An algorithm for determining the most stable vacancy clusters in diamond lattice

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- Introduction
- Vacancy clusters in silicon and diamond
- Algorithm for construction of vacancy clusters in the diamond structure of carbon
- Results
- Conclusions

Introduction

In diamond more than 500 electronic and more than 150 vibrational optical centers have been documented. Many of them are due to V_n vacancy centers.

Vacancy clusters in diamond and in silicon
are detected by electron paramagnetic resonance,
positron annihilation spectroscopy
and other methods.

Usually they are produced by electron, neutron,
or ion irradiations and by temperature annealing.

Vacancy: mono vacancy

Vacancy cluster: connected set of mono vacancies

V_n : vacancy cluster of n mono vacancies

Vacancies and vacancy clusters will be represented by the missing atoms from the bulk

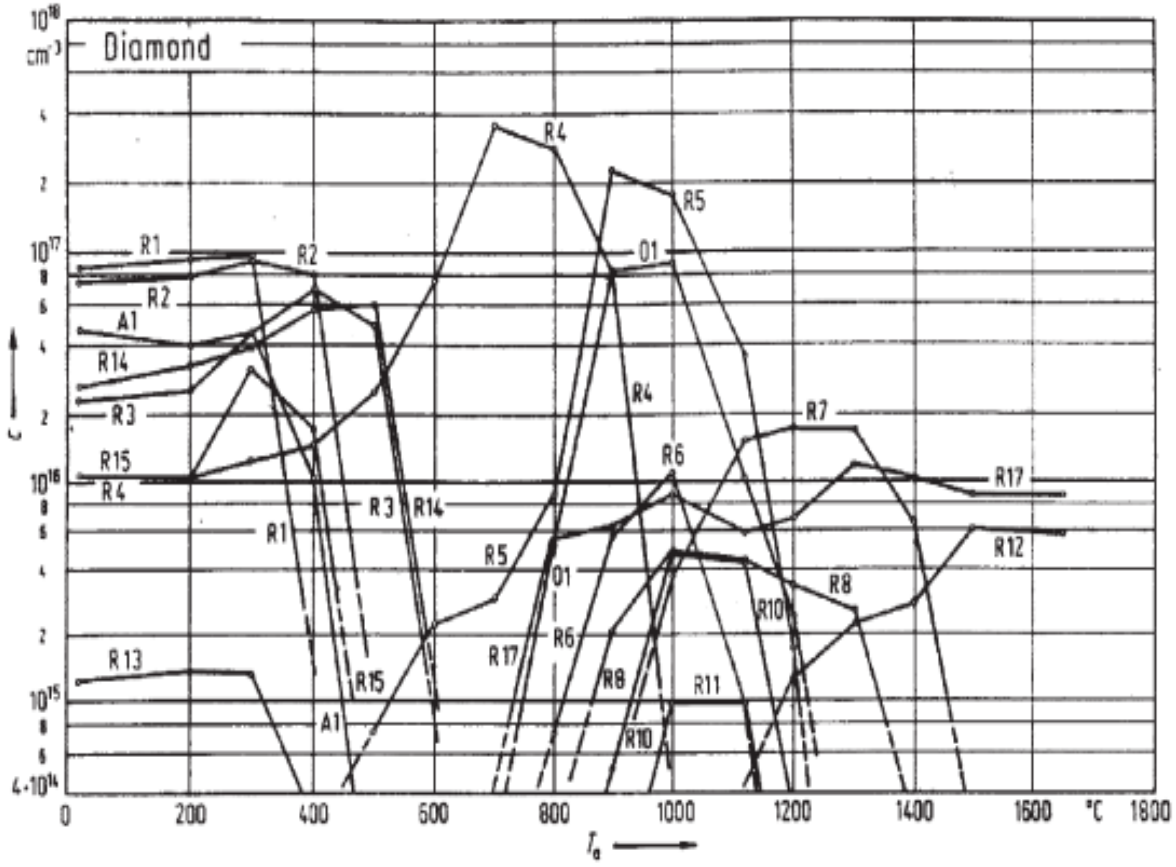
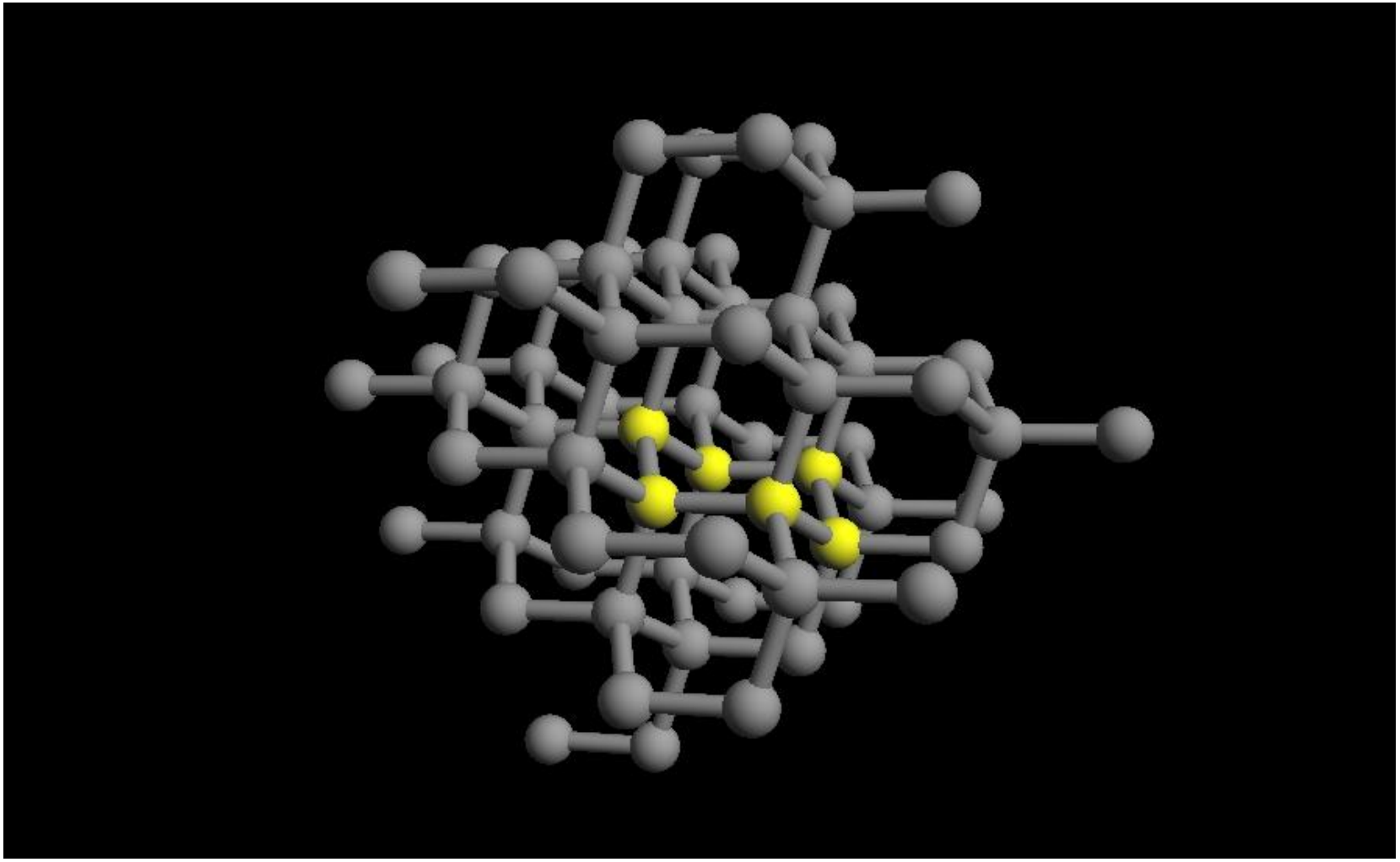
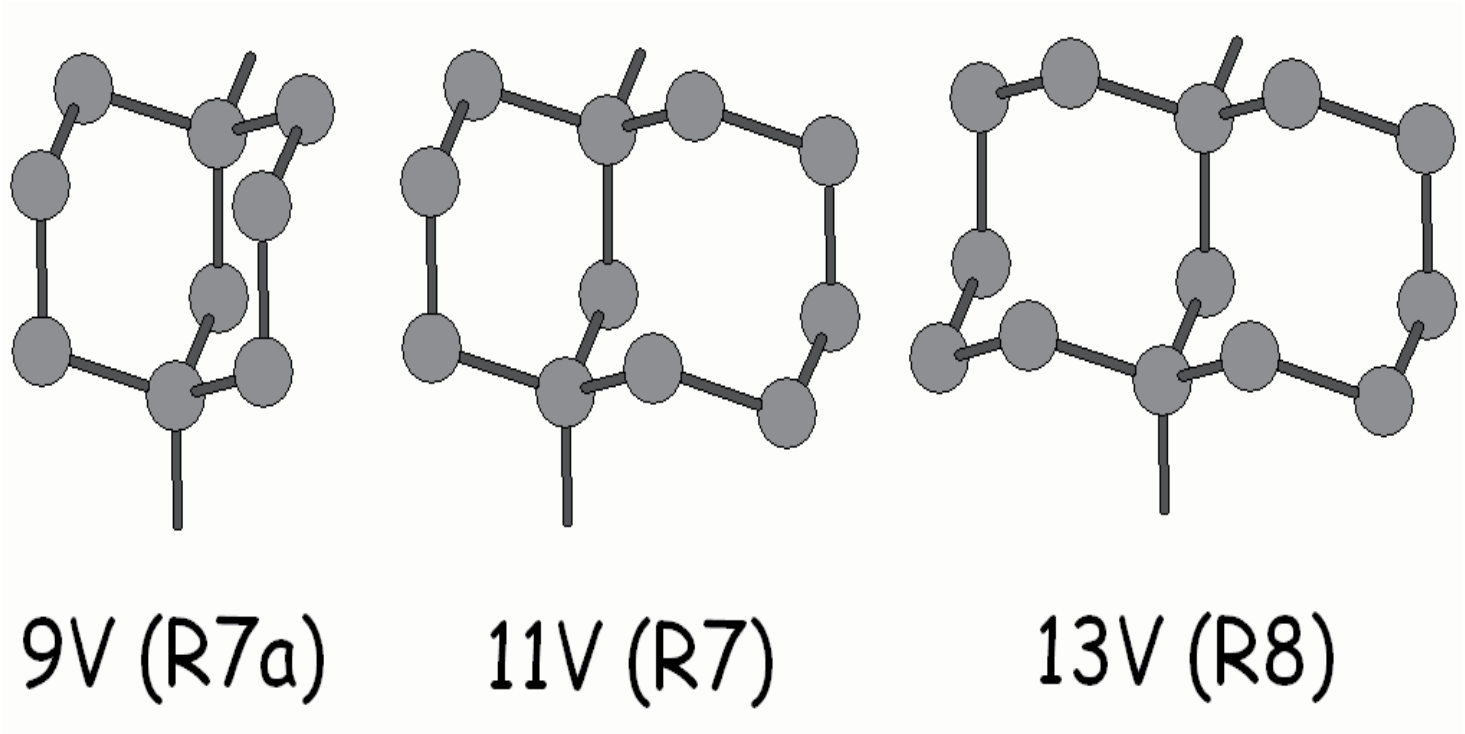


Fig. 1. Isochronal annealing-in and annealing-out of EPR spectra [4,7].

