

phys. stat. sol. (b) **118**, 173 (1983)

Subject classification: 13; 22.1; 22.1.1; 22.1.2

*Sektion Chemie der Friedrich-Schiller-Universität Jena<sup>1)</sup> (a), and Faculty of Mathematics and Physics, Charles University, Prague<sup>2)</sup> (b)*

## Tight-Binding Cluster Model for C, Si, and Ge

### II. Size and Shape Dependence of Some Cluster Properties<sup>3)</sup>

By

L. KÜNNE (a), L. SKÁLA (b), and O. BÍLEK (b)

The analytic description of the electronic structure of the s-states tight-binding cluster model of C, Si, and Ge (part I) is used for the investigation of the dependence of some electronic properties of the clusters on their size and shape. Clusters in the form of cubes, plates, and rods are considered. The rate of convergence of the cluster properties to the corresponding limit values is discussed.

Die im Rahmen der Tight-Binding-Approximation erhaltene analytische Lösung für das Eigenwertproblem des s-Bandes von C, Si- und Ge-Clustern (Teil I) wird benutzt, um die Abhängigkeit einiger elektronischer Eigenschaften dieser Cluster von ihrer Größe und Gestalt zu studieren. Drei verschiedene Clusterfolgen (Würfel, Platten und Stangen) werden untersucht. Die Konvergenz der Clustereigenschaften gegen den entsprechenden Grenzwert wird diskutiert.

### 1. Introduction

In Part I of this work [1], the analytic solution of the s-state tight-binding cluster model with the diamond lattice was presented. In agreement with the experience gained in the infinite crystal calculations [2], the correct description of the lowest part of the valence band of the diamond clusters (C, Si, and Ge) may be expected.

The analytical formulae for the energies and wave functions have one great advantage — they make it possible to calculate (in some cases even analytically) various electronic properties of arbitrarily large clusters. In this way, a detailed investigation of the size and shape dependence of these properties can be performed and qualitatively new information can be obtained.

### 2. Description of Clusters

A detailed description of the clusters, the corresponding Hamiltonian, and the analytic solution of the Schrödinger equation was given in [1] and will not be repeated here. We mention here only a few most important results.

The clusters considered here are cut-outs of the infinite crystal with (100) surface. No relaxation near the surface is taken into account. The size and shape of the clusters are specified by three numbers  $L = 4\lambda + 1$ ,  $M = 4\mu + 1$ , and  $N = 4\nu + 1$  ( $\lambda$ ,  $\mu$ , and  $\nu$  are integers) which are not equal to the number of atoms in the edge of the cluster. The total number of atoms in the cluster equals

$$\mathcal{N} = 1 + \frac{L-1}{2} \frac{M-1}{2} \frac{N-1}{2} + \frac{1}{2} \left( \frac{L-1}{2} \frac{M-1}{2} + \frac{L-1}{2} \frac{N-1}{2} + \frac{M-1}{2} \frac{N-1}{2} + \frac{L-1}{2} \frac{N-1}{2} \right). \quad (1)$$

<sup>1)</sup> Am Steiger 3, DDR-6900 Jena, GDR.

<sup>2)</sup> Ke Karlovu 3, 12116 Prague 2, Czechoslovakia.

<sup>3)</sup> Part I see phys. stat. sol. (b) **117**, 675 (1983).

The difference of the number of atoms in the sublattices  $\circ$  and  $\bullet$  (see Fig. 1 in [1])

$$\mathcal{N}\circ - \mathcal{N}\bullet = 1 + \frac{1}{2} \left( \frac{L-1}{2} \frac{M-1}{2} + \frac{L-1}{2} \frac{N-1}{2} + \frac{M-1}{2} \frac{N-1}{2} \right) + \frac{L-1}{2} + \frac{M-1}{2} + \frac{N-1}{2} \quad (2)$$

is equal to the number of the surface atoms on three faces of the cluster intersecting in one corner. This number gives also the degeneracy of the central energy level

