

応用:ナノ複合カーボン固体

sp₂-sp₃ナノ複合カーボン固体のナノドメイン解析

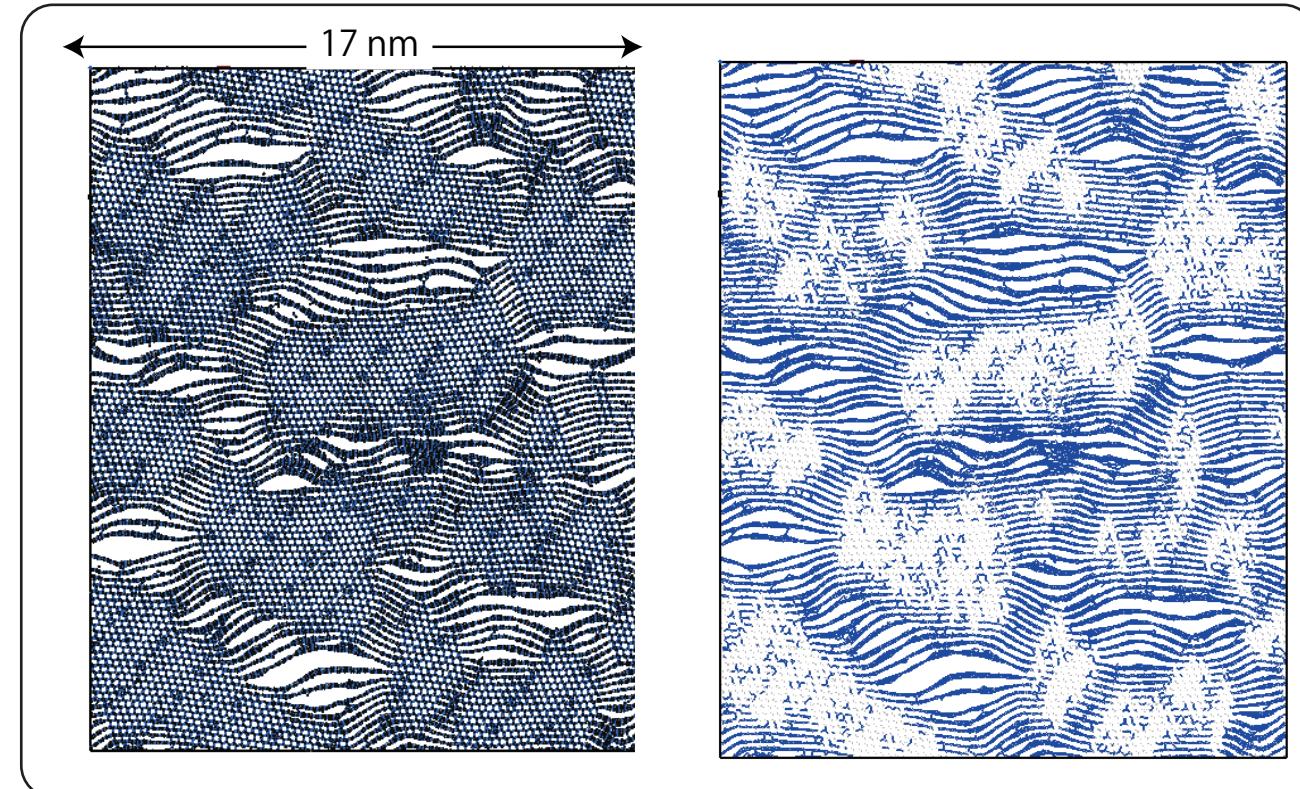
1. 背景: ナノ多結晶ダイアモンド

2. 理論

波動関数とグリーン関数

COHP解析: 量子力学的結合解析理論

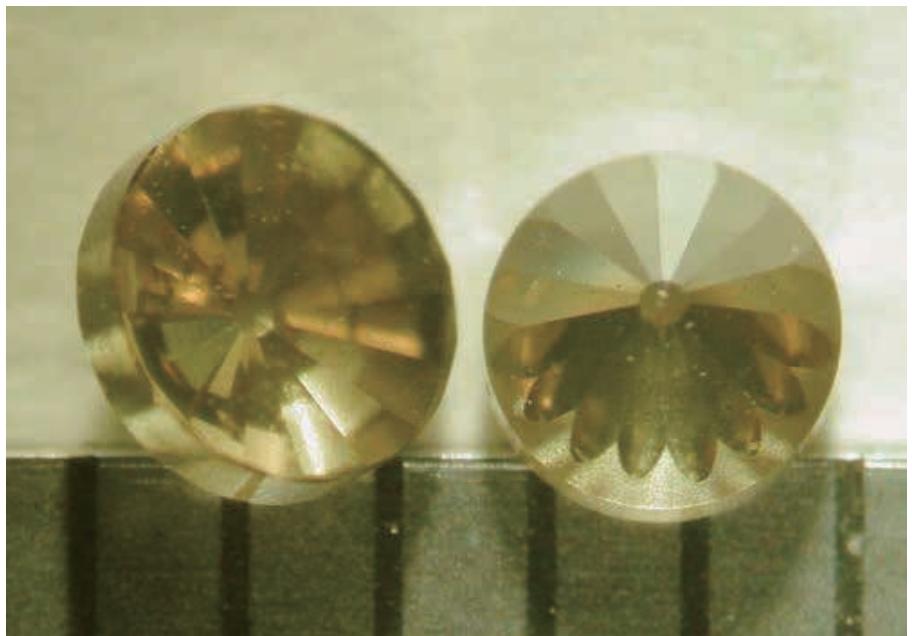
