9.8. Space groups

考试：12月31日 (Tue) 14:00 – 16:00 数 102

9.8.1 Basic definitions.

Space group:

The point group and translation symmetry operations which carry the crystal into itself.

Recall: $\{R_\alpha | \tau\}$ (Seitz) where R_α denotes point group operations and τ translation, an element of $\mathbb{E}^3$.

$$\{R_\alpha | \tau\} \vec{r} = R_\alpha \cdot \vec{r} + \vec{\tau}$$

$$\{R_\beta | \vec{\tau}'\} \{R_\alpha | \vec{\tau}\} = \{R_\beta R_\alpha | R_\beta \vec{\tau} + \vec{\tau}'\}$$

$$\{R_\alpha | \tau\} \{R_\alpha | \tau\}^{-1} = \{E | 0\}$$

$$\Rightarrow \{R_\alpha | \tau\}^{-1} = \{R_\alpha^{-1} | -R_\alpha^{-1} \tau\}$$

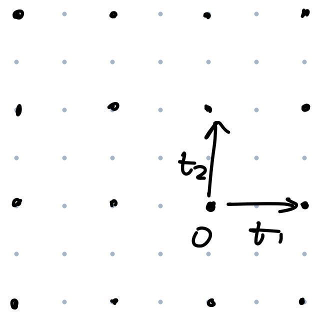
$$\{R_\alpha | \tau\} \{R_\alpha^{-1} | -R_\alpha^{-1} \tau\} = \{R_\alpha R_\alpha^{-1} | R_\alpha(-R_\alpha^{-1} \tau) + \tau\}$$

$$= \{E | 0\}$$

And the translational subgroup T is an ablelian normal subgroup.

$\{\alpha | \tau\} \{E | t\} \{\alpha | \tau\} = \cdots \{E | \alpha t\}$ another translation.

Bravais lattice. (in 2D)



$\forall T \in \Lambda$ → lattice

$T = n_1 \vec{t}_1 + n_2 \vec{t}_2$

Now the space group contains point group symmetry operations and translations. The two parts pose restrictions onto each other

(see 陶瑞宝 Chap 5; Bradley & Cracknell)

In 1D:

2D: 4 lattice systems, 5 Bravais lattices
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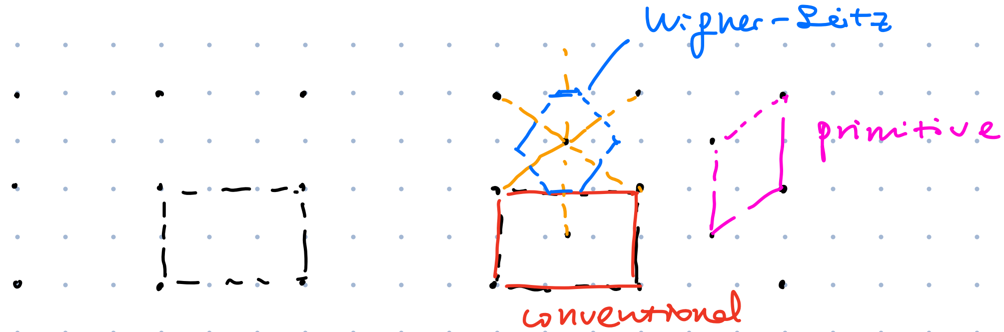
3D: 7 lattice systems. 14 Bravais lattices

see figures.

The parallelepiped formed by t_1, t_2, t_3 is the primitive unit cell. vs. conventional cell.



(op) (oc)

<u>Symmorphic space groups:</u>

$\forall \{R_\alpha | \tau\}$: $R_n \in \Lambda$: the Bravais lattice

$$\{R_\alpha | \tau\} = \{R_\alpha | R_n + \tau_\alpha\} = \{E | R_n\}\{R_\alpha | \tau_\alpha\}$$

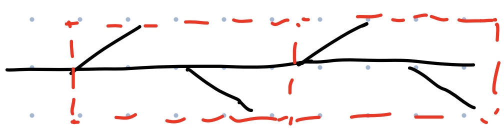
If for a space group with a proper choice of origin. $\forall \{R_\alpha | \tau\} \in SG$ can be decomposed such that $\tau_\alpha = 0$: <u>symmorphic</u> (73)

$(1 \to T \to G \to P \to 1)$ $P \cong G/T$

otherwise non-symmorphic (153)

$\Big\}$ <u>230</u>

(screw axis / glide plane)



Mirror + $\frac{1}{2}$ translation

As a dual of the real space lattice and unit cells, there are

Reciprocal lattices & Brillouin zones

reciprocal lattice vectors $\vec{g}_i$

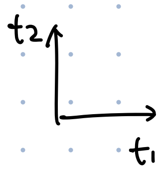
$$\vec{g}_i \cdot \vec{t}_j = 2\pi\delta_{ij}$$

$$\Rightarrow \vec{g}_i = \frac{2\pi(\vec{t}_j \times \vec{t}_k)}{t_1 \cdot (t_2 \times t_3)} \qquad (i, j, k : \text{cyclic perm. of } 123)$$

A reciprocal lattice vector

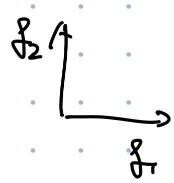
$$\vec{G}_n = n_1 \vec{g}_1 + n_2 \vec{g}_2 + n_3 \vec{g}_3$$

Brillouin zone: unit cell in the reciprocal space.

