\ J/\text{m}^2 = 0.26 \text{ eV}/\text{Å}^2\). 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 \textit{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, we have performed preliminary calculations which indicate that the presence of nitrogen aggregates can further reduce the activation energy for the formation of the metastable stacking fault. The physical reason for this is the fact that since N is a trivalent impurity in diamond, less bonds have to be broken by the shearing process that creates the defect. 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 symmetry properties, the study by Goss \textit{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 [110] 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.

We acknowledge the financial support by the Brazilian funding agencies FAPESP, CNPq, and FAEP-UNICAMP; and the computer resources granted by CENAPAD-SP.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{DOS.png}
\caption{Electronic density of states of bulk diamond and of diamond containing a planar defect. The inset shows the levels without broadening.}
\end{figure}
[23] G. S. Woods, Proc. R. Soc. London, Ser. A 407, 219 (1986).
[24] Compressed bonds usually increase vibrating frequencies, see for example, J. Xie et al., Phys. Rev. B 60, 9444 (1999).
[25] In the interstitial model, the interstitials are arranged in a square lattice whose lattice constant is $(\sqrt{2}/2)a_0$. 

P. Keblinski et al., J. Mater. Res. 13, 2077 (1998).