$$E = \alpha. \quad (3a)$$

The band of the s-states is given by

$$E_{pqr\pm} = \alpha \pm 4\beta \left[ \cos^2 \frac{p\pi}{L+1} \cos^2 \frac{q\pi}{M+1} \cos^2 \frac{r\pi}{N+1} + \sin^2 \frac{p\pi}{L+1} \sin^2 \frac{q\pi}{M+1} \sin^2 \frac{r\pi}{N+1} \right]^{1/2}; \quad (3b)$$

$$(p = 1, \dots, \frac{L-1}{2}; q = 1, \dots, \frac{M-1}{2}; r = 1, \dots, \frac{N-1}{2}),$$

where  $\alpha$  and  $\beta$  are the tight-binding parameters. For  $L, M, N \rightarrow \infty$  the formula (3b) becomes the dispersion relation  $E = E(\mathbf{k})$  of the infinite crystal known from [2]. The corresponding LCAO coefficients have the form

$$c_{\text{min}}^{pqr} = N^{pqr} \sin \left( \frac{a}{4} lk_x^{pqr} \right) \sin \left( \frac{a}{4} mk_y^{pqr} \right) \sin \left( \frac{a}{4} nk_z^{pqr} \right) \quad (4a)$$

and

$$c_{\text{max}}^{pqr\pm} = \mp N^{pqr} \left[ \cos^2 \left( \frac{a}{4} k_x^{pqr} \right) \cos^2 \left( \frac{a}{4} k_y^{pqr} \right) \cos^2 \left( \frac{a}{4} k_z^{pqr} \right) + \sin^2 \left( \frac{a}{4} k_x^{pqr} \right) \sin^2 \left( \frac{a}{4} k_y^{pqr} \right) \sin^2 \left( \frac{a}{4} k_z^{pqr} \right) \right]^{-1/2} \times \left[ \sin \left( \frac{a}{4} lk_x^{pqr} \right) \sin \left( \frac{a}{4} mk_y^{pqr} \right) \sin \left( \frac{a}{4} nk_z^{pqr} \right) \times \cos \left( \frac{a}{4} k_x^{pqr} \right) \cos \left( \frac{a}{4} k_y^{pqr} \right) \cos \left( \frac{a}{4} k_z^{pqr} \right) + \cos \left( \frac{a}{4} lk_x^{pqr} \right) \cos \left( \frac{a}{4} mk_y^{pqr} \right) \cos \left( \frac{a}{4} nk_z^{pqr} \right) \times \sin \left( \frac{a}{4} k_x^{pqr} \right) \sin \left( \frac{a}{4} k_y^{pqr} \right) \sin \left( \frac{a}{4} k_z^{pqr} \right) \right], \quad (4b)$$

where the normalizing factor  $N^{pqr}$  is given by

$$N^{pqr} = \left[ \frac{64}{(L+1)(M+1)(N+1)} \right]^{1/2}. \quad (4c)$$

For the investigation of the size and shape dependence of the cluster properties we consider three types of clusters: cubes ( $L = M = N$ ), plates ( $L = M, N = 5$ ), and rods ( $L, M = N = 5$ ). The cluster of a given form (cube, plate, or rod) is fully

specified by a given  $L$ . Numerical calculations are presented up to  $L = 401$  for the cubes ( $\mathcal{N} = 8060301$ ) and up to  $L = 1001$  for the plates ( $\mathcal{N} = 626502$ ) and rods ( $\mathcal{N} = 3255$ ).

### 3. Results and Discussion

The energy band (3b) has two parts which are symmetrical with respect to the central level  $E = \alpha$  (3a). These parts are separated by a "gap" the width of which depends on the size and shape of the cluster. The energy levels of the small cluster from Fig. 1 in [1] ( $L = 9, M = N = 5$ ) together with the corresponding density of states of the diamond crystal (taken from [2]) are shown in Fig. 1. It is obvious that the lower part of the total density of states is described well by the s-state model. We see that the distribution of the levels of the cluster corresponds to the density of the s-states of the infinite crystal except for the existence of the gap and the degenerate central level  $E = \alpha$ .