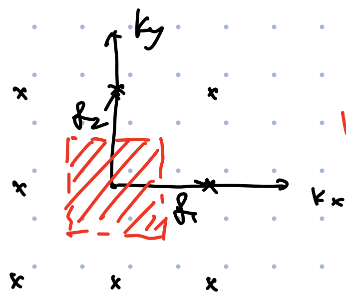


$$\vec{g}_1 = \frac{2\pi}{a}(1, 0)$$

$$\vec{g}_2 = \frac{2\pi}{a}(0, 1)$$



First Brillouin zone:



wigner-seitz

What is special about 1st BZ.? We need to talk about the rep of T.

Recall T is an abelian normal subgroup. $T \cong \mathbb{Z}^d$. $\underbrace{(\mathbb{Z}\oplus\mathbb{Z}\oplus\mathbb{Z}\cdots)}_{d}$

all its irreps are 1D.. The characters:

$$\chi_\phi(1) = e^{-i2\pi\phi} \qquad \phi \in [0, 1) \qquad \chi_\phi(m) = e^{-i2\pi m\phi}$$

Group structure requires $\chi(m+n) = \chi(m)\chi(n)$ ✓

In physics we take periodic boundary conditions

$\mathbb{Z} \to \mathbb{Z}_N$

$\chi_k(1) = e^{-ik}$ $\quad e^{-ikN} = 1 \quad k = \frac{2\pi}{N}$

$\Rightarrow \chi_k(\vec{\tau}) = e^{-i\vec{k}\cdot\vec{\tau}} \qquad \left(e^{-i\vec{k}\cdot(N_1\vec{t}_1 + N_2\vec{t}_2 + N_3\vec{t}_3)} = 1 \right)$

$\vec{k}\cdot\vec{t}_i = \frac{2\pi}{N_i}$

If $\vec{k} - \vec{k}' = G_m = (m_1\vec{g}_1 + m_2\vec{g}_2 + m_3\vec{g}_3)$, then

$\chi_{\vec{k}}(\vec{\tau}) = \chi_{\vec{k}'}(\vec{\tau})$

$\Rightarrow$ 1st BZ contains all distinct irreps of the translational subgroup. $\vec{k}'$ outside of 1st BZ labels the same irrep as some $\vec{k} = \vec{k}' - \vec{G}_m$ inside the 1st BZ.

$\boxed{\text{Bloch theorem}}$: the wave functions transform as <u>irreps</u> of T. the $\forall \hat{\tau} \in \Lambda$

$\psi(\vec{r} - \vec{\tau}) \equiv \hat{\tau}\cdot\psi(\vec{r}) = e^{-i\vec{k}\cdot\vec{\tau}}\,\psi(\vec{r})$

solved by $\quad \psi_k(\vec{r}) = u_k(\vec{r})\cdot e^{i\vec{k}\vec{r}}$ (Bloch waves) with

$u_k(\vec{r}) = u_k(\vec{r} + \vec{\tau}) \qquad \forall \vec{\tau} \in \Lambda$

They are eigenstates of the discrete translation operators. (and a Hamiltonain on the lattice)

Taking the Bloch waves $\{\psi^a_{\vec{k}}\}$ as a basis

$$\langle \psi^a_{\vec{k}} | H | \psi^b_{\vec{k}'} \rangle = H^{ab}_{\vec{k}} \delta_{kk'}$$

a, b labels states in the degeneracy space in the isotypic decomposition of the Hilbert space.

Different $\vec{k}$ (or irreps) do not couple.

→ <u>Band structure.</u>

For a given material, the Bloch states can be constructed using relevant "atomic orbitals" $\phi_a(r-R_n)$ (Wannier)

$$\psi^a_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{R_n \in T} \phi^a(\vec{r} - \vec{r}_a - \vec{R}_n) e^{i\vec{k}\cdot\vec{R}_n}$$

$$\left(\text{in fact } \psi^a_{\vec{k}}(r) = \frac{1}{\sqrt{N}} \sum_n \sum_{a'} U^{(k)}_{aa'} \phi_{a'}(r - r_{a'} - R_n) e^{ikR_n} \right)$$

to satisfy orthogonality etc.

Now we consider the <u>point group</u> part. (rotations etc.)

