Volume Expansion and Stress Tensors for Self-Interstitial Aggregates in Diamond

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Abstract

There is a need for defect modelling techniques to be able to accurately calculate experimentally observable quantities. We present the results of the calculation of volume relaxations and piezospectroscopic stress tensors for proposed models of interstitial aggregates in diamond to facilitate correlation with the experimental centres.

Theoretical Outline

- Supercell, LSDF calculations: AIMPRO [1, 2]
- Cubic supercells: 64-216 atoms
- Cartesian Gaussian wavefunction basis
- Charge density treated by plane-waves
- BHS pseudopotentials [3]

Volume dilation

Defects exerting a compressive strain on the surrounding lattice results in an expansion of the lattice. The fractional increase in volume is:

$$\frac{\delta V}{V} = \eta \frac{[\mathrm{X}]}{[\mathrm{C}]} \qquad (1)$$

[X] & [C] are the number densities of defect (X) and diamond sites. The volume change for a defect is then:

$$\delta V = \eta V_{\mathrm{ref}} \quad V_{\mathrm{ref}} = a_0^3/8 \qquad (2)$$

Piezospectroscopic Stress Tensor

- *No* imposed stress: in equilibrium defects randomly oriented.
- Stress renders different orientations with different energies.
- The change in energy is $\Delta E = \mathrm{Tr}\ B_i \cdot \epsilon$
  - ϵ = imposed strain
  - B_i = (traceless) energy-stress tensor [defect orientation i].
- Equilibrium populations of defects aligned along i for temperature $T \propto \exp(-\Delta E_i/kT)$.
- The tensor does not depend on a reorientation barrier.

Interstitial Aggregates - Experimental Background

- There are three known self-interstitial centres in diamond:
  1. **R2 EPR centre** - the single self-interstitial (Fig 1(a))
  2. **R1 EPR centre** - the di-self-interstitial (Fig 1(b))
  3. **O3 EPR centre** - the tri-self-interstitial (Fig 2(b))
- The 3H optical centre is suspected of being another form of the di-interstitial [4, 5]. (Fig 1(c))
- The platelets are believed to be large planar aggregates akin to Fig 2(c) [4, 6].

Derivation of $I_1^{\langle 001 \rangle}$ B-tensor from Experiment

- Hunt *et al* reported the populations of different orientations of R2 under stress. [7]
- 0.6 GPa along [100] at 520K leads to a 30% drop in the concentration of R2 parallel to stress.

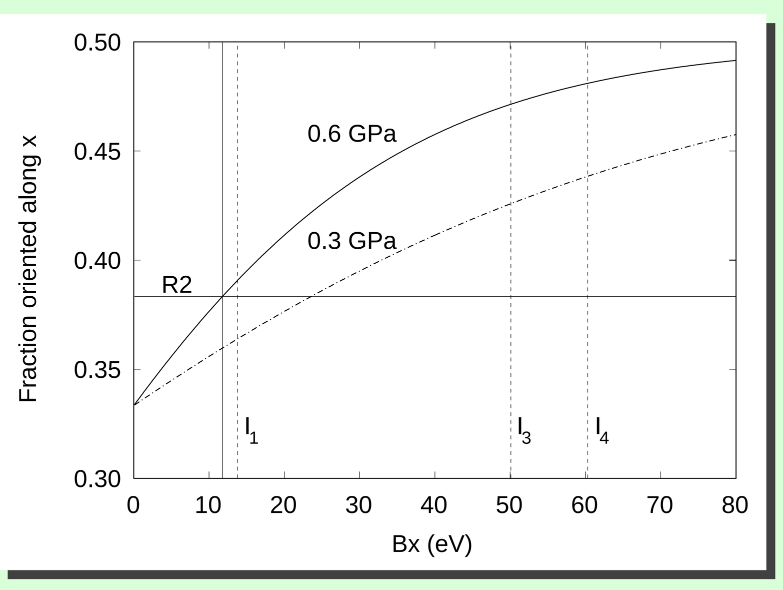
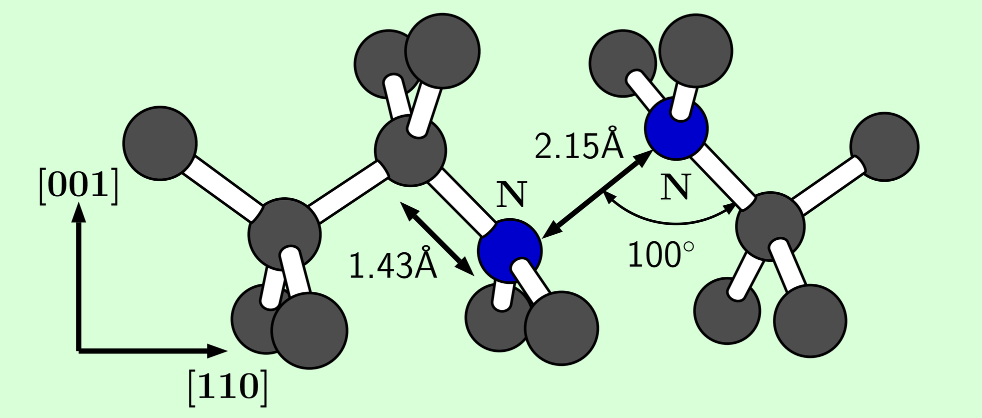


