Small aggregates of interstitials and models for platelets in diamond

2000 J. Phys.: Condens. Matter 12 10257

(http://iopscience.iop.org/0953-8984/12/49/326)

J. Phys.: Condens. Matter **12** (2000) 10257–10261. Printed in the UK PII: S0953-8984(00)17681-7

Small aggregates of interstitials and models for platelets in diamond

J P Goss†, B J Coomer†, R Jones†, C J Fall†, C D Latham†, P R Briddon‡ and S Öberg§

† School of Physics, The University of Exeter, Exeter EX4 4QL, UK
‡ Department of Physics, The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK
§ Department of Mathematics, Luleå University of Technology, Luleå S-97187, Sweden

Received 4 October 2000

Abstract. By examining the structure of small clusters of self-interstitials in diamond using local-density-functional techniques, we have developed models for the planar defects called platelets. We present the structures, energies and vibrational properties.

Recently much progress has been made in the understanding of self-interstitials and their aggregates in group IV materials. In diamond, the R2 and R1 $S = 1$ electron paramagnetic resonance (EPR) centres have been conclusively assigned to the single, [001]-orientated split-interstitial [1] and di-interstitial [2] respectively. A form of the tri-interstitial has been assigned to the O3 EPR centre [3, 4]. Both complexes can be understood in terms of complexes of R2: R1 is a reconstructed pair of [001] split-interstitials at nearest-neighbour sites whereas O3 possesses three [001] split-interstitials at next-nearest-neighbour locations (figure 1).

The structure of O3 points very clearly to the Humble [5] model for a tetra-interstitial which is completely reconstructed (i.e. there are no dangling bonds). The defect possesses a considerable strain in the [001]-direction. This defect, shown in figure 1 has been identified in silicon as the B3 EPR centre in the positive charge state [6]. However, Humble introduced this model not as a point defect, but as a building block for the (001)-platelet seen in diamond.

Platelets are created during long-term, high-temperature annealing of nitrogen containing diamonds and are a common flaw in natural diamonds. They are associated with a broad

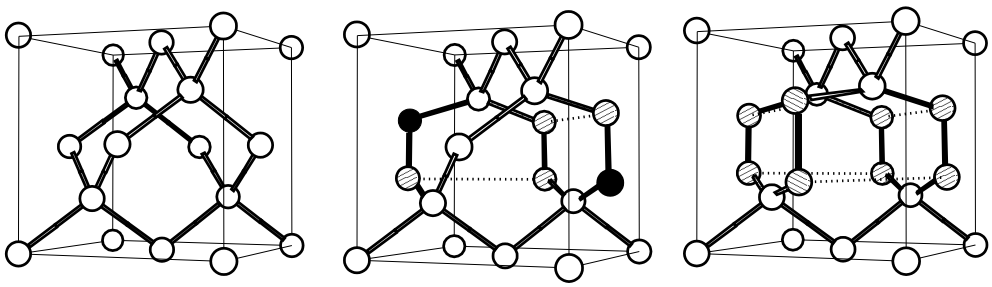

Figure 1. Schematic of the O3 centre (middle) and the tetra-intersitial strucutre (right). The dashed bonds indictate the reconstructions, which leave the grey atoms four-fold and the black atoms three-fold coordinated. Also shown (left) is a section of pure lattice for comparison.