3.8.2 k-stars and little groups

Define the <u>little group</u> of $\vec{k}$, $G_{\vec{k}}$

$$\forall g \in G_{\vec{k}},\quad g\circ\vec{k} \equiv \vec{k} \quad \text{i.e.} \quad g\cdot\vec{k} = \vec{k} + \vec{G}_m ,$$

and $T \subset G_k \subset G$.

group structure:

① $\forall g_1, g_2 \in G_{\vec{k}}$: $g_1\cdot g_2\circ\vec{k} = g_1\circ(k + G_{m_2}) = \vec{k} + (\vec{G}_{m_1} + g_1\circ\vec{G}_{m_2})$

$$= \vec{k} + \vec{G}_{m_3}$$

② $g\circ k = k + G_m \Rightarrow k = g^{-1}\circ k + g^{-1}\circ G_m = g^{-1}\cdot k + G_{m'}$

$$\Rightarrow g^{-1} \in G_{\vec{k}}$$

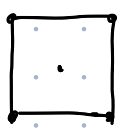
A related concept. <u>little co-group</u> $\overline{G_{\vec{k}}} = G_{\vec{k}}/T$

factors out the normal translation group T.

and $\overline{G_k} \subset P = \{\alpha : \{\alpha | t\} \in G\}$.

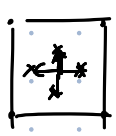
There are $\dfrac{|P|}{|\overline{G_k}|}$ k-vectors in the $\boxed{\text{k-star}}$: $\{gk \mid g \in G\}$

<u>Examples</u>. BZ of a square lattice.



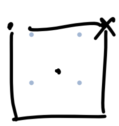
$k=0$: G_k = full space group G.

$\overline{G_k}$ full D_4



$k^* = \{\pm k(1,0)\ \pm k(0,1)\}$

G_k does not include C_4, C_2, etc.



$k^* = \{k\}$ $G_k = G$.

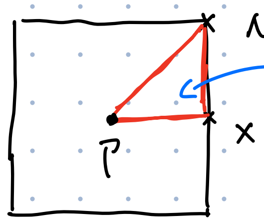
"point of symmetry": $\exists$ a neighborhood N. s.t.

no points in N except $\vec{k}$ has the symmetry

group $G_{\vec{k}}$

~ "Point of the highest sym. in the neighborhood.

others are "general points"



basic domain $\Omega = \frac{8\pi^3}{V} \cdot \frac{1}{|G_\Gamma|}$

Refs: Bilbao database

international tables for crystallography

line/plane of symmetry: line / plane in N passing through $\vec{k}$

all points have the same symmetry

9.8.3 Action of SG operations on Bloch functions

By convention, the group action on functions has the form

$$\{\alpha|\vec{\tau}\}\psi(\vec{r}) = \psi(\alpha^{-1}(\vec{r}-\vec{\tau}))$$

which means

$$\{\alpha|\vec{\tau}\}\, e^{i\vec{k}\cdot\vec{r}} = \exp(i\vec{k}.\alpha^{-1}(\vec{r}-\vec{\tau}))$$
$$= \exp(i(\alpha\vec{k}).(\vec{r}-\vec{\tau}))$$

$$k\cdot\alpha\cdot r = \sum_{ij} k_i \alpha_{ij} r_j \overset{\alpha\in O(3)}{=} \sum_{ij} \alpha^{-1}_{ji} k_i r_j = r.(\alpha^{-1}k)$$

Then

$$\{\alpha|\vec{\tau}\}\psi_k(r) = \exp(i\alpha\vec{k}.(\vec{r}-\vec{\tau}))\, u_{\alpha k}(\vec{r}-\vec{\tau})$$
$$= \psi_{\alpha k}(\vec{r}-\vec{\tau})$$

(define $u_{\alpha k}(\vec{r}-\vec{\tau}) = u_k(\alpha^{-1}(r-\tau)) = \{\alpha|\tau\}u_k(r)$)

and $\{\alpha|\tau\}\{\beta|\tau'\}\psi_k(r) = \psi_{\alpha\beta k}(r-\tau-\alpha\tau')$

$\{\alpha|\tau\}$ transforms a Bloch function $\psi_k(r)$

to another Bloch function $\psi_{\alpha k}(r-\tau)$
$(= e^{-i\alpha\vec{k}.\vec{\tau}}(r))$

$\rightarrow \{\psi_k\}$ is a representation space for space groups.

9.8.4. Band compatibility relations

Suppose a k point with little group G_k.

and a neighboring point $k+\delta k$ with $G_{k+\delta k}$

① If both are general points. $G_{\vec{k}}$ has no point group part. ($G_{\vec{k}} = G_{\vec{k}+\delta\vec{k}} = T$)

Then all irreps are 1D. and

$$\lim_{\delta k \to 0} \chi_{k+\delta k}(\{E|R_n\}) = \chi_k(\{E|R_n\})$$

satisfies continuity. no compatibility issue.

② k a high symmetry point.

① $G_{k+\delta k} \cong G_k$

② $G_{k+\delta k} \subset G_k$

For case ①. all irreps of G_k and $G_{k+\delta}$ is one-to-one.