3. sp₂-sp₃ナノ複合カーボン固体のナノドメイン解析



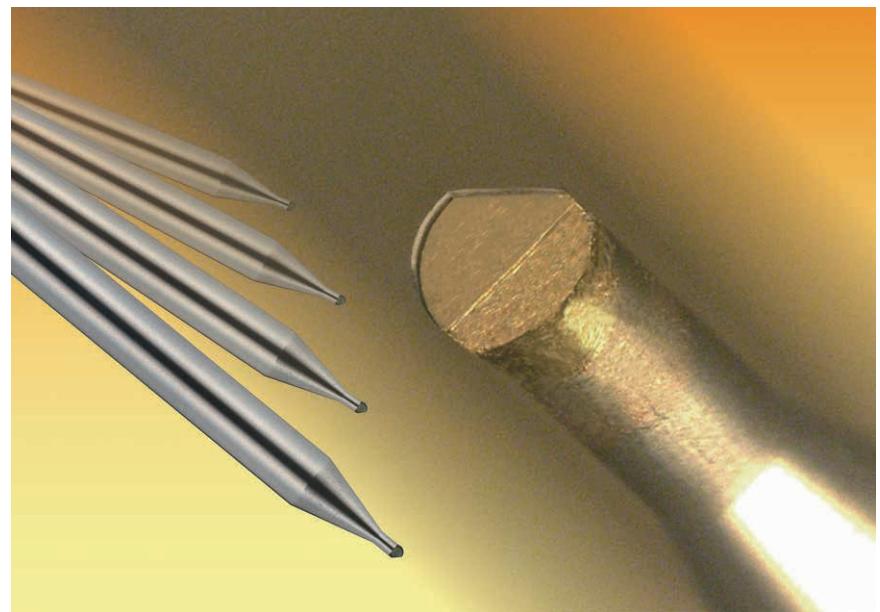
ナノ多結晶ダイヤモンド(NPD)

→「(天然)ダイヤより硬い、(人工)ダイヤ」

超高硬度ナノダイヤモンドの応用
(2006年11月愛媛大学)



「ナノ多結晶ダイヤモンド
『スミダイヤバインダレス』
切削工具を発売」
(2012年1月16日 住友電工)