Fig. 5: Fractional population of x oriented defects at 520K as a function of the magnitude of the x-B-tensor element, for an applied stress of 0.3 and 0.6 GPa along z.

- $\Rightarrow$ B=−24 eV along the defect axis, 12 eV perpendicular.

Dilatation of The A-centre



- η (Eq. 2) for the A-centre **measured** to be 0.11–0.12 [8].

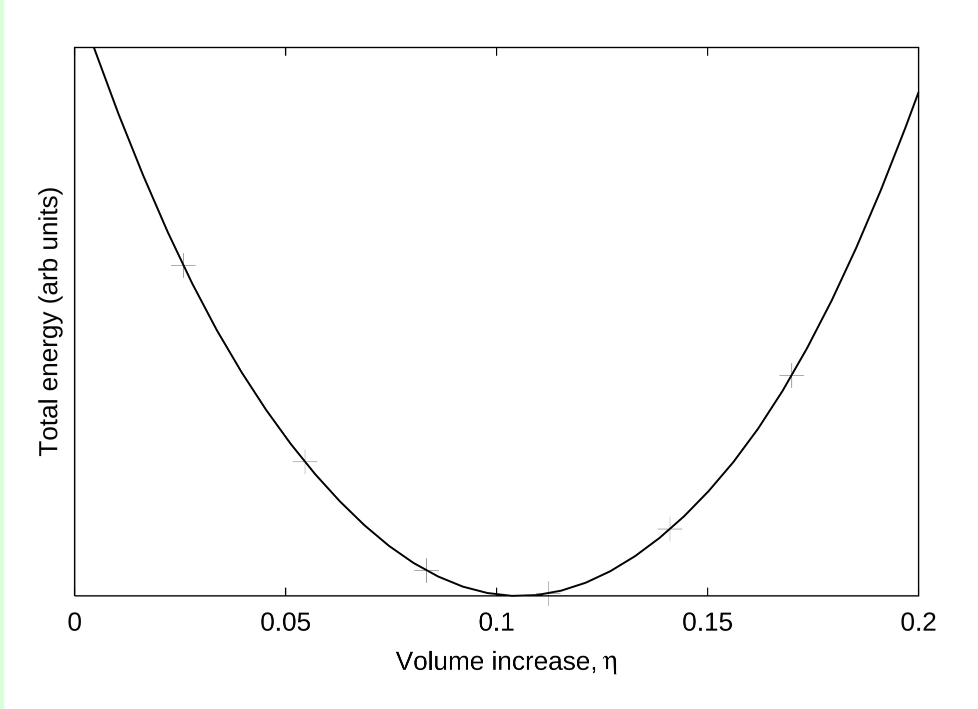


Fig. 3: Total energy of the A-centre vs. volume expansion (η). The points are calculated, the solid line a quadratic fit.

- Theory ($\eta = 0.11$) reproduces experiment very well.

Dilatation of the Lattice Vacancy

- We assume that the volume relaxation can be calculated without treating the multiplets fully.