$\lim_{\delta k \to 0} \Gamma^{k+\delta k} = \Gamma^k$, no problem

② $k+\delta k$ moves away from the high symmetry line / plane.

irreps of G_k becomes reducible at $k+\delta k$

(similar to the case of crystal field

discussed previously). Then we need to know what irreps of $G_{k+\delta k}$ occur in the irreps of G_k restricted to $G_{k+\delta}$.

$$\Gamma^{k,i}(g) \cong \bigoplus a_{ij}^{k,k+\delta k} \Gamma^{k+\delta k, j}(g)$$

We need to know the characters:

The Bloch waves

$$\psi^{A}_{a;\vec{k}}(\vec{r}) = \sum_{R_n} \phi_a(\vec{r} - \vec{r}_A - R_n)\, e^{i\vec{k}(\vec{R}_n + \vec{r}_A)}$$

sublattice

orbital

up to translation

The character of $g \in G_{\vec{k}}$ = $\psi^{A}_{a;k}(\vec{r})$ unchanged by g

$\times$ phase by T

$\alpha k = k + G_m$

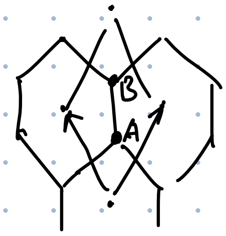
$$\chi(\{\alpha|\tau\}) = \underbrace{\{\alpha|\tau\}(\phi_a(\vec{r} - \vec{r}_A - R_n))}\, e^{i(\alpha k)\cdot(\vec{R}_n + \vec{r}_A - \vec{\tau})}$$

$$= e^{-ik\tau} \sum_{A} \underline{\delta_{\{\alpha|\tau\}r_A, r_A}}\; \underline{\chi_a(\alpha)}\; e^{i\vec{G}_m\cdot\vec{r}_A}$$

character of orb.

if the orbital is moved back

As an example. we consider the band structure of graphene.

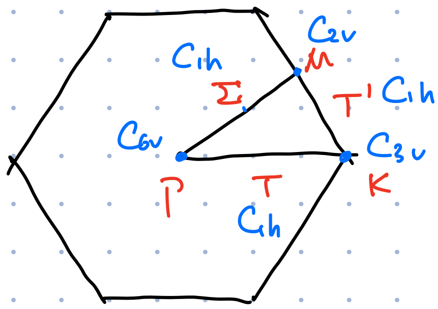


Two sublattices

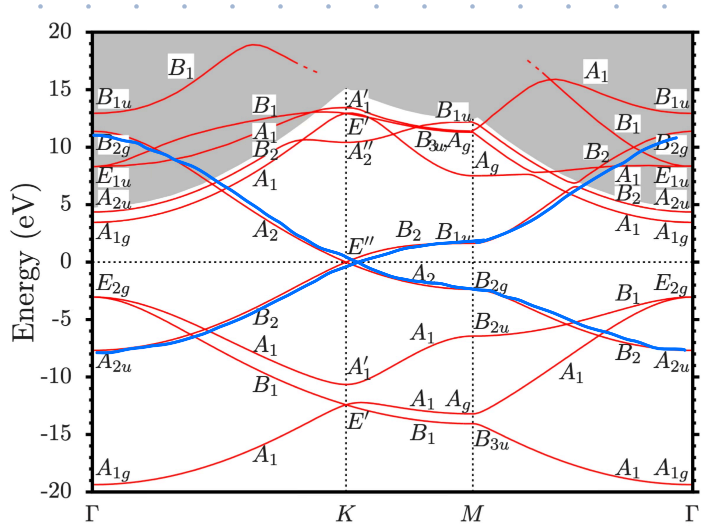
$p6mm = T \rtimes C_{6v}$ (in fact shoud be D_{6h} in 3D, by includiny σ_h)

$\{\alpha | \tau\} = \{E | R_n\}\{\alpha | 0\}$ $\qquad D_{6h} = C_{6v} \times \underset{\{1, \sigma_h\}}{C_{1h}}$

The Brillouin zone is



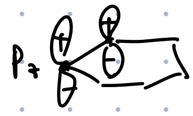
Its band structure :



$C : 2s^2 2p^2$

And we only consider p_z orbitals (blue bands)

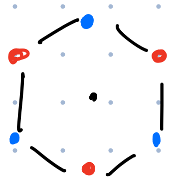
(odd under σ_h). others s. p_x. p_y are even under σ_h.



