Vibrational modes of three-membered self-interstitial clusters in silicon

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Abstract
A selection of the vibrational modes of two variants, compact and non-compact,
of three-membered self-interstitial clusters in crystalline Si is studied by first-
principles calculations in order to contribute to the possible identification of a
three-bodied cluster with the W centre in Si. Internal vibrational modes of the
compact clusters are found between 19 meV ('translation' modes) and 47 meV
(breathing mode), in fair agreement with the phonon replica spectrum of W.
However, the compact cluster does not possess the local mode above the bulk
phonon range associated with W. A local mode is instead exhibited by the
non-compact cluster variant. The latter, though, is energetically disfavoured
over the compact one. The combined results on the vibration and energetics
suggest that neither of the two clusters can be identified with W.

(Some figures in this article are in colour only in the electronic version)

Various device-fabrication-related processes, most notably interstitial-driven anomalous
impurity diffusion, involve the clustering of self-interstitial atoms in ion-implanted Si. A
prominent point-like defect therein, known as the W centre, is usually believed to be related
to excess self-interstitials, allegedly in clusters of size $n = 3$ [1, 2]. The W centre has been
studied for some time [3–5], but its identification is not yet firmly established. We recently
studied small self-interstitial clusters in Si [6] and considered the ground state for $n = 3$,
the compact I_3 cluster, as a candidate [7] for the identification of W. A non-compact cluster
variant [8] was also proposed to this end.

   Here we concentrate on the vibrational replica structure [4] of the main PL emission of
W, which includes at least one strictly local vibrational mode at 70 meV. The vibrational
frequencies of the compact cluster appear to be compatible with the vibronic replica spectrum
of W, except for the local mode, which is absent. This seems to bar its possible identification
with W. The non-compact cluster variant [8] does exhibit the local mode, but unfortunately
it is energetically quite disfavoured over the compact one (1.4 eV above it). We conclude that
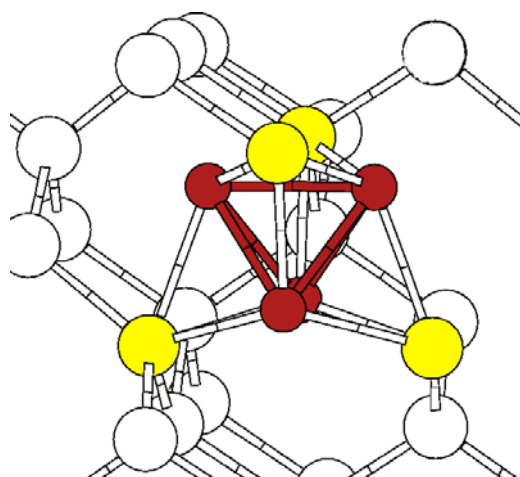neither of these variants of I_3 can be identified with the W centre.

Figure 1. The compact I_3 self-interstitial cluster. Cluster atoms: dark grey; bulk-like first neighbours: light grey; bulk atoms: white.

The calculations are done at the first-principles level within generalized-gradient [9] density-functional theory and the ultrasoft pseudopotential plane wave repeated-supercell approach using the Vienna *ab initio* simulation package (VASP) code [10]. Data reported here are obtained with standard body-centred-cubic 32-atom and simple-cubic 64-atom supercells. The results are in fact fairly insensitive to cell size. We use multiprojector ultrasoft potentials provided with VASP [10] with two s, two p and one d projectors ($r_c = 1.31$ Å) and non-linear core corrections, a 151 eV plane wave cut-off and a $4 \times 4 \times 4$ k-space summation mesh. Atomic positions are relaxed so that all force components are below 0.01 eV Å^{-1}. The theoretical lattice constant $a_{Si} = 5.462$ Å is used throughout. The vibrational properties are studied for the neutral charge state, because this is the state relevant to the prevailing conditions of observation of the W line (n-type or undoped self-implanted samples, where we predict [6] moderately n-type conditions).

The calculated equilibrium structure of the compact and non-compact I_3 clusters, shown in figures 1 and 2, respectively, agree well with recent tight-binding [11] and *ab initio* results (compact: [12]; non-compact: [8]). Energetically, we find the non-compact variant to be disfavoured over the compact by 1.4 eV. The compact I_3 (dark grey in figure 1) is a perfect tetrahedron with edges aligned with the (110) axes and the central point at a lattice site. The side lengths are identical within numerical error (2.488 ± 0.002 Å or 5% more than the theoretical Si–Si bond length of 2.365 Å).