The aim of this section is to discuss within the s-states model the dependence of the density of states, band width and "gap" width on the size of the cluster and its shape.

#### 3.1 Density of states

In Fig. 2 we show a representative selection of the lower half of the density of states (DOS) for the clusters in form of the cube, plate, and rod in dependence on the cluster size. The degenerate level  $E = \alpha$  is also shown. The size of the cluster is denoted by the numbers  $L/\mathcal{N}$  near each figure. The number of atoms in the clusters increases in the direction down. The DOS for small  $L$  is presented in the form of the histogram which becomes the smooth curve for large  $L$ . If  $L > 100$  the shape of the DOS changes very little. The shape of the DOS for the cubes, plates, and rods is different including the limit  $L \rightarrow \infty$ .

The greatest difference between the cluster and the corresponding infinite crystal DOS is the existence of the highly degenerate central level  $E = \alpha$  which can significantly influence the physical and chemical properties of the cluster. Increasing the size of the cube the relative weight of the energy level  $E = \alpha$  decreases and for the infinite crystal it goes to zero. Because of the nonzero limit value of the ratio "number of surface atoms to total number of atoms",

$$\frac{\mathcal{N}\circ - \mathcal{N}\bullet}{\mathcal{N}} = 0.2 \quad \text{for plates with } N = 5 \quad (5a)$$

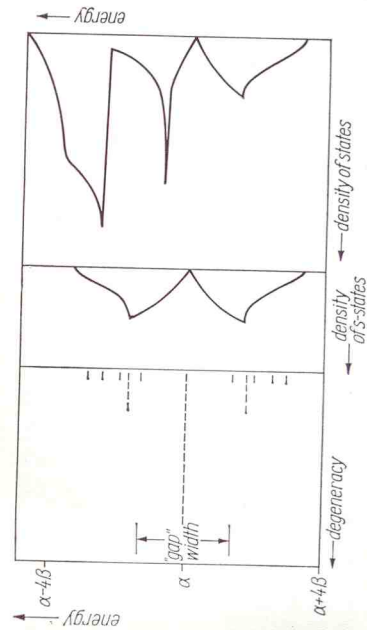


Fig. 1. The energy levels of the cluster with  $L = 9$  and  $M = N = 5$  in comparison with the density of s-states and the total density of states of the diamond crystal [2]