J. M. Baker, Diam. and Rel. Mater. 16 (2007) 216-219

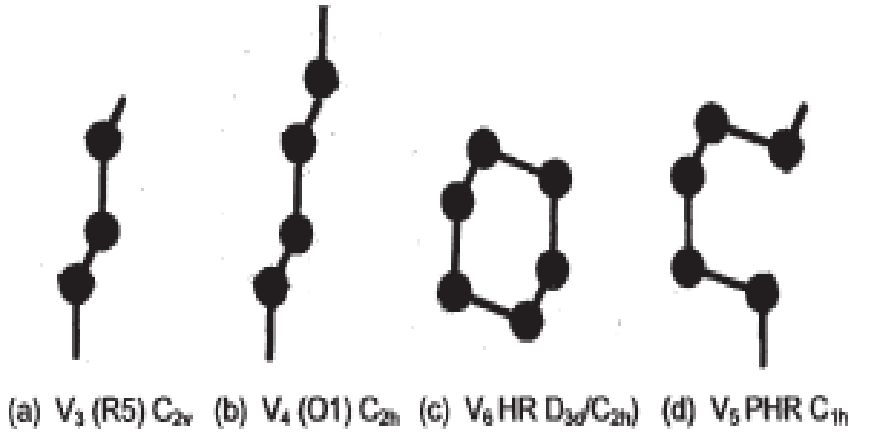
Representation of a V_6 vacancy cluster

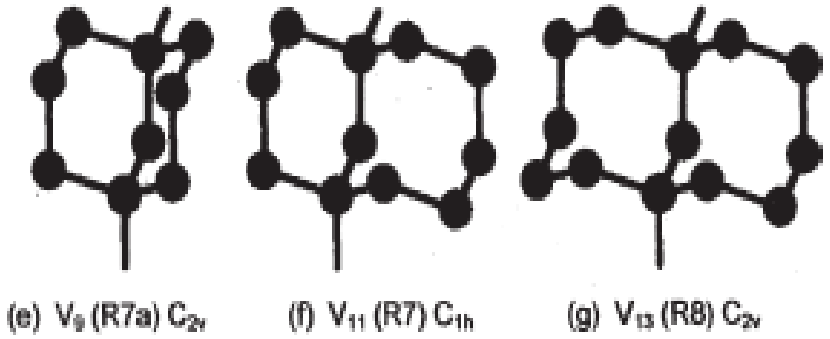


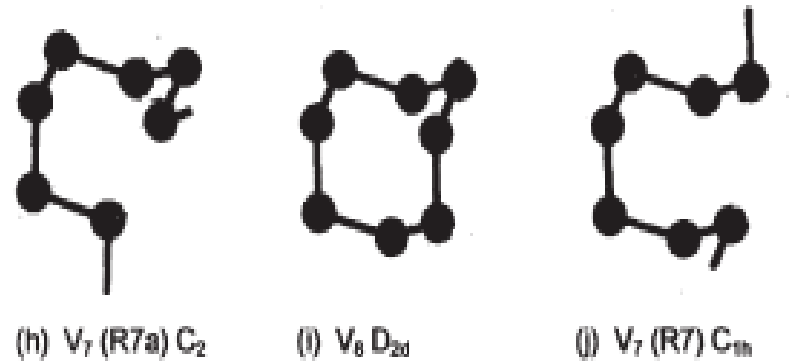


K. Iakoubovskii and A. Stesmans

Phys. Stat. Sol (a) 201. (2004) 2509-2515







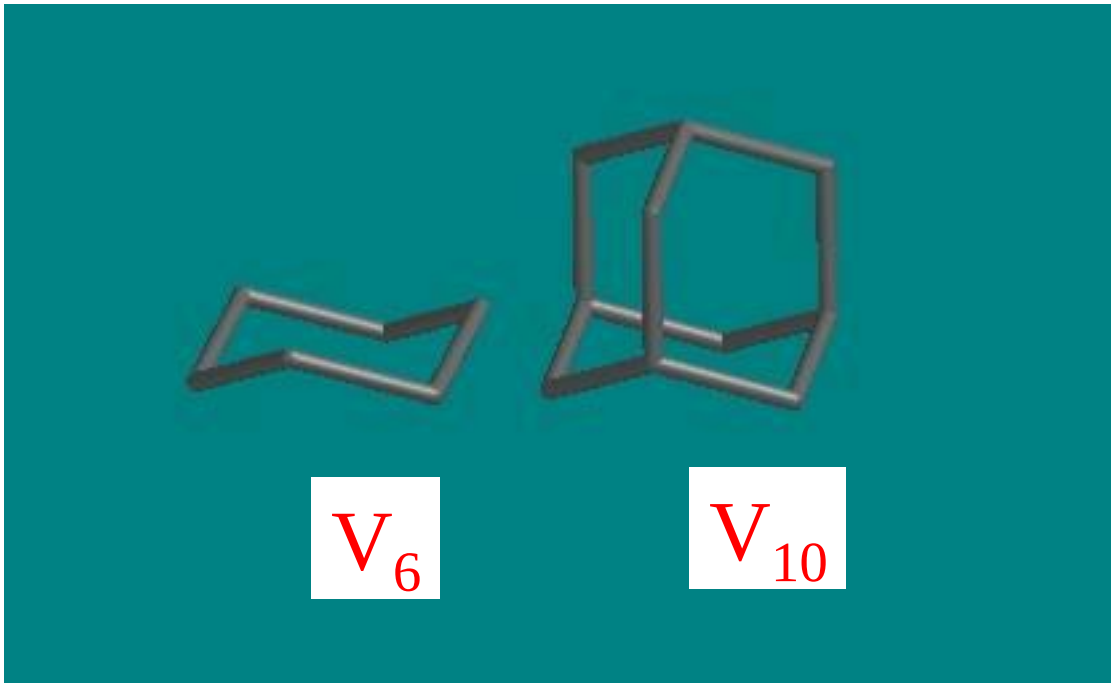
J. M. Baker, Diam. and Rel. Mater. 16 (2007) 216-219

Based on the counting of dangling bonds, it has been proposed that closed ring structures of vacancies V_6 and V_{10} should be especially stable in silicon.

$$E_f = \frac{1}{2} N_{DB} E_{bond}$$

$$E_{bond} = 2.35eV$$

$$E_B(n) = \frac{1}{2}(4n - N_{DB})E_{bond}$$

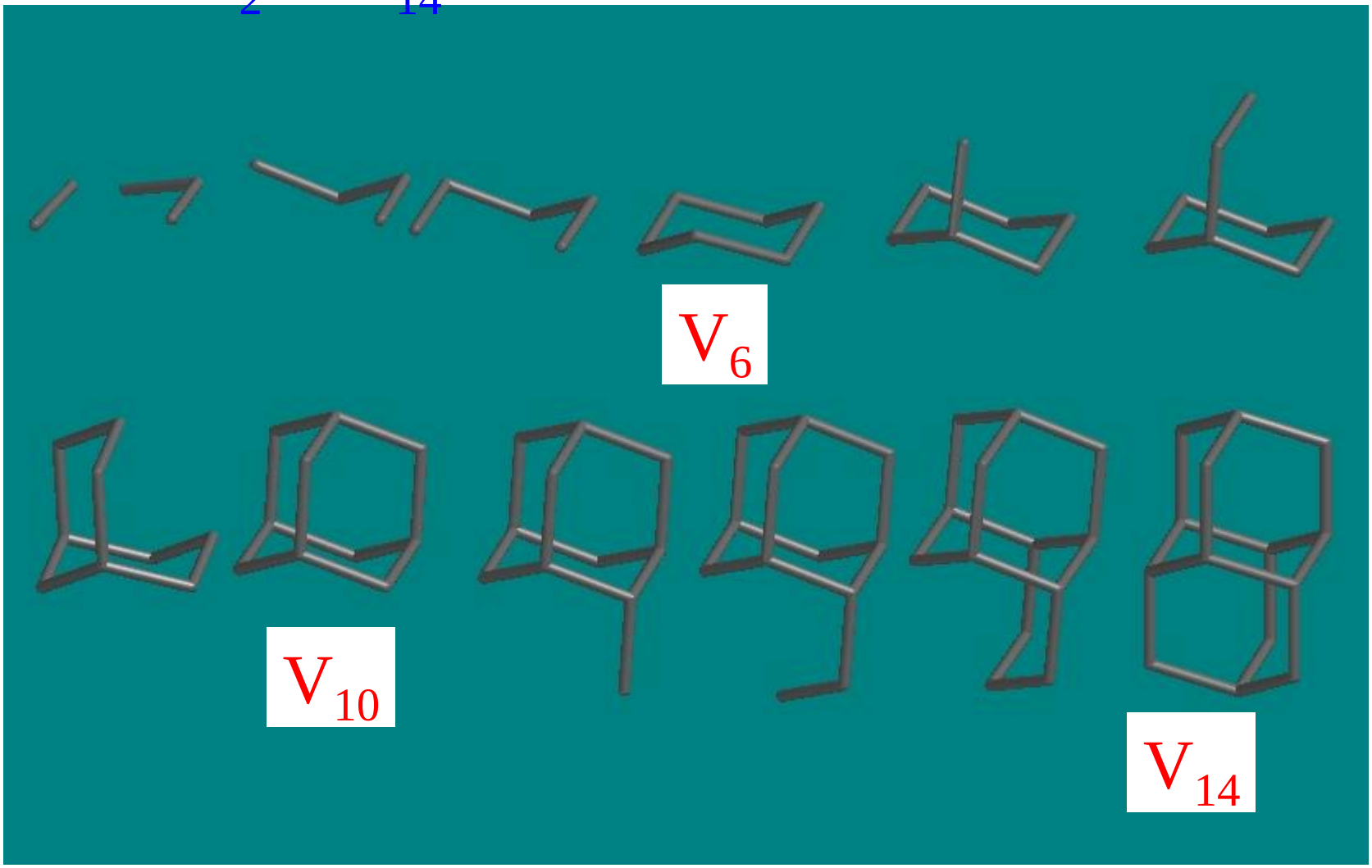


(D.J. Chadi and K.J. Chang, Phys. Rev. B38, 1523, (1988).)

Adamantane like vacancy clusters:

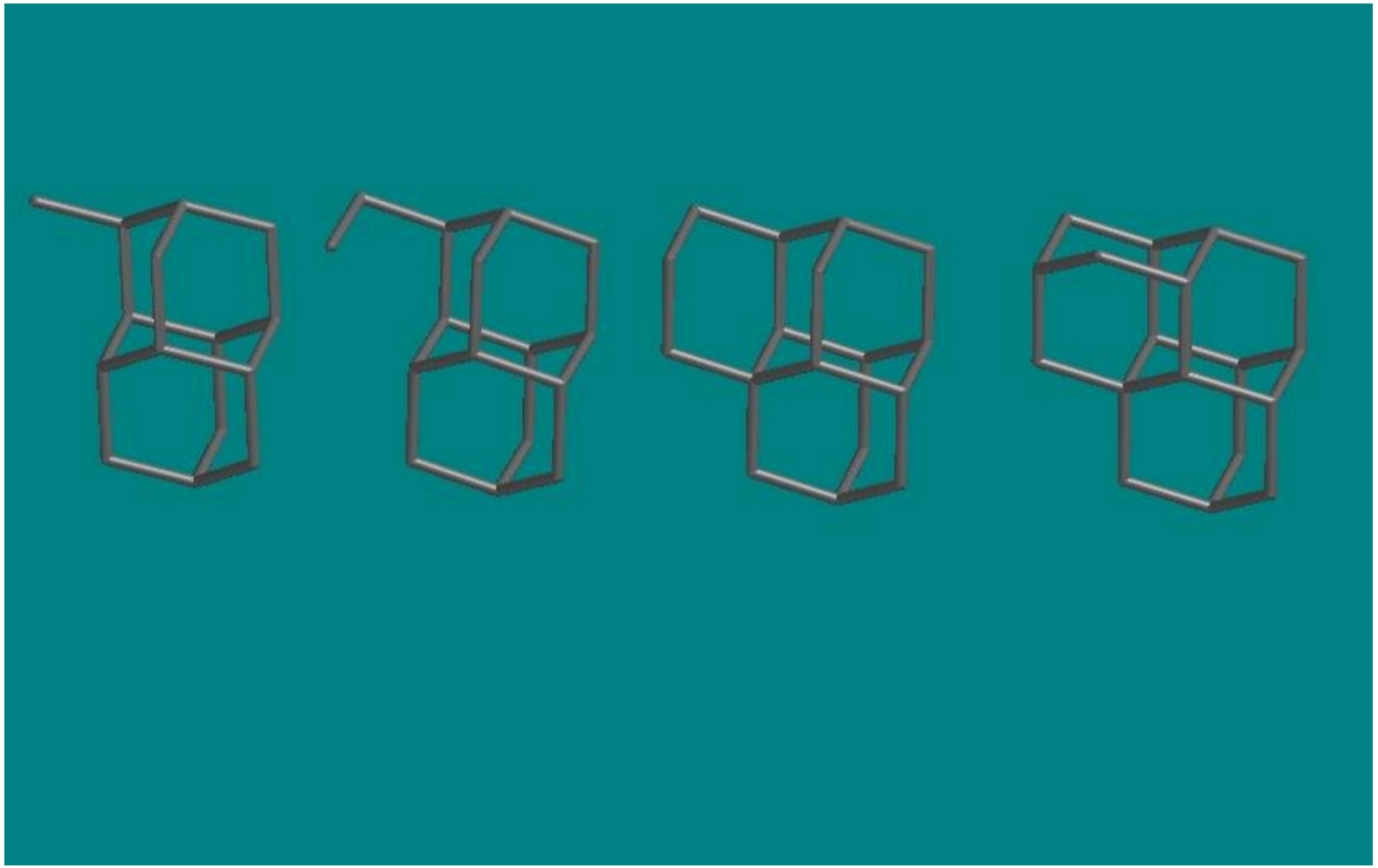
Vacancy cluster constructed by minimizing the number of dangling bonds in the vacancy cluster

Adamantane like vacancy clusters from V_2 to V_{14} in silicon.

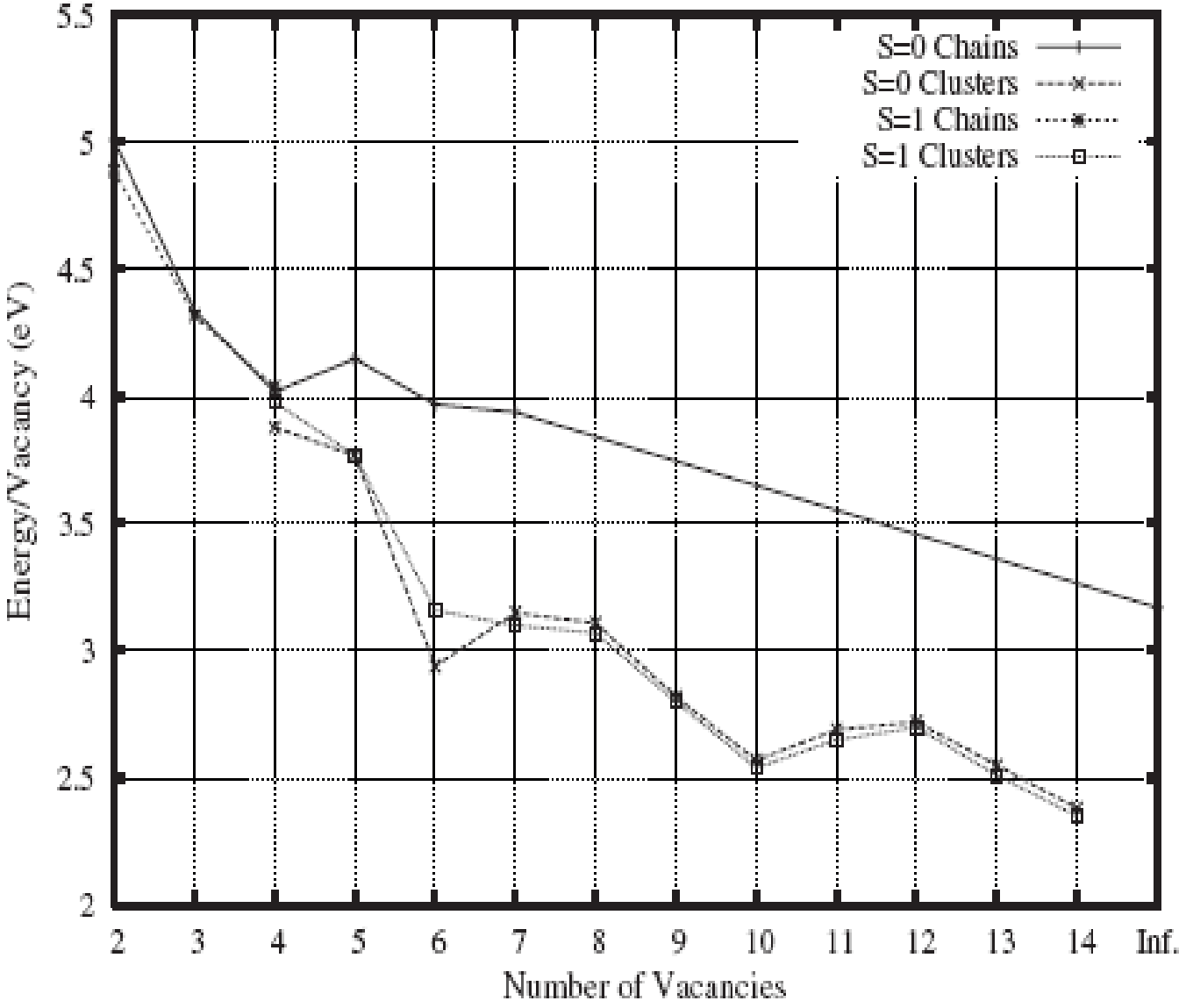


J. L. Hastings et al., Phys. Rev. B56, 10215 (1997)
A. Bongiorno et al. Europhysics Letters 59, 608 (2000)
T.E.M. Staab et al., Phys. Rev. B65, 115210 (2002)

Adamantane like vacancy clusters from V_{15} to V_{18} in silicon.