$p_z \xrightarrow{C_{6v}/D_{6h}} A_1/A_{1g}$ The orbital character is 1

characters:

Γ: C_{6v}. $\chi_P(g) = e^{-ik\tau}\, \underline{\delta_{\{\alpha|\tau\}r_A, r_A}}\, \underline{\chi_a(\alpha)}$



E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{d_i}	σ_{v_i}
2	0	2	0	2	0

C_{6v} C_{1h}

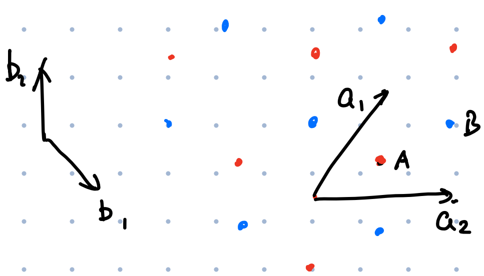
$T_P = A_1 + B_2 = \Gamma_1 + \Gamma_3$ $(A_1 + B_2) \times A''$

$= \underline{A_{2u} + B_{2g}}$

K: C_{3v}

E	$C_3^{\pm}$	σ_{v_i}
2	$\omega + \bar{\omega}$ $= -1$	0

$\omega = i\frac{2\pi}{3}$



$(e^{iG_m \cdot r_A})$

$C_{3v} \otimes C_s = D_{3h}$

$T_K = E = \Gamma_3$ $\underline{E \times A'' = E''}$

M: C_{2v}.

E	C_2	σ_{d_2}	σ_{v_2}
2	0	2	0

$T_M = A + B_2 = \Gamma_1 + \Gamma_2$ $(B_{1u} + B_{2g})$

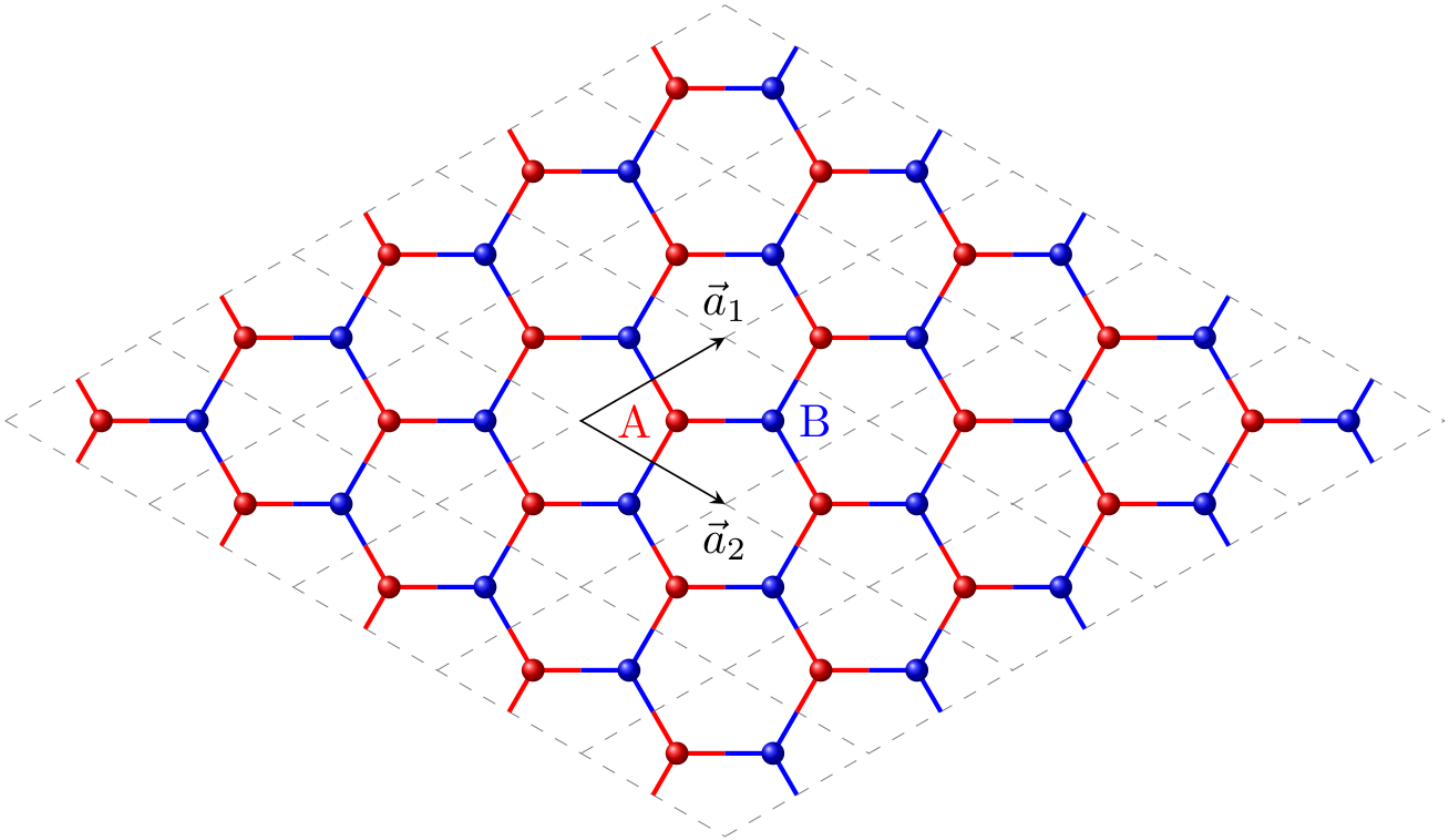
$\Gamma \to T \to K$ only need to look at the