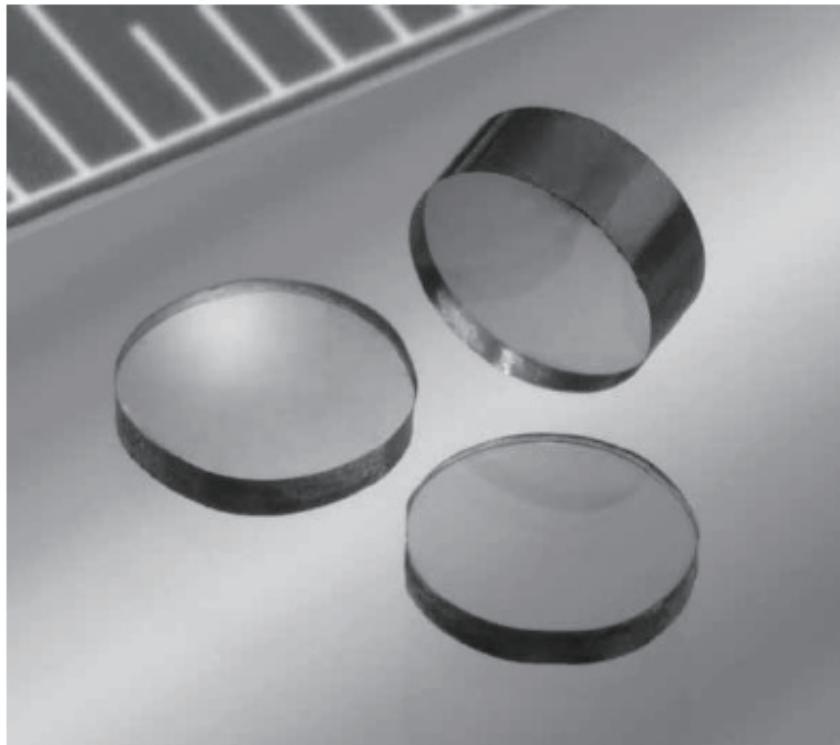


入船(愛媛大)らによる

T. Irifune, et al., Nature 421, 599 (2003)

Background: Nano-polycrystalline diamond(NPD)

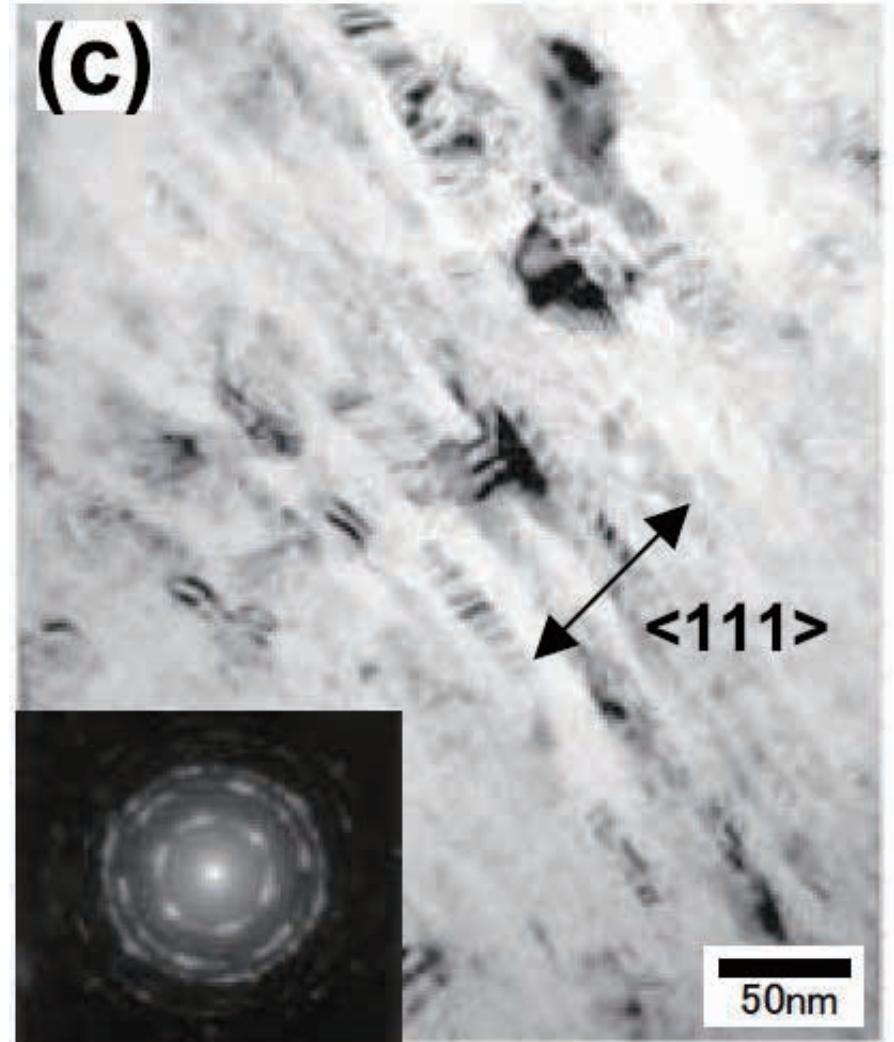
Ultra-hard material
(\rightarrow industrial application)



[1]