luminescence band [7, 8] centred at 1.25 eV, which impairs the efficiency of optical windows made from diamonds. They have attracted considerable attention in the past and many early models (e.g. [9]) of their structure were based on nitrogen aggregates. However, EELS studies [10] and the isotopic dependence of the B′ infrared-absorption associated with the platelet [11] have cast doubt on the presence of a substantial amount of nitrogen in the platelet and instead a model based on aggregated interstitials has been proposed. The most recent favour a condensation of carbon interstitials onto a {001} plane [10]. As all bonds are saturated, an array of I_4 units, as suggested by Humble [5], and shown schematically in figure 2(a), is expected to have particularly low energy. However, it is possible to switch the bond reconstruction from one I_4 unit to a neighbouring one with the requirement that each reconstructed bond lies perpendicular to its neighbouring reconstructed bonds. Thus one of the reconstructed bonds in figure 2 is broken and the atoms with dangling bonds form bonds with neighbouring I_4 units. This leads to a plethora of possible models. One such model is shown in figure 2(c). The presence of a C_2 [100] axis shows that the [110] and [1$\bar{1}$0] projections are equivalent, in conflict with recent transmission electron microscopy (TEM) studies [10]. These models cannot then be fully correct. Figures 2(d) and (e) show sets of parallel bonded chains along [1$\bar{1}$0], and along with the model illustrated in figure 2(d) consisting of an alternating arrangement of Humble I_4 units, these are asymmetric between these projections. Any of these is a possible model for a periodic platelet structure, although a combination of all these topologies might well occur in practice [10].

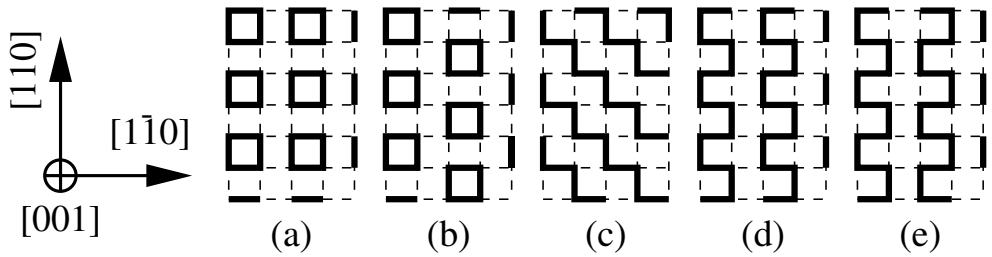

Figure 2. The proposed structures for the platelet. The grid represents the lattice of atom sites in a (001) plane. Each site is occupied by [001]-split interstitial. The reconstuctions between adjacent sites are indicated by the dark lines, and in models (a) and (b) correspond to the dark bonds in figure 1. (a) is a regular array of tetra-interstitials, and (b) where they are staggered. (c)–(e) consist of the [100]-chain, and the in- and anti-phase [110]-chains.

We have used a local-density-functional approach (supercell AIMPRO [13, 12]) to simulate these defects. The platelets are modelled using unit cells consisting of sixteen (001) layers of atoms, with 4, 8 or 16 atoms per plane depending on the periodicity of the platelet model. The calculations have been performed using the Monkhorst–Pack [14] scheme of k-points with a 2^3 mesh of points. Formation energies per interstitial, E^f, can be calculated using the formula $E^f = (E_{\text{platelet}} - nE_{\text{C}})/N$, where E_{platelet} is the total energy of the platelet supercell containing n atoms and N interstitials, and E_{C} being the energy per atom of pure diamond.

E^f varies by around 0.5 eV between the models, as listed in table 1. The lowest energy structure is that shown figure 2(a) which does not reflect the asymmetry of the ⟨011⟩ and ⟨01$\bar{1}$⟩ directions observed experimentally. We note that the formation energy per interstitial is reduced further if the volume of the platelet unit cell is allowed to relax (table 1). This leads to a value of around 1 eV per interstitial which is dramatically lower than the formation energy for the isolated interstitial at around 12 eV. Importantly the alternating squares model