A. Bongiorno et al. Europhysics Letters 59, 608 (2000)
T.E.M. Staab et al., Phys. Rev. B65, 115210 (2002)



L. S. Hounsome et al.

Phys. Stat. Sol (a) 202. (2005) 2182-2187

Our goal is to:

a. Enumerate all distinct structures of V_n vacancy clusters with increasing n.
b. Evaluate a large number of V_n vacancy clusters at a realistic level of quantum mechanics
c. Interpret the driving forces of the distortions.

I. Laszlo, M. Kertesz, B. Slepetz, Y. Gogotsi
Diamond Relat. Mater. (2010),
doi:10.1016/j.diamond.2010.05.001

The method

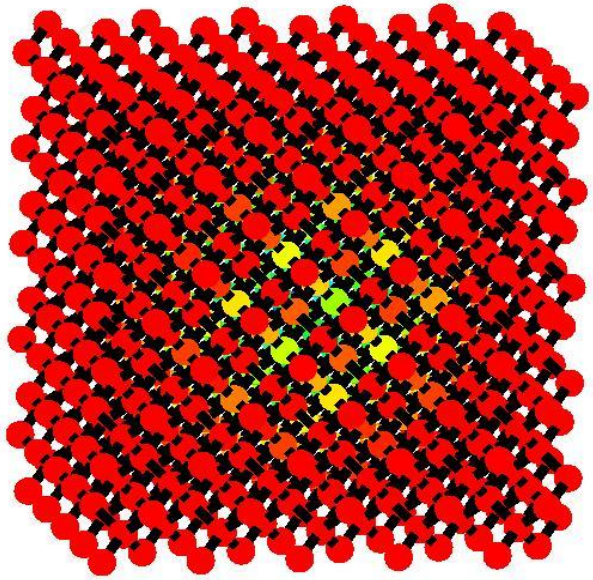
-Super cell of N=216 atoms in diamond structure

-The V_n vacancy is represented by taking away the V_n atomic cluster from the super cell

-Periodic boundary condition

- TBDFT for the interactions

D. Porezag et al. Phys. Rev B51 (1995) 12947



-Conjugate gradient method for minimizing the E^n_{vac} total energy of the system of (216-n) atoms.

(-1 < n < 15)

I. Laszlo, M. Kertesz, B. Slepetz, Y. Gogot
Diamond Relat. Mater. (2010),
doi:10.1016/j.diamond.2010.05.001

Relative stability of n-vacancy cluster geometries

Formation energy

$$E_F^n = E_{vac}^n - \frac{N-n}{N} E_{cryst}^N$$

E_F^n Formation energy of n-vacancy cluster

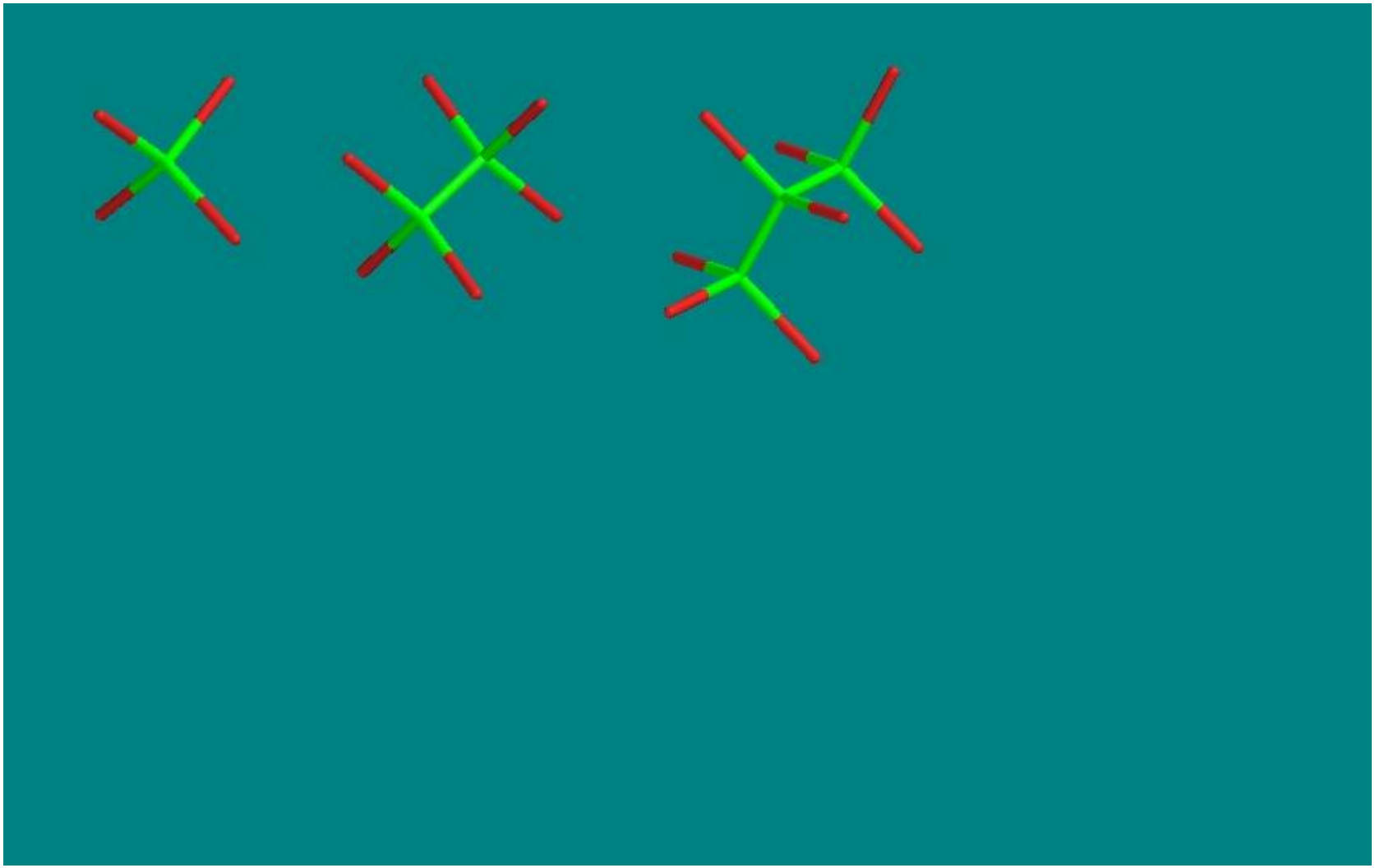
E_{vac}^n Total energy of super cell with N-n atoms

$$E_{cryst}^N = E_{vac}^0$$

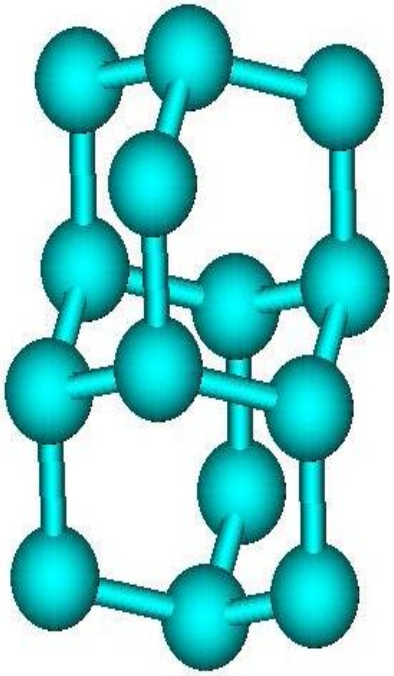
$$E_{FV}^n = \frac{E_F^n}{n}$$

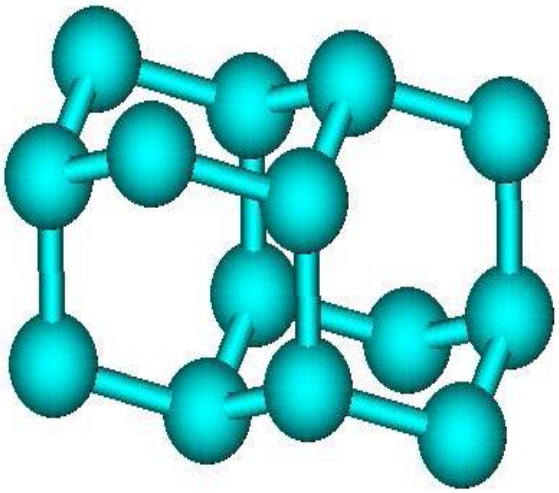
Formation energy per vacancy

Algorithm for the construction a diamond vacancy clusters



Selection of equivalent structures





Diagonalization of the modified adjacency matrix $D_{ij}=\exp(-ar_{ij})$ of the corresponding complete graph.

r_{ij} is the Euclidean distance in the diamond lattice Between vertices i and j. a= 1.0 Angstrom

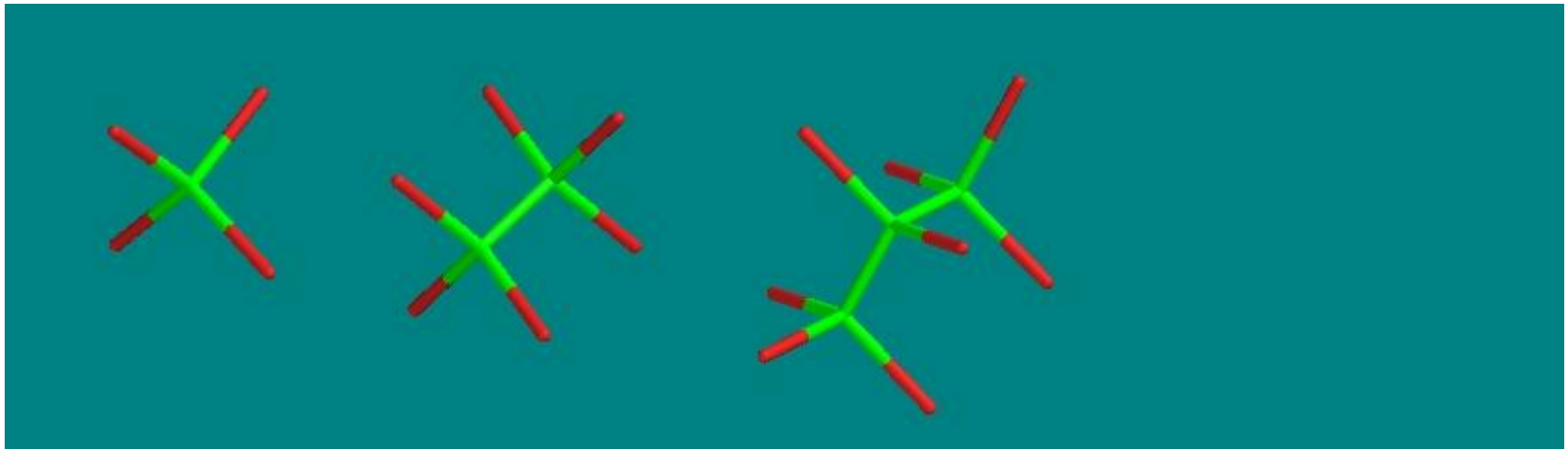
The number of all possible V_n vacancy clusters

n : number of vacancies

p : number of generated vacancy clusters

q : number of in equivalent vacancy clusters

n	p	q
1	1	1
2	4	1
3	6	1



n	p	q
1	1	1
2	4	1
3	6	1
4	8	3
5	30	7
6	83	24
7	328	88
8	1357	385
9	6617	1713
10	32417	8112
11	167511	38865
12	869139	190081
13	4574468	937194
14	24139560	4660000

I. Laszlo, M. Kertesz, B. Slepetz, Y. Gogo
Diamond Relat. Mater. (2010),
doi:10.1016/j.diamond.2010.05.001

Algorithm for generating connected vacancy clusters

1. Start with V_1 and increase n one by one
2. Generate all possible V_n from V_{n-1}
3. Eliminate the equivalent vacancy clusters. I_n is the number of in-equivalent structures
4. Optimize the geometries of all I_n structures
5. Calculation of formation energies for all V_n
6. Keep only the M_n lowest energy vacancy clusters
7. n=n+1 and GO TO 2. (The process terminates at a predetermined value n.)