T. Irifune, et al., Nature 421, 599-600 (2003)

Characteristic nanoscale lamella structure



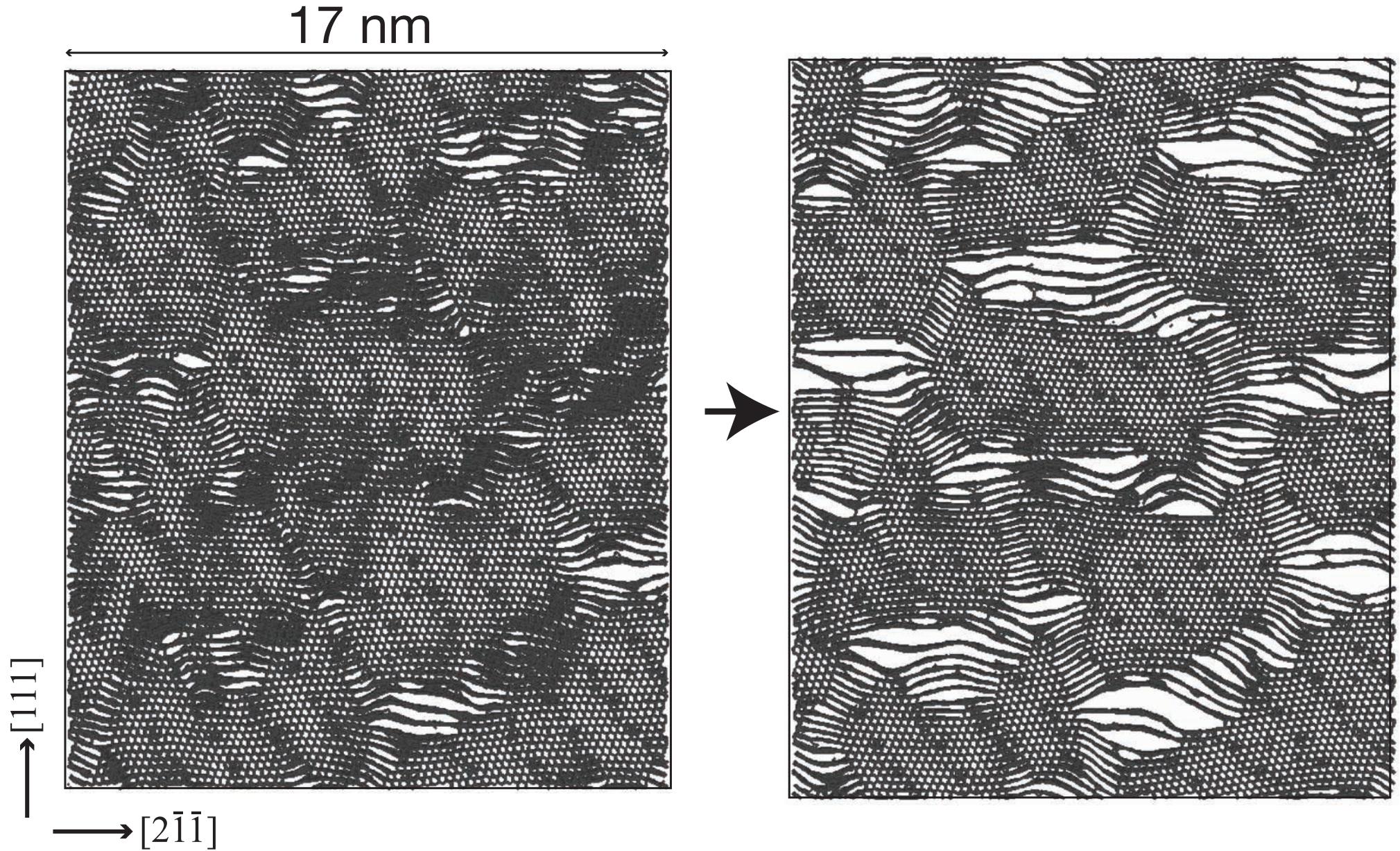
[2]

[1] 角谷均・入船徹男, SEI テクニカルレビュー172、
82-88頁, 住友電工 (2008)

[2] 角谷均・入船徹男, 高圧力の科学と技術16, 207 (2006)