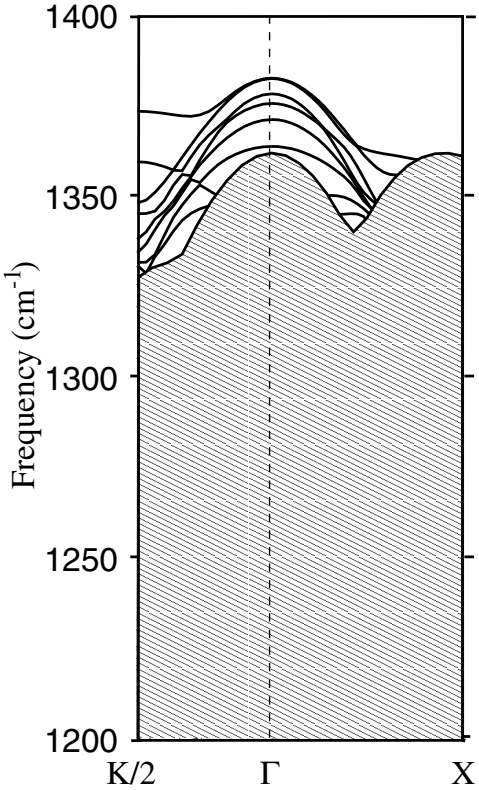

Figure 3. Phonon bands of bulk diamond projected on the (001) plane (hashed area) and high-energy phonon modes localized in the (001) plane of the platelet shown in figure 2(a) (solid lines). The phonon dispersion is shown in the [110] (K/2-Γ)) and [100] (Γ-X) directions in the folded Brillouin zone.

Table 1. Formation energies per interstitial (eV) for the various platelet models (figure 2) for the bulk lattice constant and for the relaxed unit cell. Also, for each model the dilation of the lattice in units of a_0 are reported.

	Model				
	(a)	(b)	(c)	(d)	(e)
Bulk lattice constant	3.58	3.69	4.01	3.82	3.75
Relaxed unit cell	1.04	0.90	1.27	1.20	1.14
Lattice dilation	0.44	0.39	0.38	0.41	0.42

(figure 2(b)) now has the lowest formation energy per interstitial, and this model possesses the experimentally observed asymmetry. However, we note that our calculations neglect processes relating to the nucleation process of the platelets and the strain at the platelet boundaries which might further affect the formation energy.

The TEM studies [15] have shown that the platelet leads to a displacement of {100} planes by 0.4 a_0 although displacements as low as 0.33 a_0 have been reported for smaller platelets [16]. For I_4, we find that the displacement is 0.34 a_0, with the value increasing to 0.38 to 0.44 a_0 for the relaxed platelet models. In addition, the calculated infra-red active vibrational modes of I_4 at 1349, 1362, 1401, 1420, 1421 and 1569 cm^{-1} are in reasonable agreement with bands

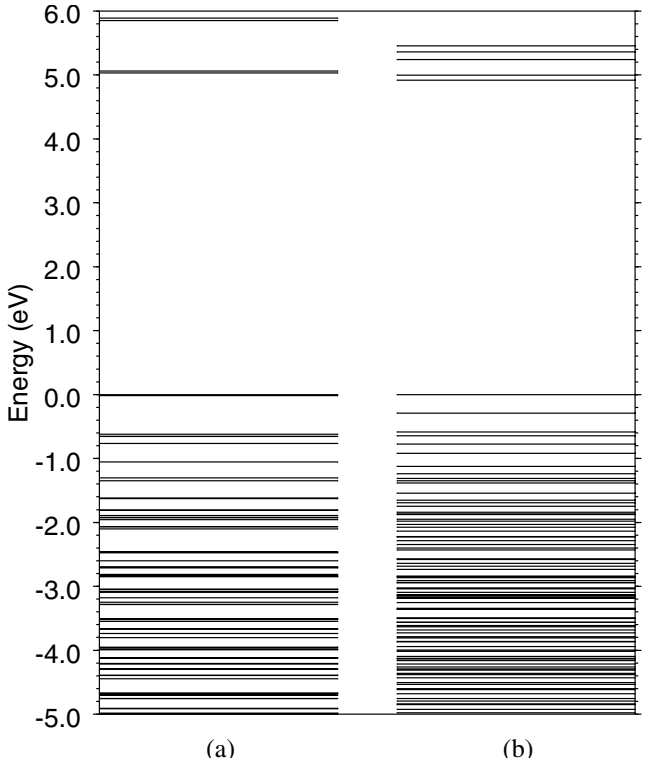

Figure 4. Plot of the Kohn–Sham eigenvalues for (a) a pure diamond unit cell, and (b) the relaxed structure illustrated in figure 2(b).

at 1372, 1426, and possibly 1520 and 1540 cm^{-1}, assigned to platelets [17].