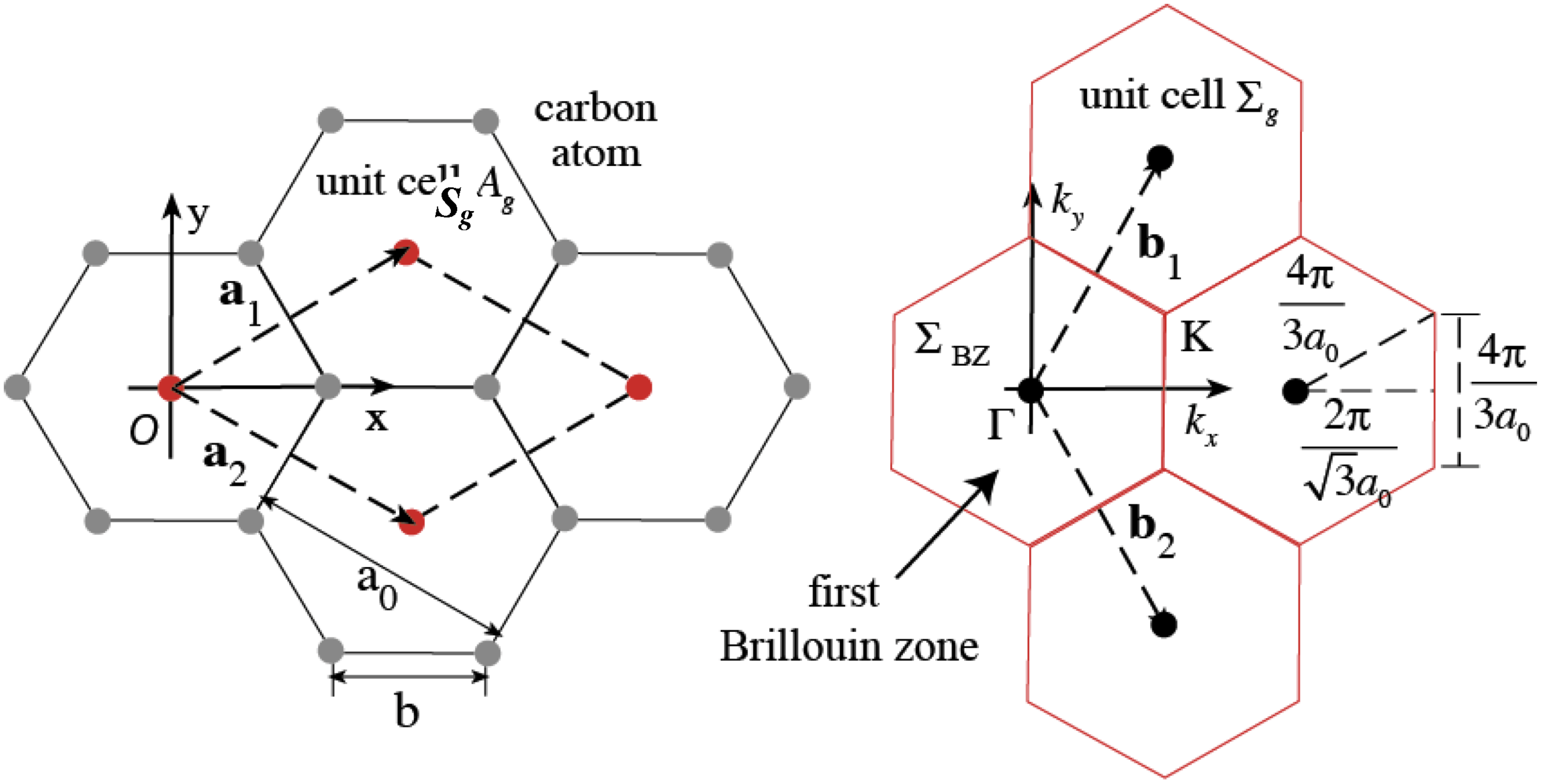
C_{6v} C_{1h} C_{3v} character of E & σ_h

	E	σ_h	
$\underline{C_{6v}}$	1	1	$A_1 = \Gamma_1$
	1	-1	$B_2 = \Gamma_3$
C_{1h}	1	1	$A' = \Gamma_1$
	1	-1	$A'' = \Gamma_2$