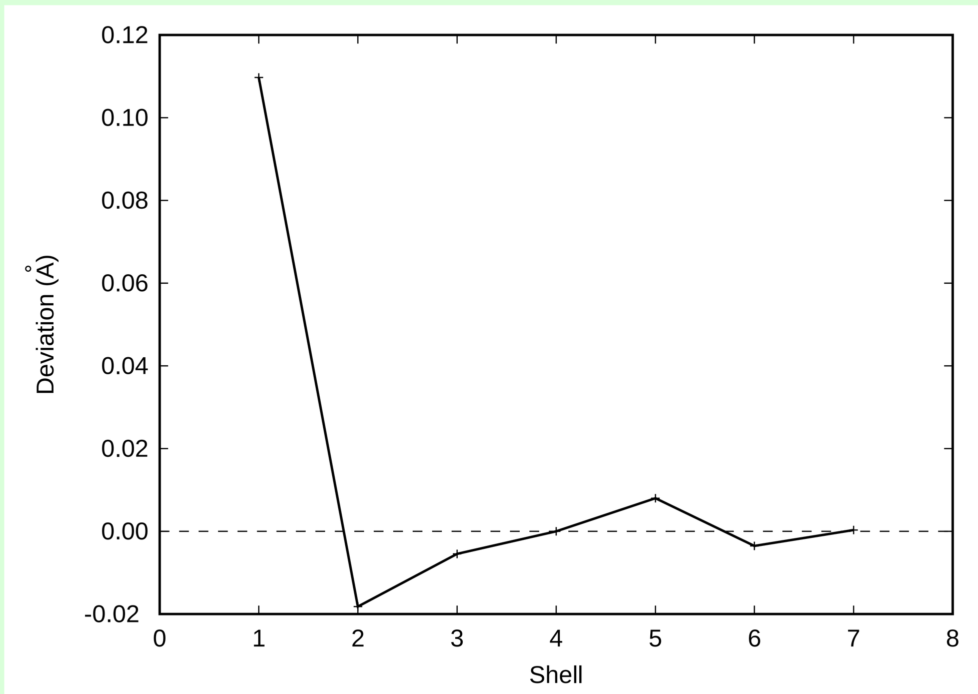


Fig. 4: The difference in the radial distance of the shells of atoms surrounding the vacancy between the relaxed and unrelaxed tetrahedral structures (a positive deviation corresponds to an outward relaxation).

Dilatation & B-tensors for interstitial aggregates

Table 2: Principal values and directions for the diagonal stress-energy tensors (eV per unit strain) and volume relaxation per interstitial (units of V_{ref}) for interstitial aggregate models. n is the number of additional C atoms.

Defect	n	η/n	B_1	B_2	B_3
R2 expt†	1	-	−24	12	12
$I_1^{\langle 001 \rangle}$ (R2) Fig.1(a)	1	1.9	−27.6 [001]	13.8 [100]	13.8 [100]
I_2^{NN} (R1) Fig.1(b)	2	1.7	−44.4 23° to $[00\bar{1}]$	41.9 23° to [110]	2.6 $[1\bar{1}0]$
I_2^{2NN} Fig.1(c)	2	1.7	−55.6 [001]	21.4 $[1\bar{1}0]$	34.3 [110]
$(I_2^{\mathrm{2NN}})^+$ Fig.1(c)	2	1.1	−51.4 [001]	18.1 $[1\bar{1}0]$	33.3 [110]
π-I_2 Fig.2(a)	2	1.7	−66.0 6° to $[1\bar{1}1]$	29.2 6° to $[\bar{1}12]$	36.4 [110]
I_3 (O3) Fig.2(b)	3	1.6	−89.7 2° to [001]	45.9 2° to [100]	43.8 [010]
I_3:D_{2d} Fig.1(d)	3	1.6	−100.1 [001]	50.1 [100]	50.1 [010]
I_4 Fig.2(c)	4	1.5	−120.5 [001]	60.3 [100]	60.3 [010]

† – values inferred from experimental data.

Summary & Conclusions

- Theory agrees with the measured η (Eq.2) of the A-centre.
- The dilatation of all interstitial aggregates is very large.
- Dilatation due to isolated vacancy practically zero.
- Dilatation of irradiated material due to self-interstitials.
- $\Rightarrow$ X-ray measurements determine η for the interstitial.
- The B-tensor increases with self-interstitial aggregate size.
- Relatively small stresses could align during aggregation.
- The B-tensors for the R1 and O3 centres could be measured.
- The B-tensor of the 3H optical centre would help with the assignment to the I_2^{2NN} structure and charge state.
- B-tensors for unassigned, interstitial-related centres (eg 5RL, TR12) would be very useful.