I. Laszlo, M. Kertesz, B. Slepetz, Y. Gogotsi
Diamond Relat. Mater. (2010),
doi:10.1016/j.diamond.2010.05.001

Algorithm for generating connected vacancy clusters

Up to n=7, we included all possible vacancy clusters, for n > 7 we used the following parameters

$M_7 = M_8 = M_9 = M_{10} = M_{11} = 5$ and

$M_{12} = M_{13} = 7$

The number of all possible V_n vacancy clusters

n : number of vacancies

p : number of generated vacancy clusters

q : number of in equivalent vacancy clusters

n	p	q
1	1	1
2	4	1
3	6	1
4	8	3
5	30	7
6	83	24
7	328	88

List of V_{4_L} parent structures for V_{5_k} structures

SN serial number

SNP serial number of parent structures

	V_5		
SN	SNP		
1	1		
2	1	2	
3	1	3	
4	1	2	3
5	1		
6	3		
7	2		

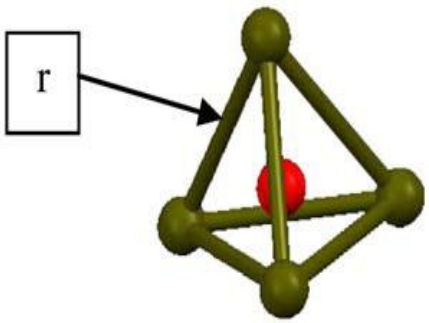
V_{5_k} SN = k

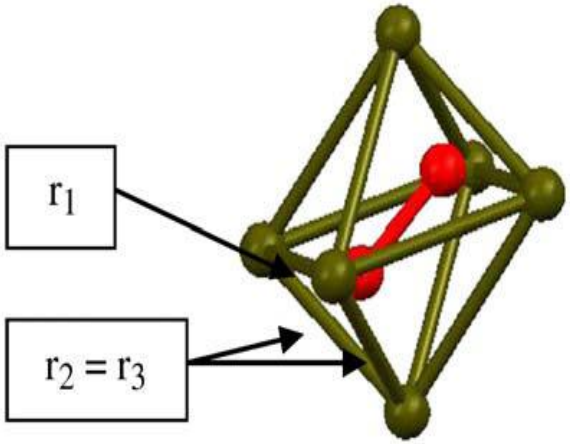
V_{4_L} SNP = L

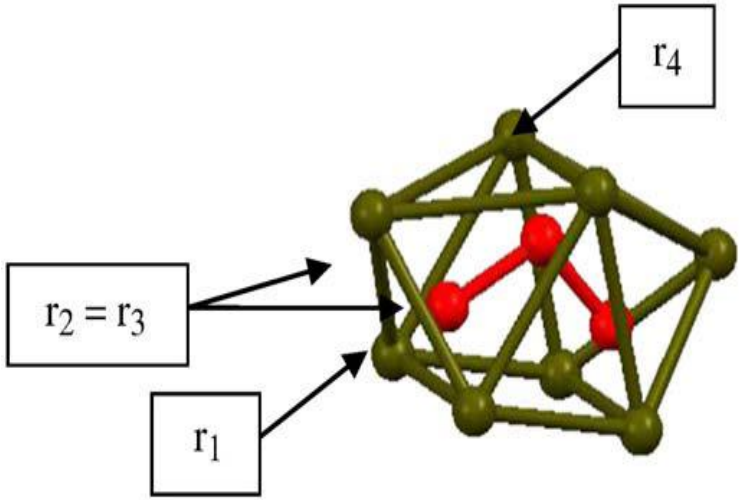
V_6			
SN	SNP		
1	1		
2	1	5	
3	1	3	
4	1	3	4
5	1	2	5
6	1	4	
7	1	2	
8	2	3	
9	2	4	
10	2	3	4
11	3		
12	3	6	
13	3		
14	4	6	
15	3	4	5
16	4		
17	2	4	5
18	3	4	
19	3	4	6
20	2	4	7
21	3		
22	3	5	
23	5		
24	6		

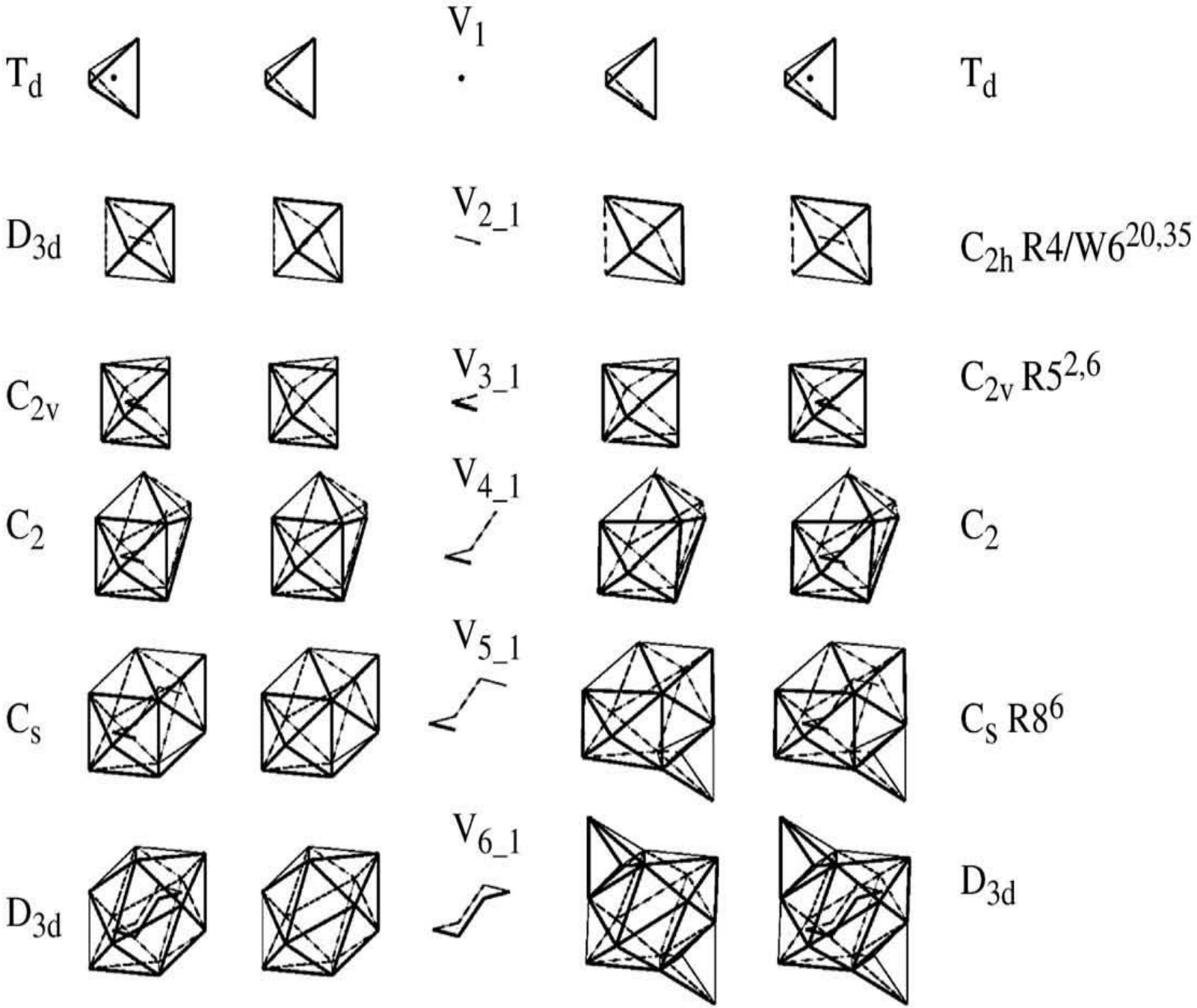
V_7				
SN	SNP			
1	1	3	4	6
2	1	2	5	7
3	2	5	7	
4	2	6	15	
5	2	3		
6	2			
7	3	7	8	
8	2	3	15	
9	2	22		
10	2			
11	7			
12	3	11		
13	4	5	15	20
14	4	5	8	15
15	5			
16	3	12		
17	3	6	19	
18	2	23		
19	4	12	14	
20	3	13		
21	2	4	22	
22	2	5	23	
23	3	4	21	
24	3	4	18	
25	2	4	17	
26	4	11	13	
27	5	10	22	
28	3	5	22	
29	2	5	17	
30	3	5	10	
31	14	20		
32	4	19		
33	6	14	18	
34	6	7	20	
35	4	10	13	
36	10	18	20	
37	12			
38	6	10		
39	8	12		
40	12			
41	7	10	17	
42	17	20		
43	5	17	23	
44	9	16	20	
45	4	7	9	10
46	4	6	16	18
47	8	11	13	
48	11	22		
49	10	11	15	
50	12	14	15	

51	5	6	9	17
52	5	7	9	17
53	8	9	10	18
54	15	17	23	
55	9	15	17	18
56	15	18	22	
57	12	24		
58	8	10	21	
59	13	21		
60	10	12	19	
61	8	19	20	
62	11	21		
63	10	17	18	
64	8	17	22	
65	11	12	19	
66	13	22		
67	17	19	22	
68	14	19	24	
69	12	13	19	
70	10	15	16	17
71	3			
72	9	10	14	19
73	23			
74	18	19	21	
75	18			
76	12	19	24	
77	24			
78	13	15	18	
79	12	18	19	
80	12	21		
81	12	22		
82	15	21	22	
83	22			
84	14	16	18	19
85	15	22	23	
86	14	17		
87	15	19		
88	22	23		