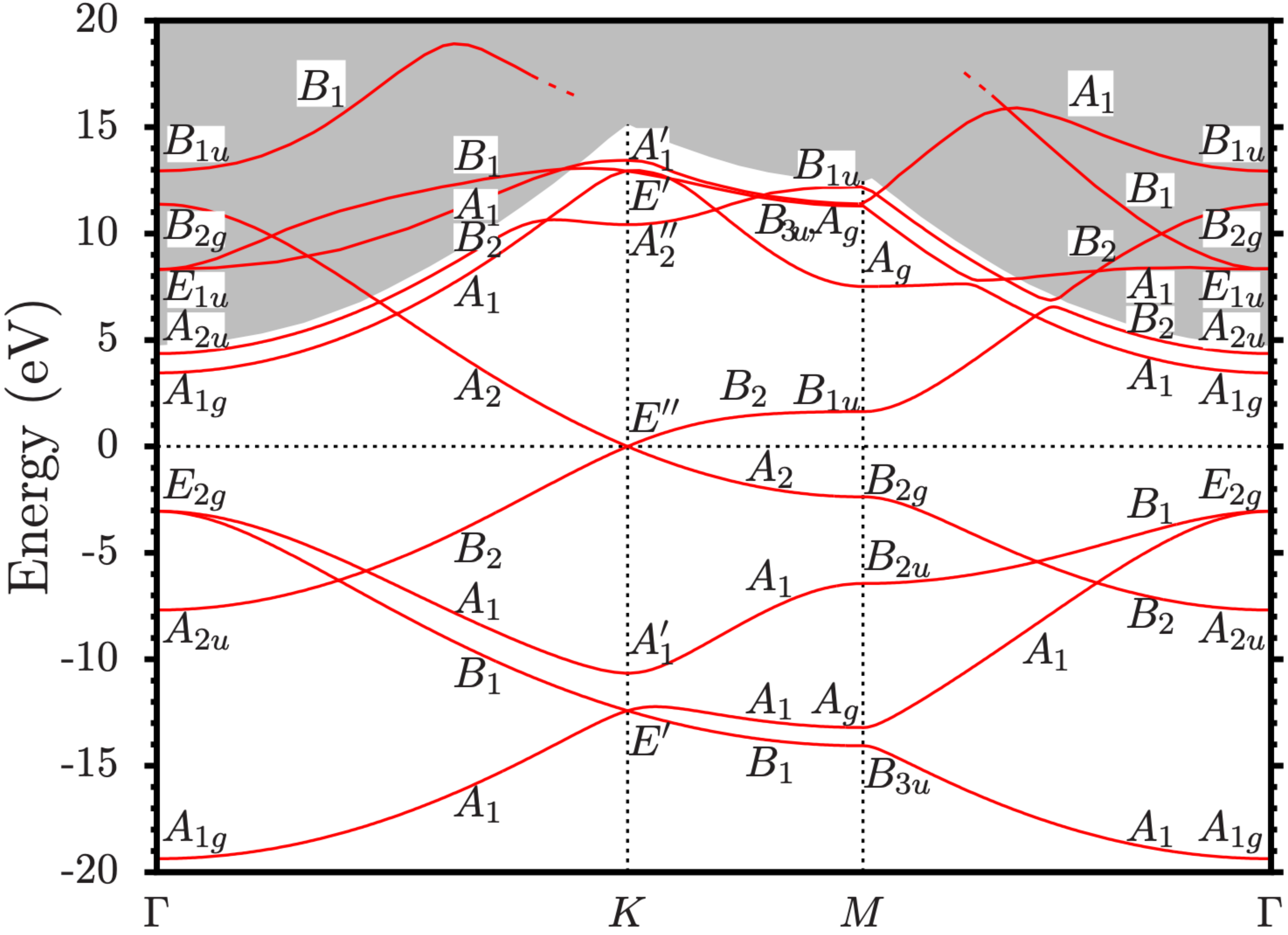
$\Gamma_1 \to T_1$

$\Gamma_3 \to T_2$


$\vec{a}_1$
A
B
$\vec{a}_2$



(a) Bravais lattice (b) Reciprocal lattice



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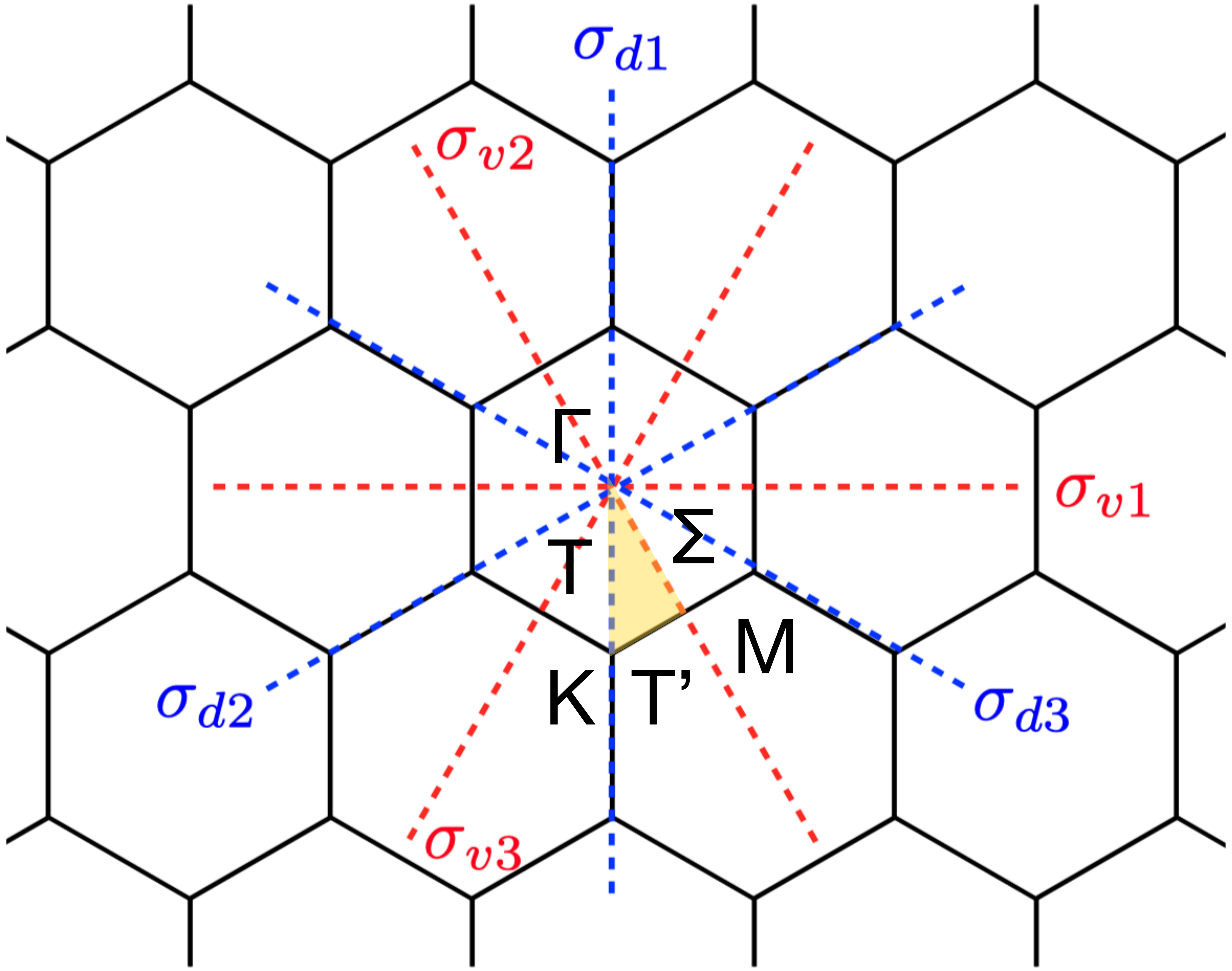

σ_{d1}
σ_{v2}
Γ
σ_{v1}
T
Σ
M
K
T'
σ_{d2}
σ_{d3}
σ_{v3}

$622\ (D_6)$		$6mm\ (C_{6v})$		$\bar{6}2m\ (D_{3h})$		E E E	C_2 C_2 σ_h	$C_3^{\pm}$ $C_3^{\pm}$ $C_3^{\pm}$	$C_6^{\pm}$ $C_6^{\pm}$ $S_3^{\pm}$	C'_{2i} σ_{di} C'_{2i}	C''_{2i} σ_{vi} σ_{vi}
A_1	Γ_1	A_1	Γ_1	A'_1	Γ_1	1	1	1	1	1	1
A_2	Γ_2	A_2	Γ_2	A'_2	Γ_2	1	1	1	1	−1	−1
B_1	Γ_3	B_2	Γ_3	A''_1	Γ_3	1	−1	1	−1	1	−1