The non-compact I_3 is instead obtained starting from three additional Si atoms placed at the centre of the three parallel bonds surrounding a tetrahedral interstitial site. Relaxation results in the formation of a three-atom ring (dark grey in figure 2). All the additional atoms are four-fold-coordinated, and form bonds of length 2.21, 2.23 and 2.28 Å with their neighbours. The bond lengths are displayed for clarity in figure 2. The presence of three-bond-centred Si interstitials severely compresses the Si–Si bond between the topmost atoms in figure 2 with a bond of length 2.21 Å. The local vibrational mode discussed below is localized on the topmost atom in the figure. The perturbation also propagates to the lower shell of axial bonds, which are still only 2.26 Å long.

The symmetry of the defects is defined by the space group of a defected crystal, i.e. Si containing a I_3 centre. This turns out to be T_d and C_{3v} for the compact and non-compact
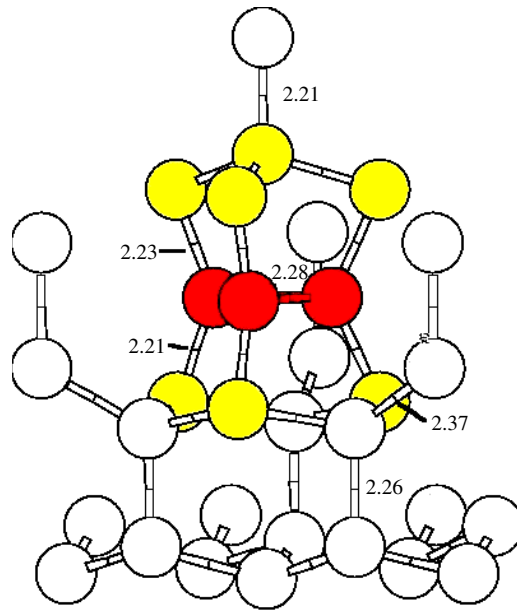
Figure 2. The non-compact I_3 self-interstitial cluster. Cluster atoms: dark grey; bulk-like first neighbours: light grey; bulk atoms: white. Bond lengths in ångströms are displayed (bulk bond length is 2.365 Å).

variants, in agreement with the C_{3v} symmetry deduced from the stress *response* of the vibronic structure [4]. Computationally, the cluster structures were obtained without imposing symmetry *a priori*.

To calculate the vibrational modes, we employ two methods. In the first, the frozen-phonon approach [13], one calculates the vibrational frequency freezing into the system a given displacement pattern. If the pattern corresponds to a normal mode, the total energy change in the harmonic regime is, by definition,

$$\Delta E_{\text{tot}}(u) = \frac{\omega^2}{2} \sum_i m_i u_i^2 = \frac{N_{\text{Si}} m_{\text{Si}} \omega^2 u^2}{2},\tag{1}$$

where the second equality applies to the present single-species case, each of the N_{Si} silicon atoms involved in the mode being displaced by u from its equilibrium position. The frequency can be extracted from the quadratic term in a polynomial fit to $\Delta E_{\text{tot}}(u)$. (Alternatively, when applicable, one may extract the mode harmonic force constant from the force/displacement ratio and thence the frequency using an appropriate reduced mass.)

The second method involves no assumptions about the specific modes of the system and consists in explicitly calculating the matrix $\partial F_i^s / \partial u_j^{s'}$ of the derivatives of the force component i on an atom s with respect to the displacement component j of atom s' for all atoms presumed to be involved in the vibrations of the system. This coincides with the dynamical matrix at the Brillouin zone centre; diagonalization gives the vibrational eigenfrequencies and eigenvectors at $\mathbf{k} = \mathbf{0} = \Gamma$. Of course, this is appropriate in the case of a symmetry-breaking, isolated defect described in a supercell approach.

The compact cluster is weakly bound to the surrounding bulk. This can be seen, for example, from the low bond-charge density between the bulk and cluster atoms in the (110)-plane cross section shown in figure 3, as well as from the distances of the first-neighbour bulk
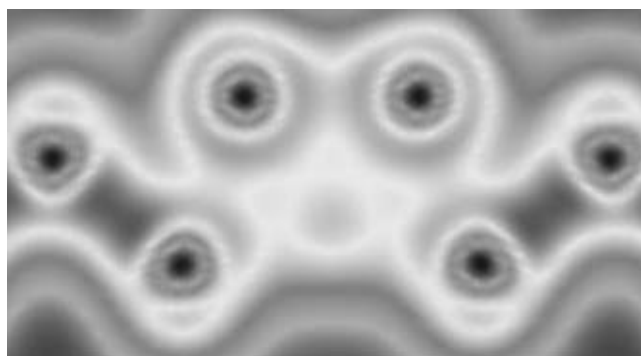
Figure 3. Charge density of the I_3 compact cluster in a (110) plane. Dark spots coincide with atomic locations. Only two cluster atoms (the two top central atoms) are visible in this section.