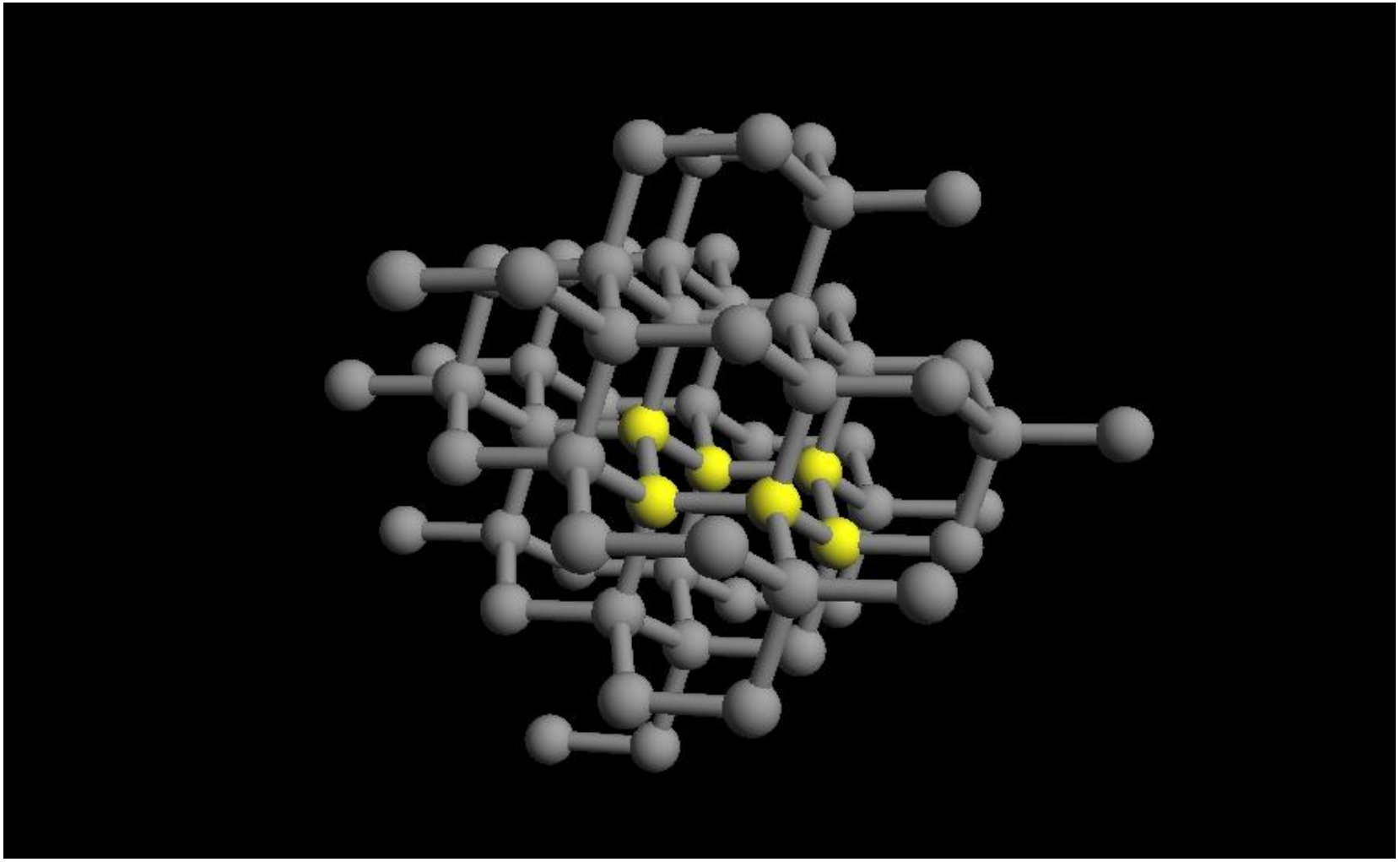

r

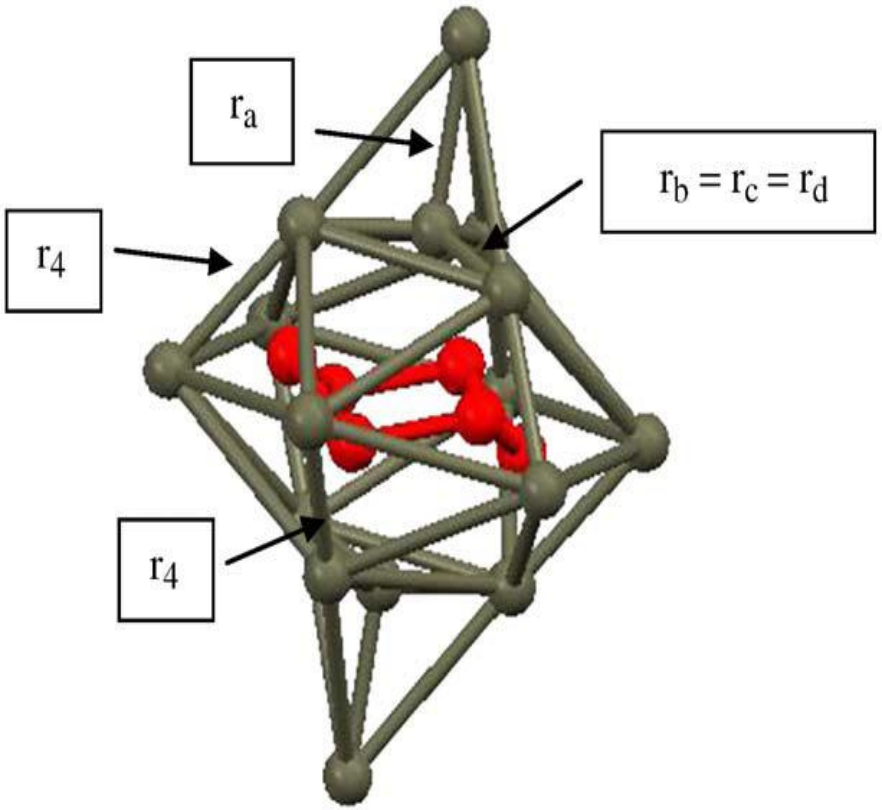

r1
r2 = r3

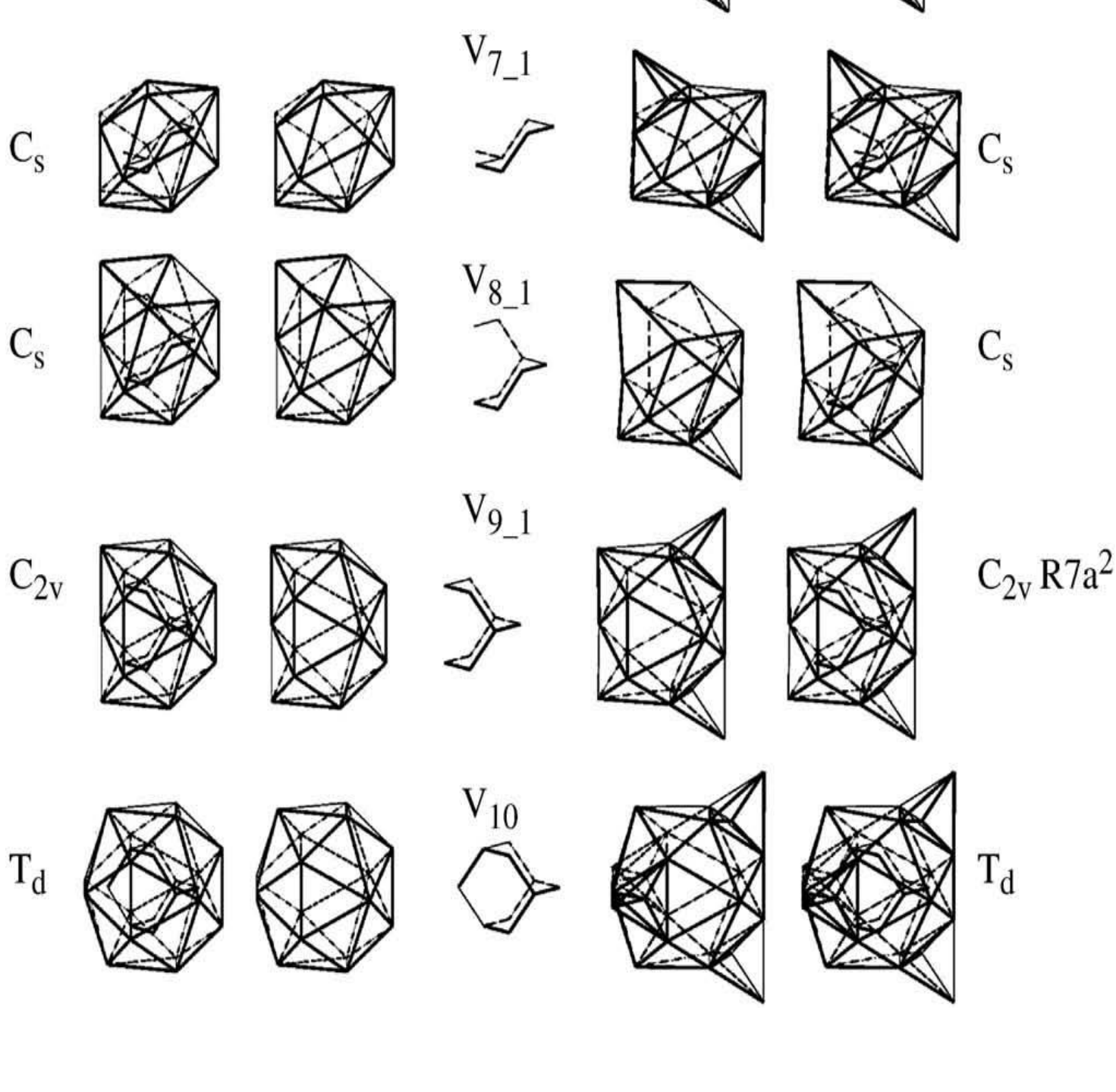

r4
r2 = r3
r1

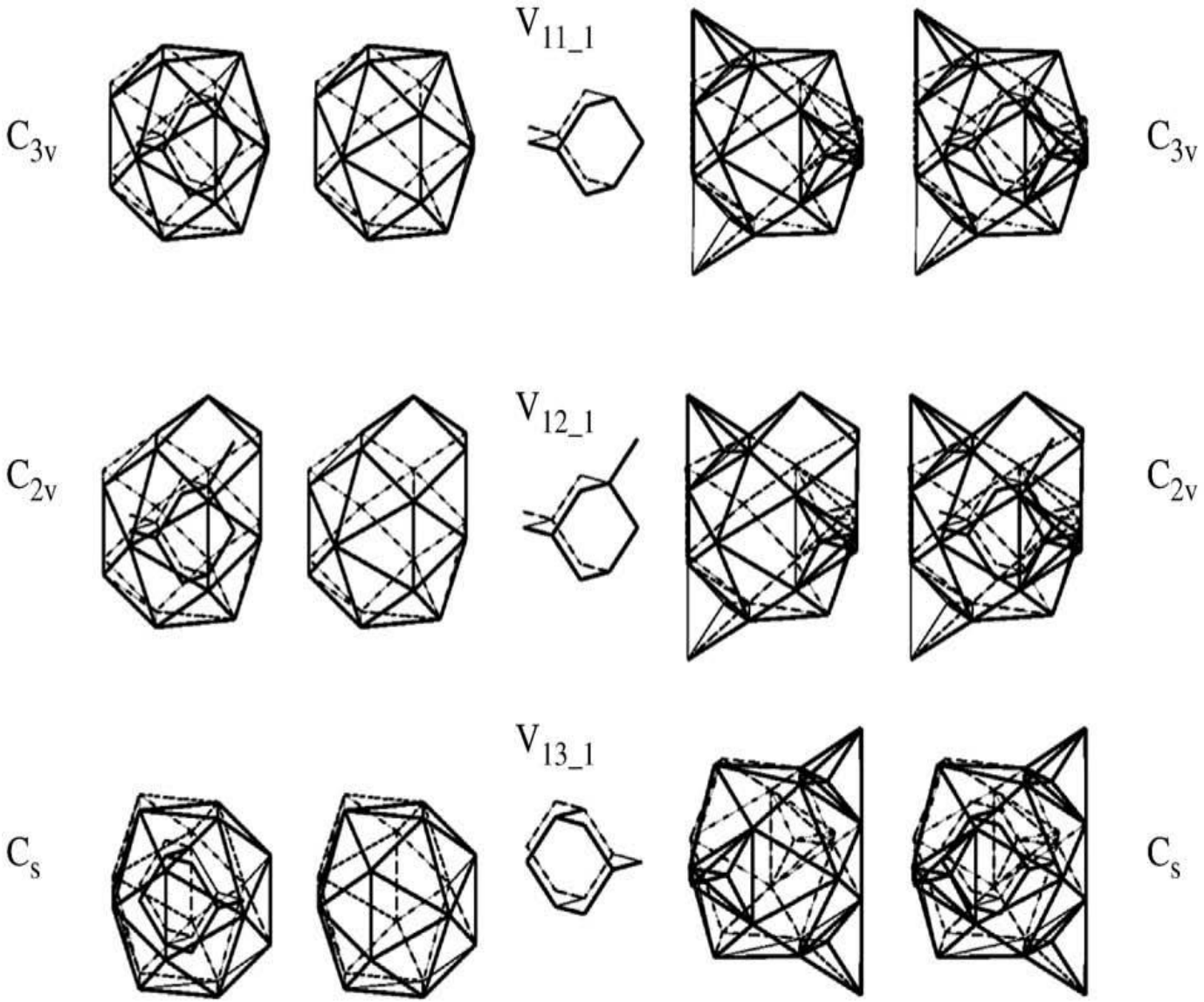

T_d
V_1
T_d
D_{3d}
V_{2_1}
C_{2h} R4/W6[20,35]
C_{2v}
V_{3_1}
C_{2v} R5[2,6]
C_2
V_{4_1}
C_2
C_s
V_{5_1}
C_s R8[6]
D_{3d}
V_{6_1}
D_{3d}