B_2	Γ_4	B_1	Γ_4	A''_2	Γ_4	1	−1	1	−1	−1	1
E_2	Γ_6	E_2	Γ_6	E'	Γ_6	2	2	−1	−1	0	0
E_1	Γ_5	E_1	Γ_5	E''	Γ_5	2	−2	−1	1	0	0

$$6/mmm = 622 \otimes \bar{1}\ (D_{6h} = D_6 \otimes C_i)$$

$32\ (D_3)$				E	$C_3^{\pm}$	C'_{2i}
		$3m\ (C_{3v})$		E	$C_3^{\pm}$	σ_{di}
A_1	Γ_1	A_1	Γ_1	1	1	1
A_2	Γ_2	A_2	Γ_2	1	1	-1
E	Γ_3	E	Γ_3	2	-1	0

$\bar{3}m = 32 \otimes \bar{1}\ (D_{3d} = D_3 \otimes C_i)$

$mm2\ (C_{2v})$				E	C_{2z}	σ_y	σ_x
		$222\ (D_2)$		E	C_{2z}	C_{2y}	C_{2x}
A_1	Γ_1	A	Γ_1	1	1	1	1
B_2	Γ_4	B_3	Γ_4	1	-1	-1	1
A_2	Γ_3	B_1	Γ_3	1	1	-1	-1
B_1	Γ_2	B_2	Γ_2	1	-1	1	-1

$mmm = 222 \otimes \bar{1}\ (D_{2h} = D_2 \otimes C_i)$