atoms from the cluster atoms: these are around 2.6 Å, which is much larger than both the interatomic distances of 2.36 Å in the bulk and 2.48 Å within the cluster. We therefore assume that the cluster is effectively decoupled from the bulk and consider only force constants related to motions of the cluster atoms in the dynamical-matrix calculation, and only cluster internal modes in the frozen-phonon calculation. The natural choice of the modes to be considered is clearly that of the twelve independent normal modes of a tetrahedron.

In figure 4 (see also, for example, [14]) we sketch the non-translational normal modes of a tetrahedron (A non-degenerate breathing, E two-fold-degenerate twist, T_2 three-fold-degenerate stretch and T_2' three-fold-degenerate bend) labelling them by name, multiplicity and calculated energy quantum. Considering the T_2 three-fold-degenerate translation-like mode (which corresponds to a free translation for an isolated molecule), multiplicity sums up to 12 as it should. The translation-like mode has a vibrational quantum of 19 meV; as seen in figure 4, all other energies fall within the interval 27–46 meV. The highest frequency is that of the totally symmetric breathing mode; the lowest is that of the translation mode and this confirms *a posteriori* the weak coupling of the cluster to the rest of the crystal.

Since the actual overall symmetry of the simulated system is the identity group C_1, degeneracy removal of the modes is expected. From cross-checks of frozen-phonon and dynamical-matrix calculations we estimate that degeneracy is obeyed to well below ±1%.

We now compare the calculated modes with the experimental PL spectrum of the W centre in figure 5. A reliability reference is the calculated Si LO–TO mode energy at Γ of 62.4 meV, −2.5% from experiment, typical of the GGA approximation [15]. Assuming a ±5% error bar is thus quite safe. For all spectral features the general proviso holds that the coupling is mainly to the bulk phonon continuum [4] (see also below). This is especially true of the high frequency part, where no internal modes of the cluster are present. Nevertheless, the compact-cluster vibrational energies seem compatible with the W replica-spectrum features. The main peak at ∼20 meV may involve the translation mode at 19 meV. The broad feature between 25 and 50 meV may include all the proper internal modes of the cluster. With the assumed error bar, the breathing mode could account for the high-energy shoulder of the named feature.

Above approximately 45 meV, no cluster modes are present. The spectral structure in that region must then be due to the (relatively weak [4]) coupling with optical modes, at least up to approximately 64 meV (the LO–TO energy at zone centre). Besides the contributions from the cluster modes, as mentioned, the interaction signatures with the bulk phonon continuum are dominant. The phonon dispersion and density of states (DOS) of Si [16] suggest that the
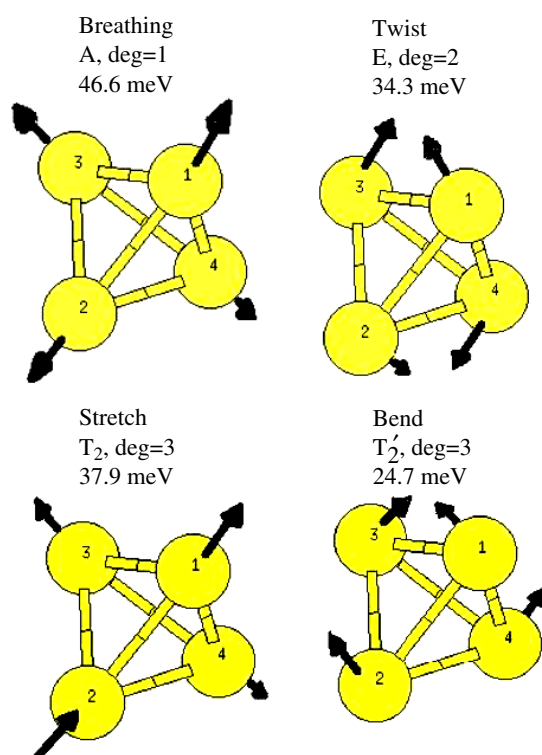
Breathing
A, deg=1
46.6 meV

Twist
E, deg=2
34.3 meV

Stretch
T_2, deg=3
37.9 meV

Bend
T_2', deg=3
24.7 meV

Figure 4. The normal modes of a tetrahedron. The corresponding calculated energies for compact I_3 are attached to each mode.

bulk modes involved in the 5 meV wide structure around 17 meV are mainly the zone-border modes at the K and X points (e.g. the Σ_3 TA mode at K, for example, has the correct 18 meV energy). For the 40 meV feature, the bulk phonon DOS weight comes mainly from the LA modes along the Λ line, with a maximum 46 meV L_2 mode at L. As mentioned, the 35–45 meV internal modes of the clusters may contribute to this structure and to its substantial linewidth.