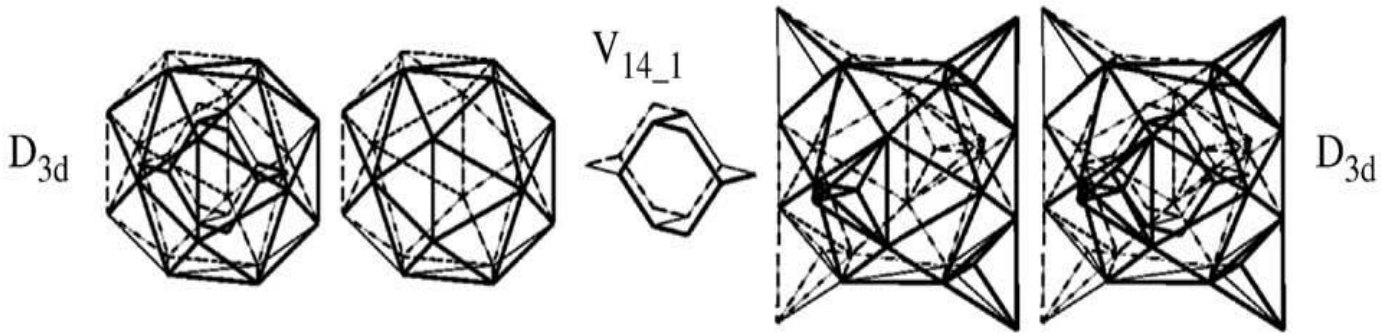
Representation of a V_6 vacancy cluster

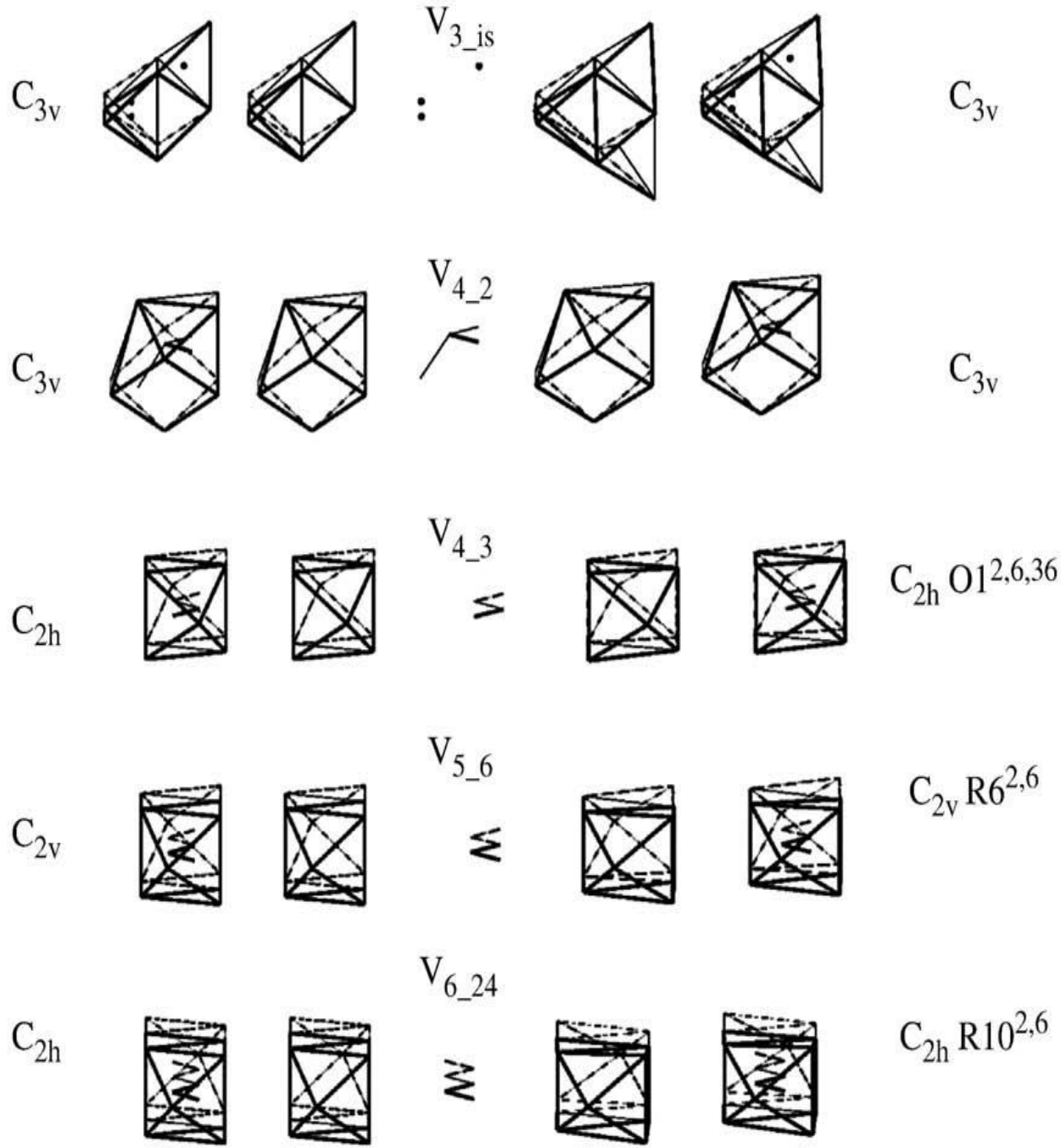



r_a
$r_b = r_c = r_d$
r_4
r_4

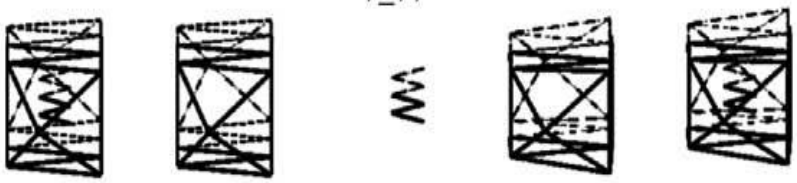

V_{7_1}
C_s
C_s
V_{8_1}
C_s
C_s
V_{9_1}
C_{2v}
C_{2v} R7a^2
V_{10}
T_d
T_d


C_{3v}
V_{11_1}
C_{3v}
C_{2v}
V_{12_1}
C_{2v}
C_s
V_{13_1}
C_s


D3d
V14_1
D3d

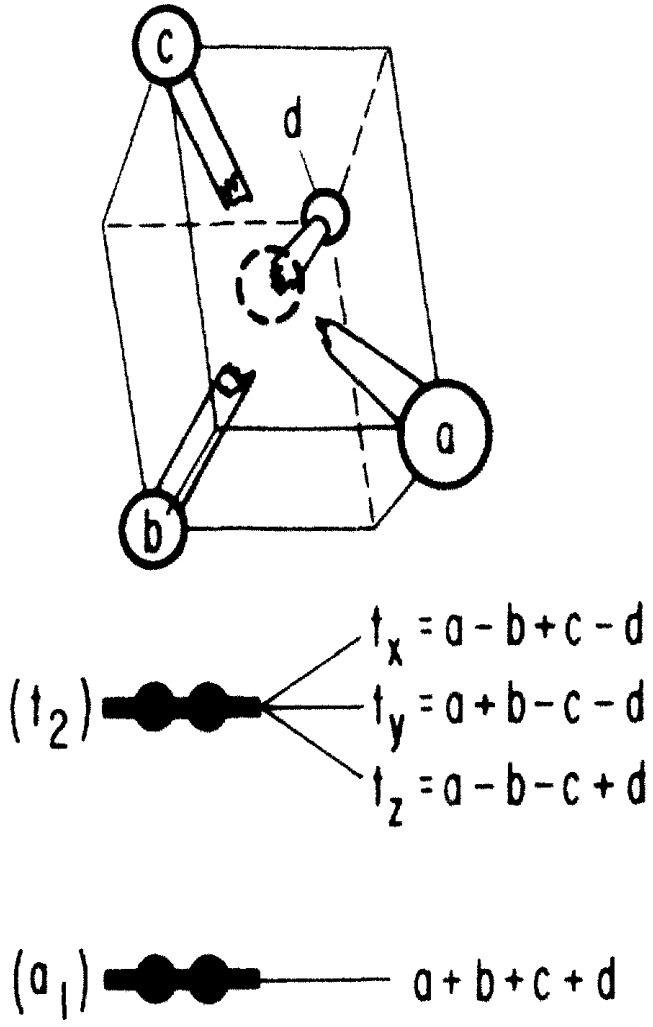

V_{3_is}
C_{3v}
C_{3v}
V_{4_2}
C_{3v}
C_{3v}
V_{4_3}
C_{2h}
$C_{2h}\ O1^{2,6,36}$
V_{5_6}
C_{2v}
$C_{2v}\ R6^{2,6}$
V_{6_24}
C_{2h}
$C_{2h}\ R10^{2,6}$