Interstitial Models

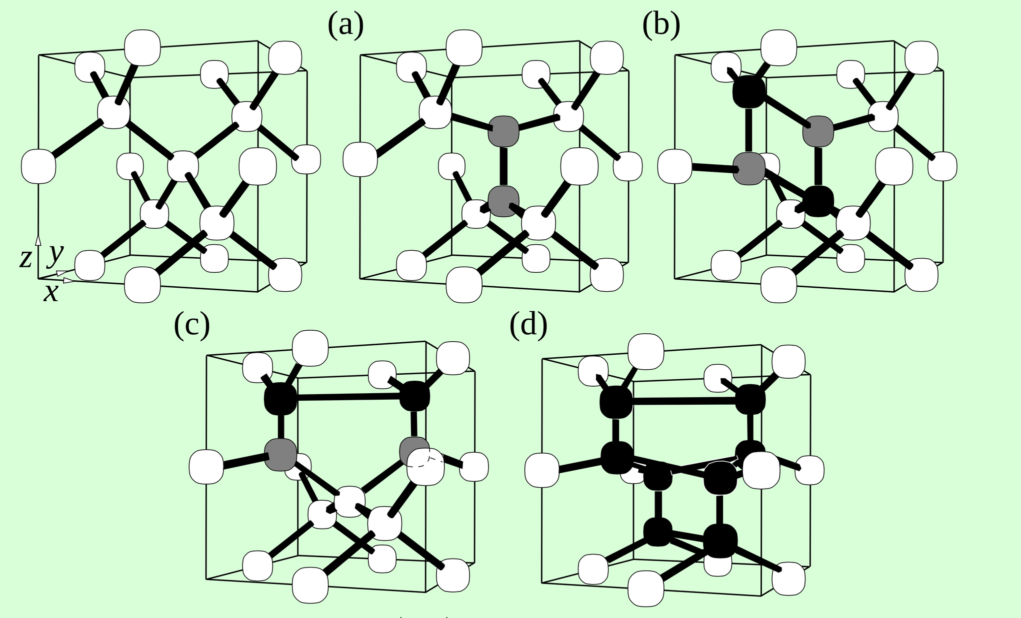


Fig. 1: Geometry of (a) $I_1^{\langle 001 \rangle}$ (R2), (b) I_2^{NN} (R1), (c) I_2^{2NN} (3H?) and (d) the low energy D_{2d} model for I_3. Interstitials atoms are shown shaded. 3- & 4-fold coordinated atoms being grey and black respectively.

Interstitial Models

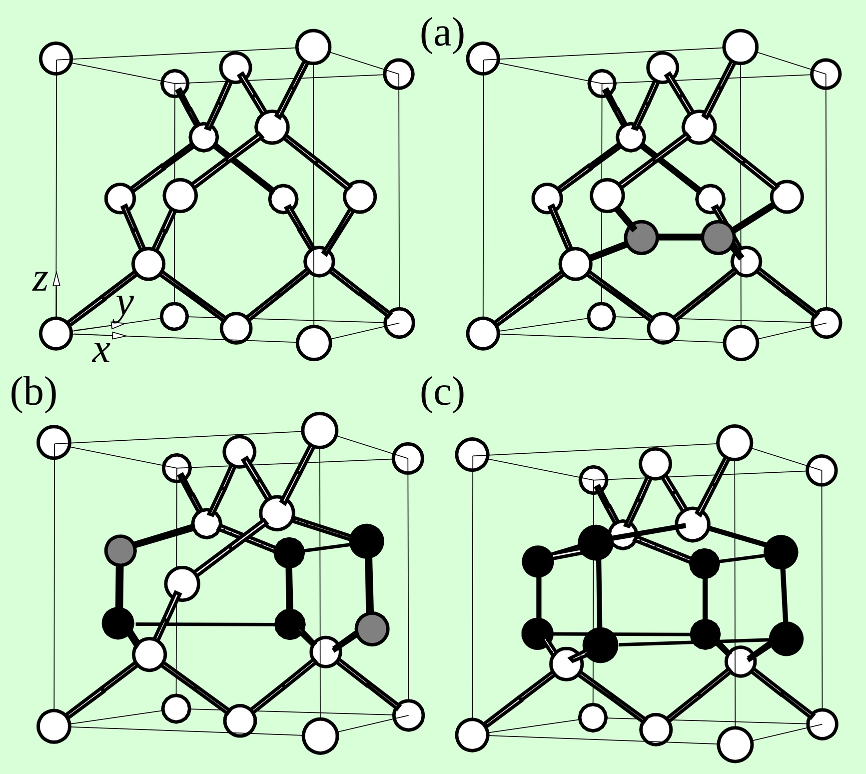


Fig. 2: Geometry of (a) the π-bonded di-interstitial, (b) C_2 symmetry I_3 (O3), and (c) I_4. Shading as in Fig. 1.

Formation energies of interstitial aggregates

Table 1: Formation and binding energies per interstitial (eV). E_b is relative to single interstitials (taken from Ref [4]).

	I_1	I_2			I_3		I_4
		NN	2NN	π-bond	C_2	D_{2d}	
Fig:	1(a)	1(b)	1(c)	2(a)	2(b)	1(d)	2(c)
Expt centre:	R2	R1	3H?	-	O3	-	platelets
E^f	12.3	9.3	9.0	8.4	7.8	7.2	5.5
E^b		3.0	3.3	3.9	4.5	5.1	6.8

- Diamagnetic/optically inactive forms are lower in energy than the observed EPR centres!

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