The actual position of the 1372 cm^{-1} (B′) band varies between platelets, but is always present. The peak position shifts from higher frequency with smaller platelets to lower frequency with the larger platelets, consistent with the view that the peak position is dictated by the amount of strain relaxation in the region of the planar defect. In figure 3, we compare the phonon modes of bulk diamond with the vibrational modes of an infinitely-extended (001) platelet with the Humble I_4 structures (figure 2(a)), although all of the structures studied are broadly similar. All vibrational modes are calculated using a Musgrave–Pople potential for bulk diamond [18]. We find a collection of vibrational modes localized in the neighbourhood of the platelet above the Raman edge of bulk diamond, consistent with the B′ band. The frequency is dependent on the amount of relaxation, consistent with the size dependence observed by experiment.

Thus we conclude that platelets can be viewed as being formed from aggregates of I_4. These models are consistent with TEM and infra-red absorption measurements. As can be seen from figure 4, which is typical of all the models examined, there is no evidence of gap states for these periodic systems. However, defects in these models, such as impurities (e.g. N) or disorder would tend to introduce dangling bond states where optical transitions and/or the high freqency local modes might be generated. Further work is needed to quantify the effects of impurities in the idealized platelet structure.

References

[1] Hunt D C, Twitchen D J, Newton M E, Baker J M, Anthony T R, Banholzer W F and Vagarali S S 2000 *Phys. Rev.* B **61** 3863

[2] Twitchen D J, Newton M E, Baker J M, Tucker O D, Anthony T R and Banholzer W F 1996 *Phys. Rev.* B **54** 6988

[3] D Hunt 1999 private communication

[4] Goss J P, Coomer B J, Jones R, Shaw T D, Briddon P R, Rayson M and Öberg S 2000 *Phys. Rev.* B, submitted

[5] Humble P 1982 *Proc. R. Soc. London (Ser. A)* **381** 65

[6] B J Coomer J P Goss, and R Jones, Öberg S and P R Briddon 2000 *J. Phys.: Condens. Mater.* submitted

[7] Wight D R, Dean P J, Lightowlers E C and Mosby C D 1971 *J. Lumines.* **4** 169

[8] Desgreniers S, Vohra Y K and Ruoff A L 1989 *Solid State Commun.* **70** 705

[9] Lang A R 1964 *Proc. Phys. Soc.* **84** 871

[10] Fallon P J and L M Brown 1995 *Phil. Mag.* A **72** 21

[11] Woods G S, Kiflawi I, K H and Evans T 1993 *Phil. Mag.* B **67** 651

[12] Coutinho J, Jones R, Öberg S and Briddon P R 2000 *Phys. Rev. Lett.* at press

[13] Jones R and Briddon P R 1998 Identification of Defects in Semiconductors *Semiconductors and Semimetals* vol 51A ed M Stavola (Boston: Academic Press) ch 6

[14] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188

[15] Cherns D, Kaneko K, Hovsepian A and Lang A 1997 *Phil. Mag.* A **75** 1553

[16] Barry J C, Bursill L A and J L Hutchison 1985 *Phil. Mag.* A **51** 15

[17] Woods G S 1989 *Phil. Mag. Lett.* **59** 339

[18] Musgrave M J P and Pople J A 1962 *Proc. R. Soc. London (Ser. A)* **268** 474