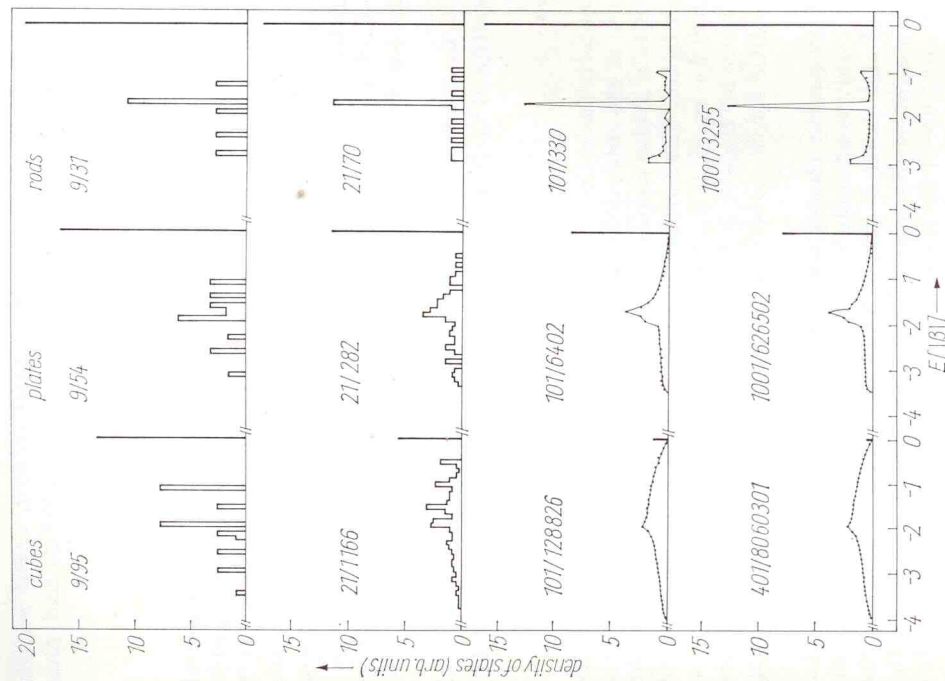


Fig. 2. The lower half of the density of states for three geometrical forms of the clusters in dependence on the number of atoms. The numbers near the figures in the form  $L/\mathcal{N}$  give  $L$  and  $\mathcal{N}$ . The energy is given in  $|\beta|$ -units, we put  $\alpha = 0$  here

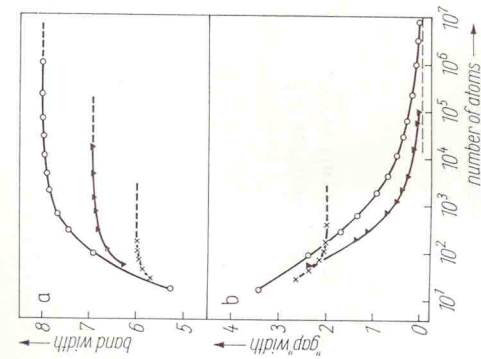


Fig. 3. The bandwidth BW and the "gap" width GW as functions of the total number of atoms  $\mathcal{N}$  in the clusters in form of cubes (O), plates ( $\blacktriangledown$ ), and rods ( $\times$ ). The broken lines show the corresponding limits

and, as a result, the bandwidth

$$\text{BW} = 8 |\beta| \left[ \cos^2 \frac{\pi}{L+1} \cos^2 \frac{\pi}{M+1} \cos^2 \frac{\pi}{N+1} + \sin^2 \frac{\pi}{L+1} \sin^2 \frac{\pi}{M+1} \sin^2 \frac{\pi}{N+1} \right]^{1/2} \quad (6)$$

increases (see Fig. 3a). This increase is greatest for the cubes, smaller for the plates and rods. The broken lines on the right-hand side in Fig. 3 indicate the corresponding limit values obtained from (6):

$$\text{BW} = \begin{cases} 8 |\beta| & \text{for cubes } (L, M, N \rightarrow \infty), \\ 4 \sqrt{3} |\beta| & \text{for plates } (L, M \rightarrow \infty, N = 5), \\ 6 |\beta| & \text{for rods } (L \rightarrow \infty, M = N = 5). \end{cases} \quad (7)$$

The rate of convergence decreases along the sequence rods, plates, and cubes. For example, to get the limit value (7) with an accuracy better than 1%, the clusters with  $L/\mathcal{N}$  equal to  $41/8631$ ,  $33/690$ , and  $21/70$  for the cube, plate, and rod, respectively, must be taken.

### 3.3 "Gapwidth"

The "gap" width between the two symmetrical parts of the energy band is given by the energy levels (3b) with the smallest value of the square root. For its discussion it is convenient to rewrite the radicand of the square root into the form

$$R = \cos^2 \frac{\pi p}{L+1} \cos^2 \frac{\pi q}{M+1} + \sin^2 \frac{\pi r}{N+1} \left( 1 - \cos^2 \frac{\pi p}{L+1} - \cos^2 \frac{\pi q}{M+1} \right). \quad (8)$$

It was verified by inspection that in case of  $L = M$  and  $L \geq N$  this radicand has the smallest value if  $p = 1$  and  $q = (L-1)/2$ . In this case, the value of the expression in the parentheses in (8) equals zero, independently of the third quantum number  $r$ .

and

$$\frac{\mathcal{N}^0 - \mathcal{N}^\bullet}{\mathcal{N}} = 0.3846 \quad \text{for rods with } M = N = 5, \quad (5b)$$

the relative weight of the level  $E = \alpha$  remains nonzero even in the limit of the infinite plates and rods.