V_{7_77}

C_{2v}  C_{2v} R11^{2,6}

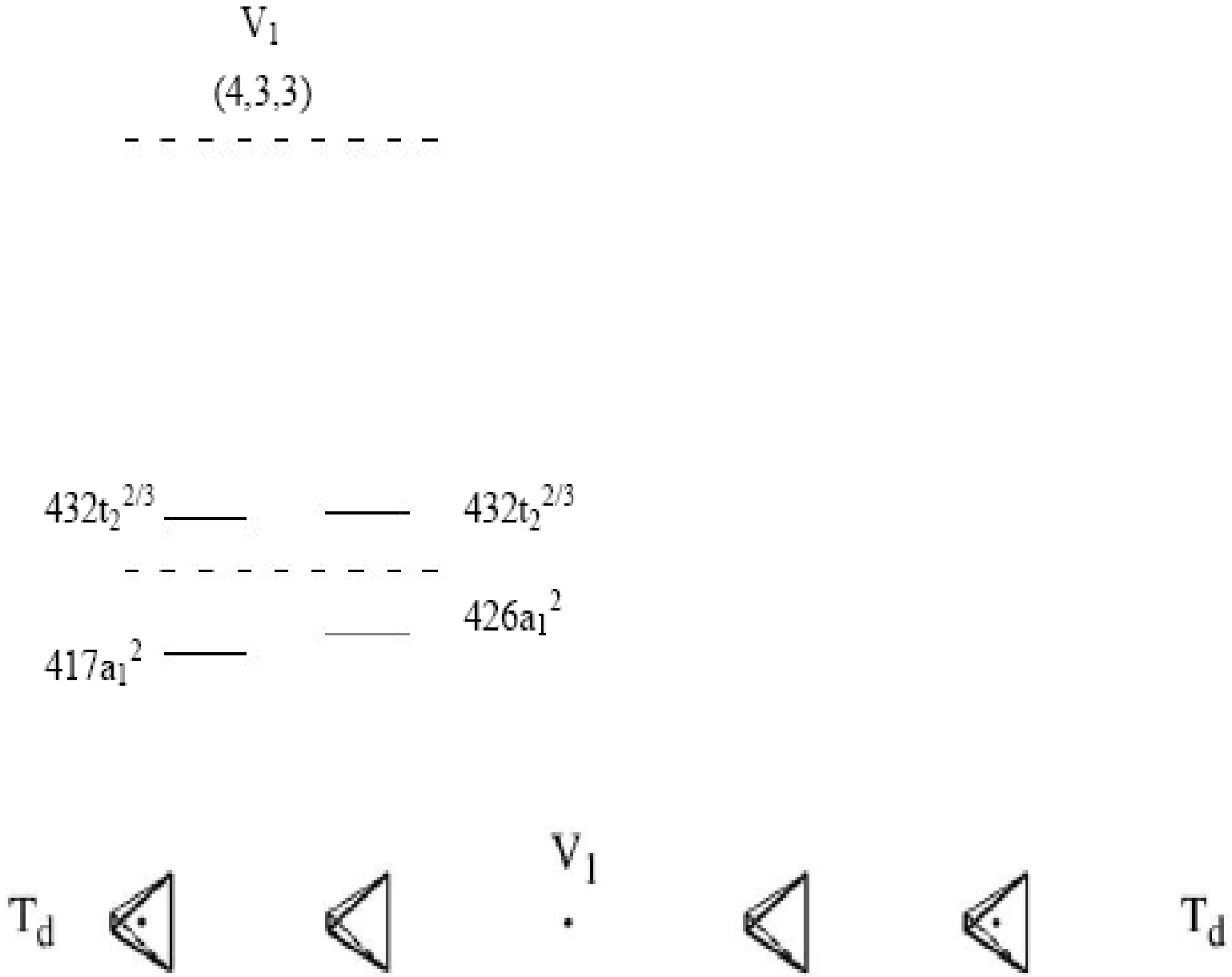
V_{8_chain}

C_{2h}  C_{2h} KUL11^{2,6}



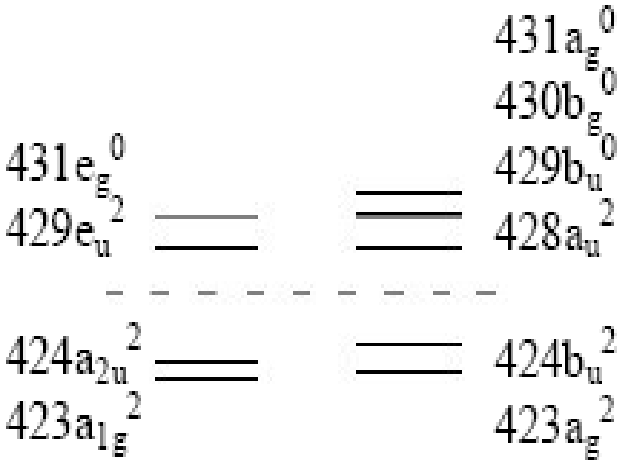
Coulson and Kearsley,

Proc. Roy. Soc. Ser. A241 (1957) 433

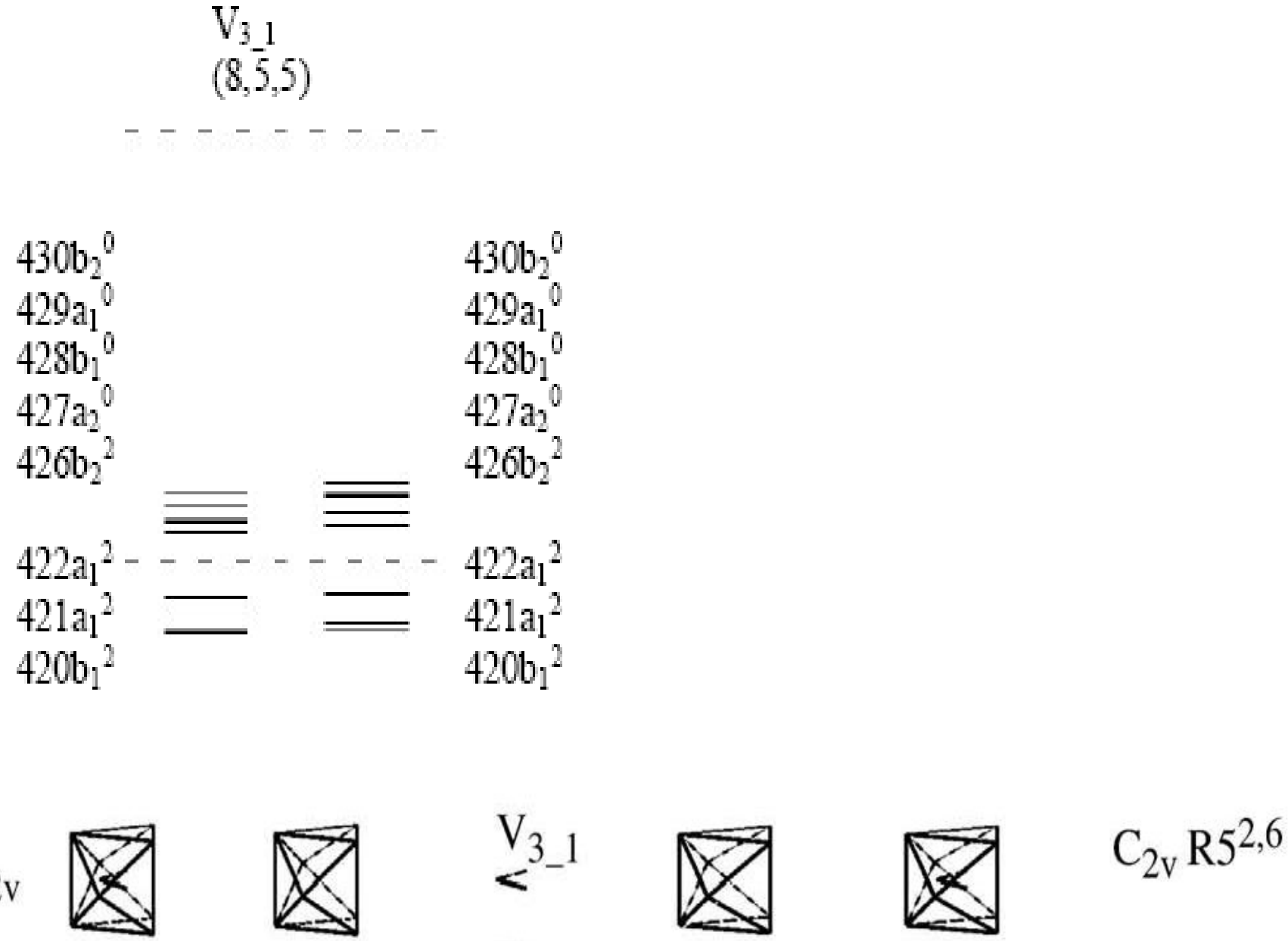

V1
(4,3,3)
432t2 2/3
432t2 2/3
426a1 2
417a1 2
Td
V1
Td

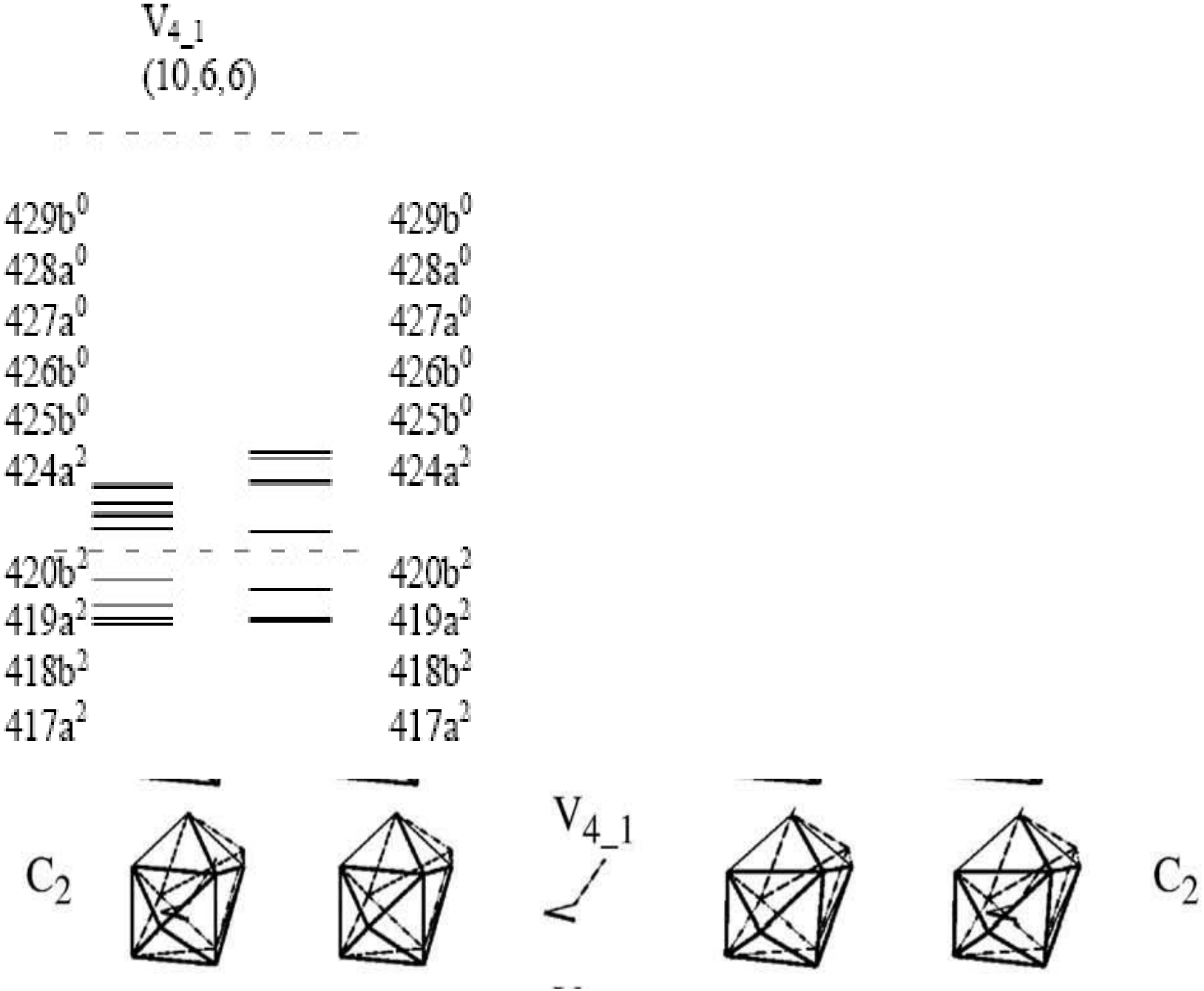
V_{2_1}

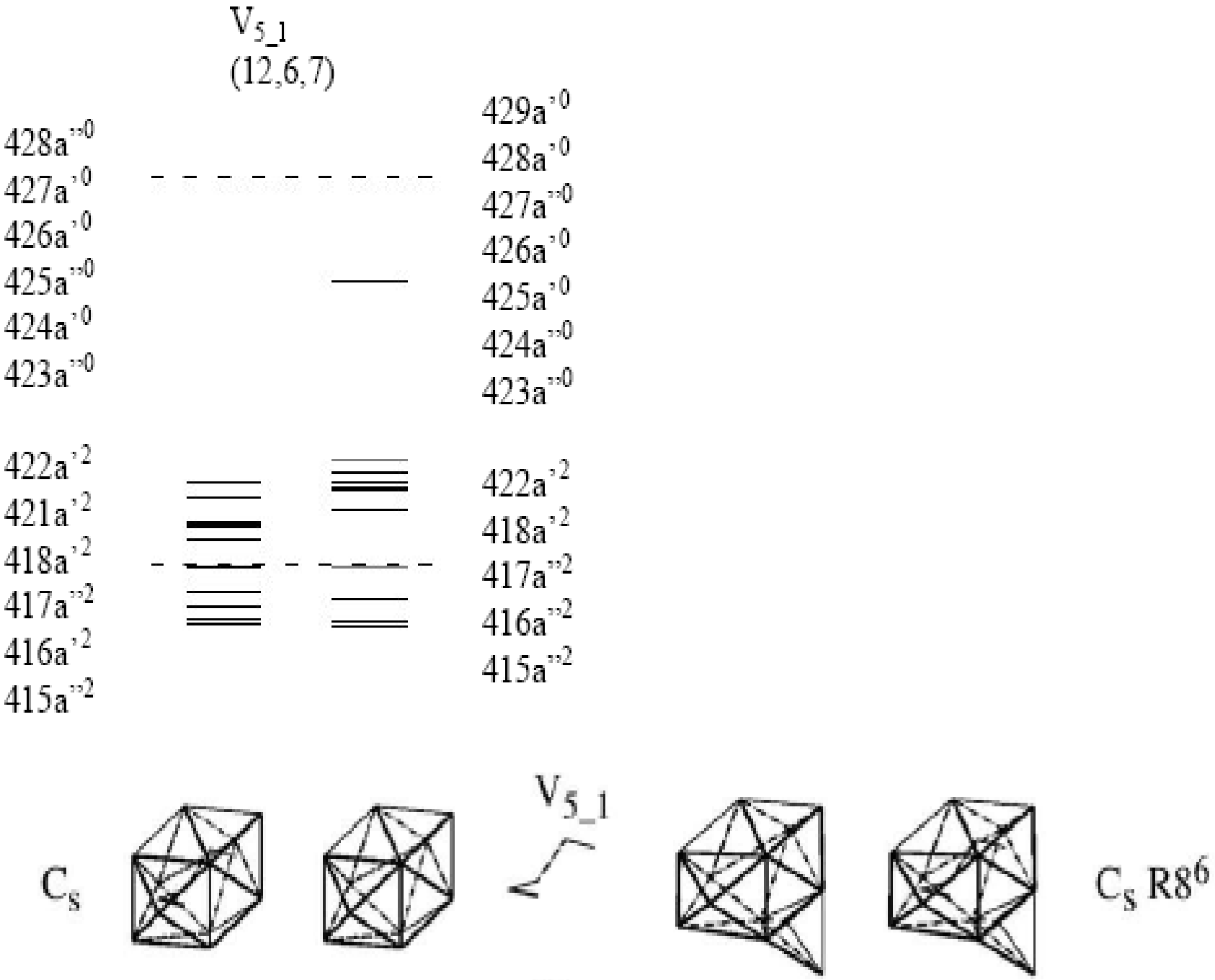
(6,4,4)

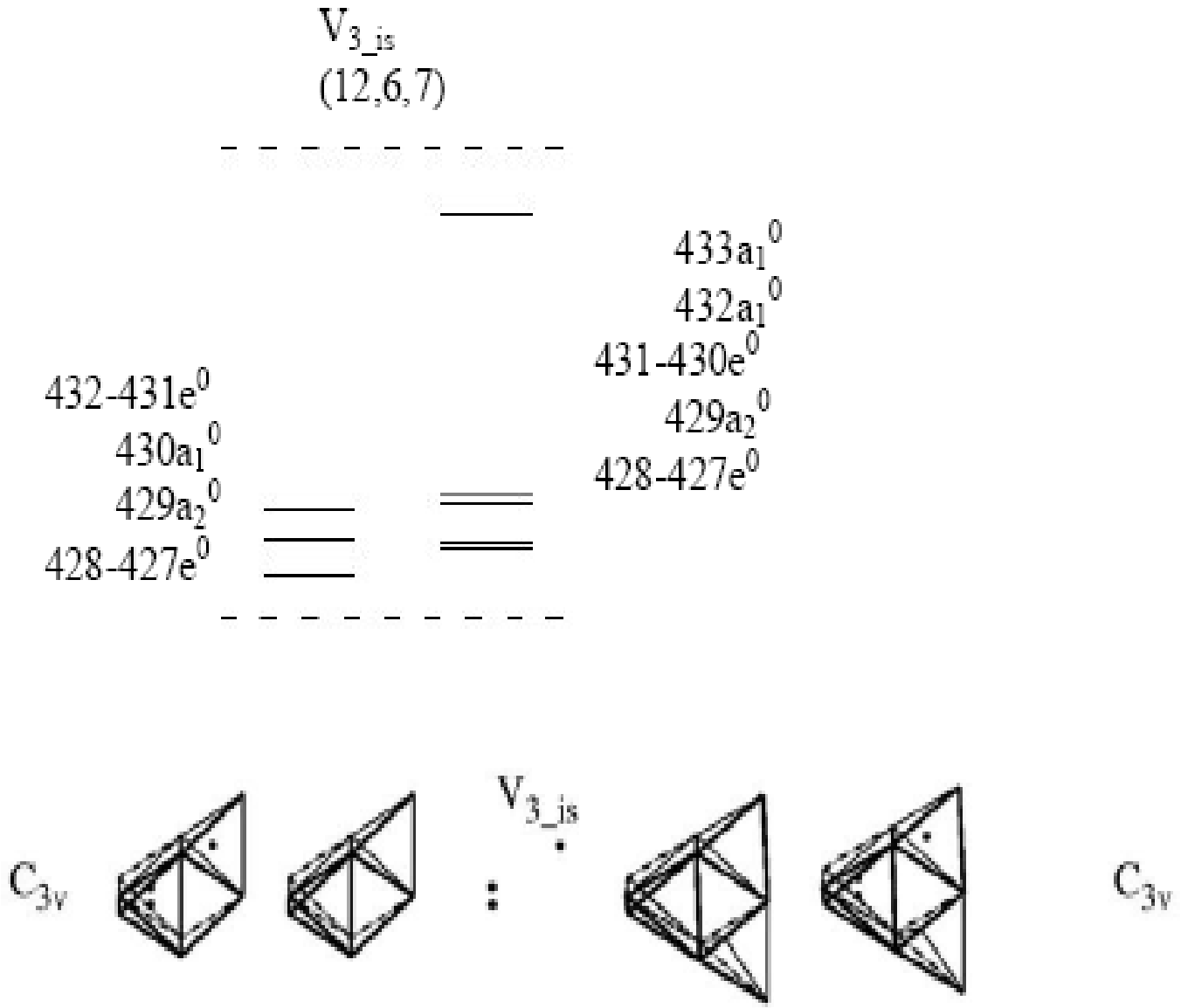


D_{3d}   $\underset{\sim}{V_{2\_1}}$   C_{2h} R4/W6^{20,35}

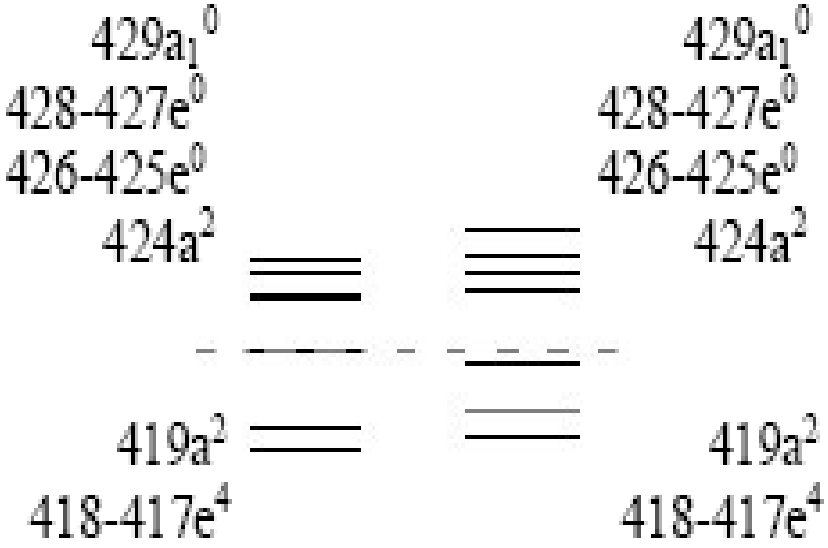

V3_1
(8,5,5)
430b2 0
429a1 0
428b1 0
427a2 0
426b2 2
422a1 2
421a1 2
420b1 2
430b2 0
429a1 0
428b1 0
427a2 0
426b2 2
422a1 2
421a1 2
420b1 2
C2v
V3_1
C2v R5 2,6

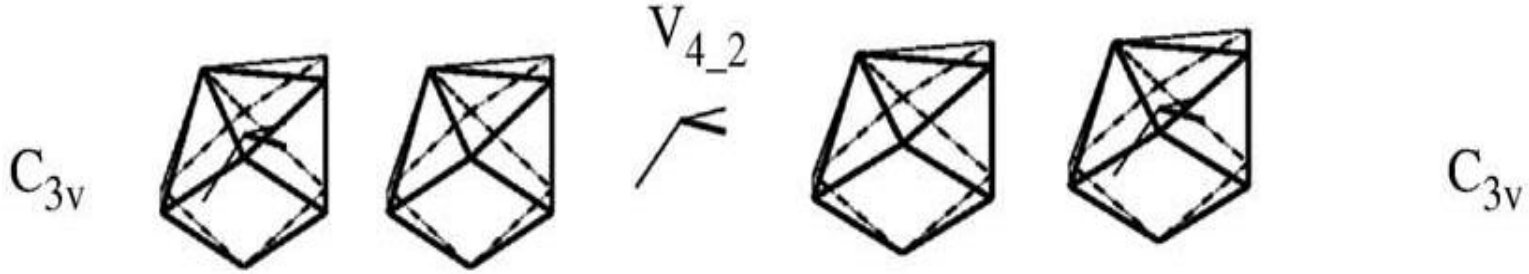

V4_1
(10,6,6)
429b0
428a0
427a0
426b0
425b0
424a2
420b2
419a2
418b2
417a2
429b0
428a0
427a0
426b0
425b0
424a2
420b2
419a2
418b2
417a2
C2
V4_1
C2