The replica peak at 70 meV, which was identified [4] as a local mode associated with the defect, is not matched by any of the internal vibrations of the compact cluster, their highest frequency being 46 meV. This casts severe doubts on the possible identification of this cluster with the W centre. We then look for the local mode in the alternative non-compact structure [8] of I_3. As indicated earlier in [8] we find that the compression of the bond along the trigonal axis to a single cluster-neighbouring atom in the non-compact variant (the topmost atom in figure 2) causes a local vibrational mode to appear at 66 meV. This is lower than the experimental value of 70 meV, but clearly higher than the calculated LO–TO bulk mode of 62.5 meV, the lower frequencies being due to the GGA approximation [15]. This would strike a point in favour of the non-compact I_3 as a candidate W centre. However, its formation energy is 1.4 eV higher than that of the compact variant. The non-compact cluster is therefore unstable towards the compact one—assuming it can form at all. Thus the non-compact cluster cannot be the W centre, unless some kinetic mechanisms are identified which trigger its formation, preempting that of the compact variant, and prevent its decay into the latter. Missing these, we are forced to conclude that neither variant of a three-bodied self-interstitial cluster can be identified as the W centre.
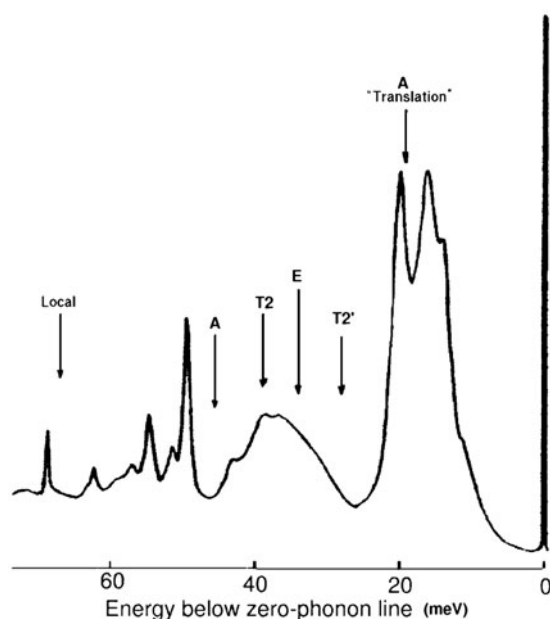
Figure 5. Experimental phonon replica PL spectrum of the W centre (reproduced from [4] with the permission of the author) compared with the calculated mode energies. All lines pertain to the compact I_3 cluster in Si, except the mode labelled 'Local', which belongs to the non-compact I_3 instead.

In summary, we have studied a selection of the vibrational properties of two I_3 self-interstitial clusters in Si via first-principles gradient-density-functional frozen-phonon calculations. The internal modes of the compact cluster have energies between 19 meV ('translation') and 46 meV (breathing). We compared the calculated energies of the compact I_3 cluster with the phonon replica spectrum of the W centre, finding a good match with observed spectral structures. The 70 meV local mode could not, however, be identified among the modes of the cluster. The non-compact variant of the cluster proposed in [8] does instead exhibit a mode localized upon a unique Si–Si bond on the trigonal axis, appearing at 66 meV by theory, a reasonable match with experiment given the softer GGA-calculated frequencies. While the absence of the local mode in the compact cluster seems to bar its identification as W, the existence of this mode for the non-compact I_3 is not sufficient to grant identification of the latter with the W centre, because the formation energy of the non-compact I_3 is 1.4 eV higher than that of the compact one. Also, a further analysis of the dissociation energetics and extrinsic levels of the clusters is necessary for such identification, as the W centre exhibits, besides the vibronic structure [4], a photoluminescence (PL) emission at 1.018 eV [4] and activation and decay energies of the PL emission of 0.85 and 2.0 eV [5], respectively. While several of the experimental signatures of W are reproduced by *ab initio* calculations [7] on I_3, a satisfactory identification of W with the present candidate I_3 may turn out to be impossible.

Acknowledgments

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