In case of very large cubes and plates, the gap between the two symmetrical parts of the energy band goes to zero. In case of rods it remains nonzero even in the limit  $L \rightarrow \infty$ . This is discussed in Section 3.3 in detail.

### 3.2 Bandwidth

Independently of the size and shape of the cluster the lower band edge of the s-band is determined by  $p = q = r = 1$  and by the positive sign of the square root in (3b) (for  $\beta < 0$ ). Because of the symmetry the upper band edge is given by the same quantum numbers but by the negative sign before the square root. Increasing the number of atoms  $\mathcal{N}$  the lower band edge decreases, the upper band edge increases

For this reason the formula for the "gap" width is the same for cubes and plates,

$$GW = 4 |\beta| \sin \frac{2\pi}{L+1}. \quad (9a)$$

In case of rods ( $L = M = 5$  and  $N \rightarrow L$ ) the radicand (8) has the smallest value for the quantum numbers  $p = q = (L-1)/2 = 2$  and  $r = 1$  which give the "gap" width

$$GW = 2 |\beta| \left[ 1 + 8 \sin^2 \frac{\pi}{L+1} \right]^{1/2}. \quad (9b)$$

The behaviour of the "gap" width in dependence on  $L$  or  $\mathcal{N}$  is therefore qualitatively different for the rods on one side and the cubes and plates on the other side. Increasing  $L \rightarrow \infty$  the "gap" width becomes

$$GW(L \rightarrow \infty) = \begin{cases} 0 & \text{for cubes and plates,} \\ 2 |\beta| & \text{for rods } (M = N = 5). \end{cases} \quad (10)$$

Whereas the GW goes to zero for the cubes and plates, the corresponding value for the rods is different from zero. This nonzero value depends on  $M$  and  $N$  and decreases with increasing  $M$  and  $N$ . The rate of convergence of the GW to the limit value (10) is shown in Fig. 3b. It is obvious that the convergence is quickest in case of the rods, slower for the plates and cubes. The difference between the plates and cubes follows from that the same number  $L$  is related to a different number of atoms  $\mathcal{N}$  in the corresponding cluster.

We can conclude from Fig. 3 that the rate of convergence of the "gap" width is slower than the rate of convergence of the bandwidth. To get for the cubes the same accuracy of the bandwidth and "gap" width the number of atoms in case of the "gap" width must be roughly 100 times greater.

#### 4. Conclusions

The detailed investigation of the size and shape -dependence of the electronic structure of the diamond clusters shows certain analogies with the electronic structure of the infinite crystal but also some differences which can play an important role in the explanation of the cluster properties.

The rate of convergence of the investigated cluster properties is slow, similarly as in the case of the s.c., b.c.c., and f.c.c. clusters [3 to 5]. Starting with  $L = 101$  the form of the density of states and the bandwidth or "gap" width change little. It means that at least about 300, 6000, and 100000 atoms for the rods, plates, and cubes, respectively, must be taken into account to approach the limit corresponding to  $L \rightarrow \infty$ . Similarly as in [3 to 5] the rate of convergence is determined rather by the number of atoms at the edge of the cluster than by the total number of atoms.

#### References

- [1] O. BÍLEK, L. SKÁLA, and L. KÜNNE, *phys. stat. sol.* (b) **117**, 675 (1983).
- [2] D. J. CHADI and M. L. COHEN, *phys. stat. sol.* (b) **68**, 405 (1975).
- [3] L. SKÁLA, *Czech. J. Phys.* **B27**, 171 (1977).
- [4] P. KADURA and L. KÜNNE, *phys. stat. sol.* (b) **88**, 537 (1978).
- [5] L. KÜNNE, L. SKÁLA, and O. BÍLEK, *Czech. J. Phys.* **B29**, 1030 (1979).