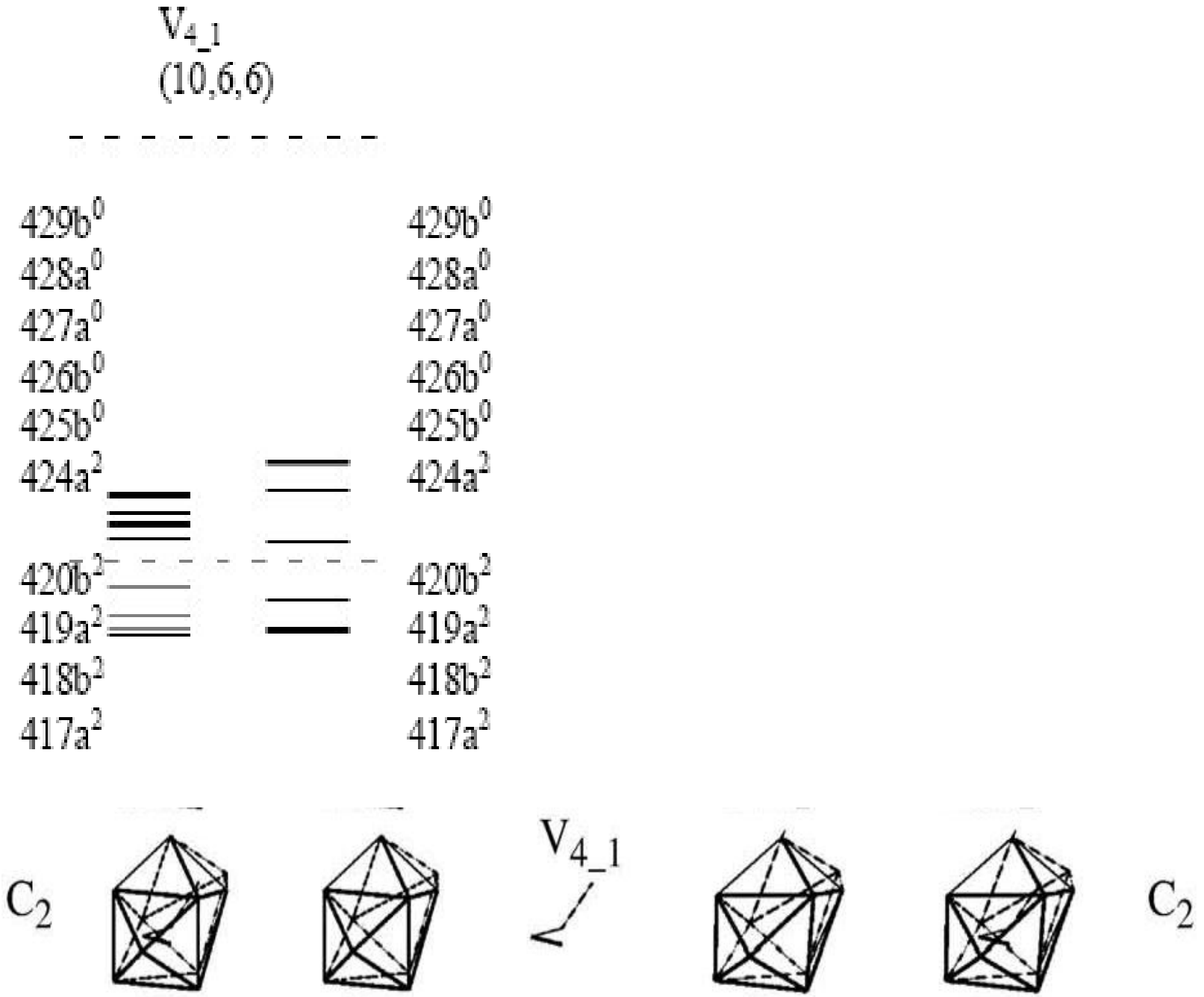

V5_1
(12,6,7)
428a''0
427a'0
426a'0
425a''0
424a'0
423a''0
422a'2
421a'2
418a'2
417a''2
416a'2
415a''2
429a'0
428a'0
427a''0
426a'0
425a'0
424a''0
423a''0
422a'2
418a'2
417a''2
416a''2
415a''2
Cs
V5_1
Cs R8^6

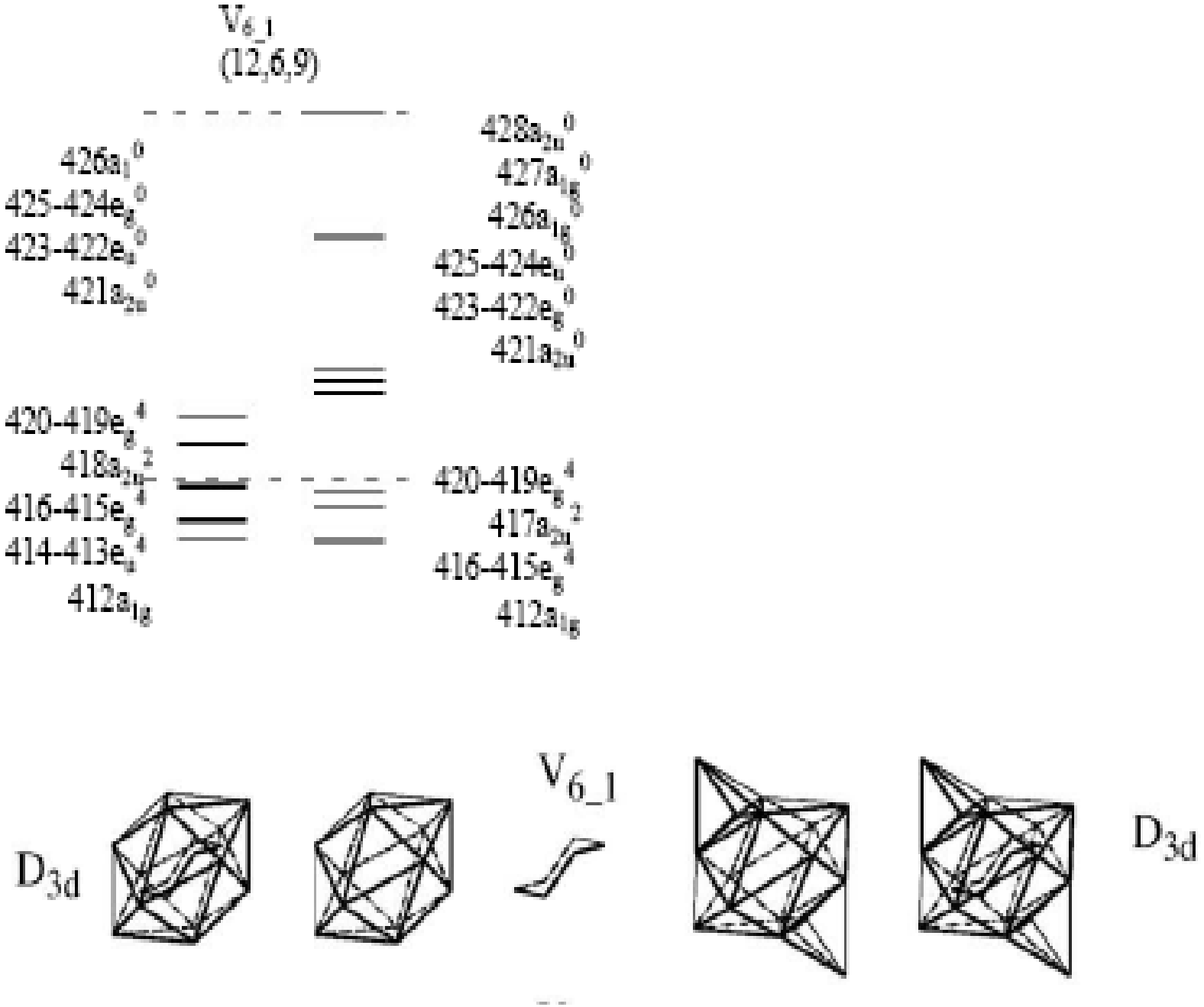

V_{3_is}
(12,6,7)
$433a_1^0$
$432a_1^0$
$431\text{-}430e^0$
$429a_2^0$
$428\text{-}427e^0$
$432\text{-}431e^0$
$430a_1^0$
$429a_2^0$
$428\text{-}427e^0$
V_{3_is}
C_{3v}
C_{3v}

V_{4_2}
(10,6,6)

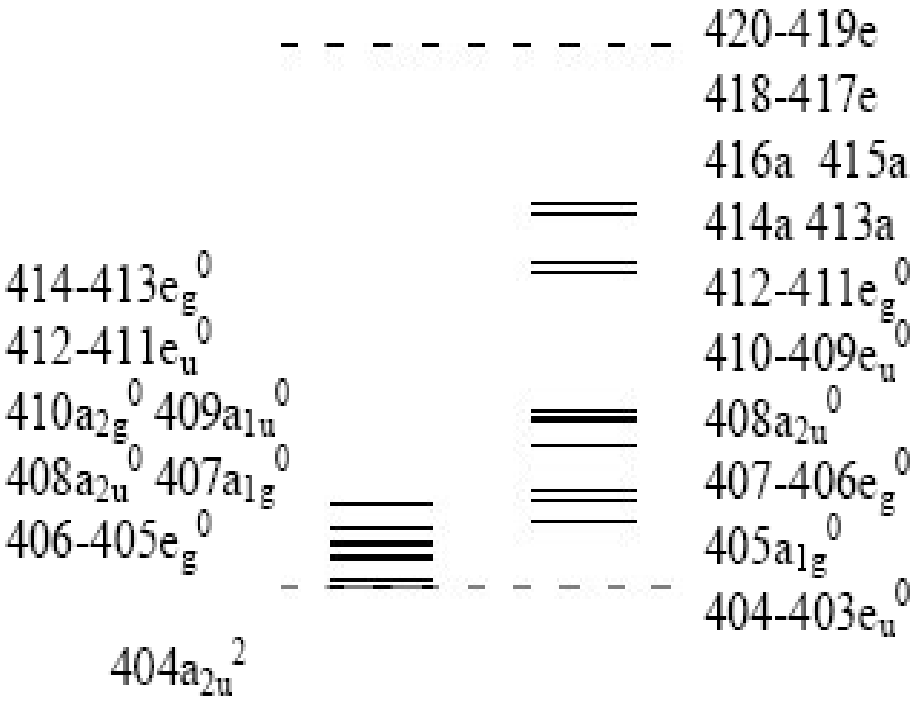

429a1 0
428-427e0
426-425e0
424a2
419a2
418-417e4
429a1 0
428-427e0
426-425e0
424a2
419a2
418-417e4

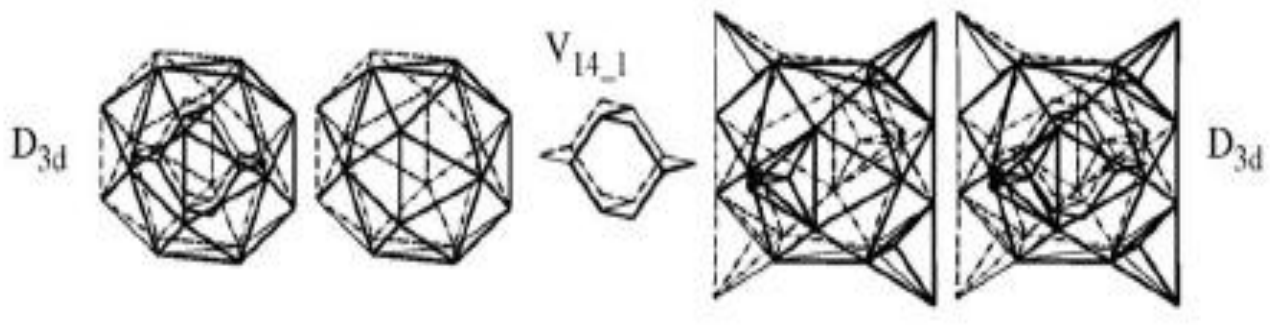

C3v
V4_2
C3v


V4_1
(10,6,6)
429b0
428a0
427a0
426b0
425b0
424a2
420b2
419a2
418b2
417a2
429b0
428a0
427a0
426b0
425b0
424a2
420b2
419a2
418b2
417a2
C2
V4_1
C2


V6_1
(12,6,9)
426a1g0
425-424eg0
423-422eu0
421a2u0
420-419eg4
418a2u2
416-415eg4
414-413eu4
412a1g
428a2u0
427a1g0
426a1g0
425-424eu0
423-422eg0
421a2u0
420-419eg4
417a2u2
416-415eg4
412a1g
D3d
V6_1
D3d

V_{14_1}
(20,10,18


420-419e
418-417e
416a 415a
414a 413a
412-411e_g^0
410-409e_u^0
408a_2u^0
407-406e_g^0
405a_1g^0
404-403e_u^0
414-413e_g^0
412-411e_u^0
410a_2g^0 409a_1u^0
408a_2u^0 407a_1g^0
406-405e_g^0
404a_2u^2


D3d
V14_1
D3d

V_1

SN	SNP	X	Y	Z	E_ε	$E_{\varepsilon V}$
1		0	0	2	7.2720	7.2720

V_2

SN	SNP	X	Y	Z	E_ε	$E_{\varepsilon V}$
1	1	1	-1	1	10.4547	5.2274

V_3

SN	SNP	X	Y	Z	E_ε	$E_{\varepsilon V}$
1	1	0	-2	0	13.8462	4.6154

V4

SN	SNP	X	Y	Z	Ef	EfV
1	1	-1	-3	1	16.4986	4.1246
2	1	2	0	0	17.1631	4.2908
3	1	1	-3	-1	17.2365	4.3091

V5

SN	SNP	X	Y	Z	Ef	EfV
1	1	-2	-2	2	18.9534	3.7907
2	1	-1	-1	-1	19.5606	3.9121
3	3	-1	1	1	19.8946	3.9789
4	3	-1	-3	1	19.9947	3.9989
5	1	0	-4	2	20.0330	4.0066
6	3	0	-4	-2	20.5336	4.1067
7	2	2	-2	2	20.5732	4.1146

Conclusions

-The adamantane like structures do not describe the vacancies in the diamond structure of carbon

-The tendency of local graphitization stabilizes the surface of diamond vacancy clusters.

-Each tetrahedron of graphitization produced an extra energy level in the gap.

-We described all possible vacancy clusters up to V_7.

-Using five extra integers we described the structure of each voids.

-There is a tendency for having graphite like vacancy surface