Formation of an sp² and sp³ nano-domain composite

The simulation result appears in the research of NPD



Basics: 波動関数とグリーン関数

以下では簡単のため、直交行列($S=I$)の場合で説明。非直交行列の場合は、後述論文を参照。

注:ベクトルの表記: $\mathbf{f} \equiv (f_1, f_2, \dots, f_M)^t$

Original (eigen-value) equation: $H\phi_k = \varepsilon_k \phi_k$ (1)

Green function:

$$G(z) \equiv (zI - H)^{-1} \quad (2)$$

$$= \sum_k \frac{\phi_k \phi_k^t}{z - \varepsilon_k} \quad (3)$$

注:クリロフ部分空間理論によるオーダーN法では、固有ベクトル計算せずに、
グリーン関数を直接求めている。



COHP analysis : Local bond-energy spectrum

COHP = Crystal Orbital Hamiltonian Populations*

*Dronskowski and Blochl: J. Phys. Chem. 97, 8617 (1993).

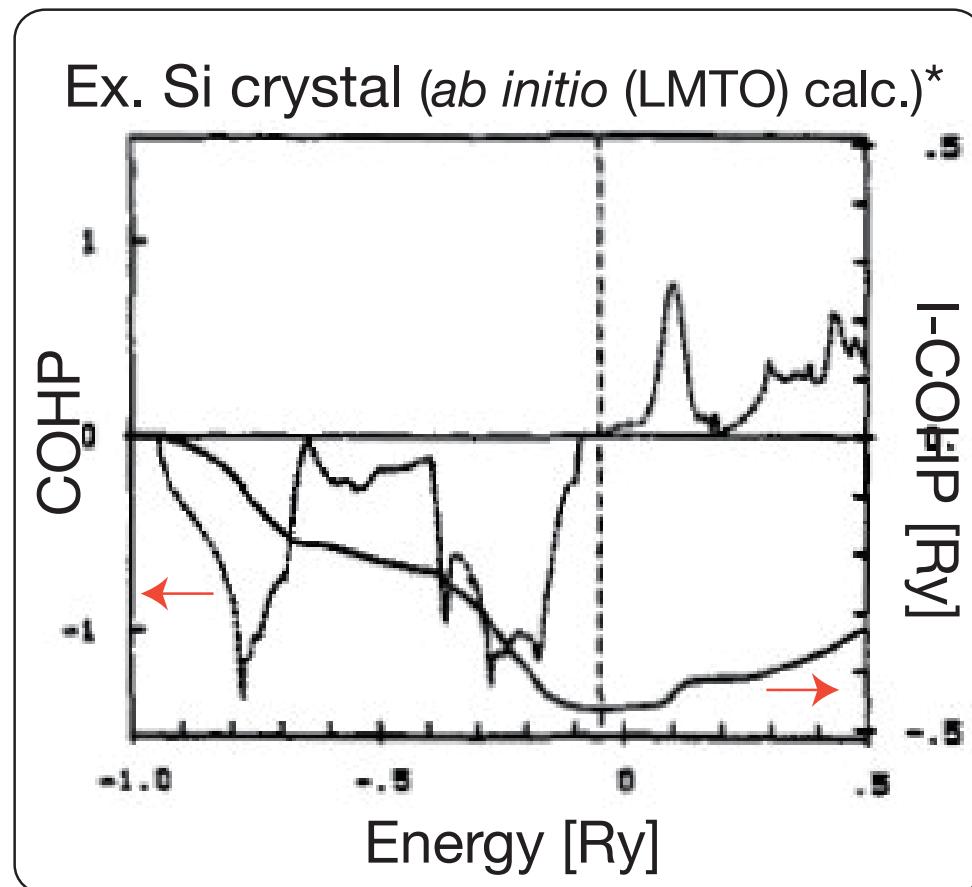
(a) Def. from the off-diagonal elements of the Green's fn.

$$C_{IJ}(\varepsilon) = -\frac{1}{\pi} \sum_{\alpha\beta} \text{Im} [G_{I\alpha;J\beta}(\varepsilon)] H_{J\beta;I\alpha}$$

I, J : atom , α, β : orbital

cf. Def. of LDOS; from diagonal elements.

$$D_I(\varepsilon) = -\frac{1}{\pi} \sum_{\alpha} \text{Im} [G_{I\alpha;I\alpha}(\varepsilon)]$$



COHP analysis : Local bond-energy spectrum

COHP = Crystal Orbital Hamiltonian Populations*

*Dronskowski and Blochl: J. Phys. Chem. 97, 8617 (1993).

(b) Sign of COHP

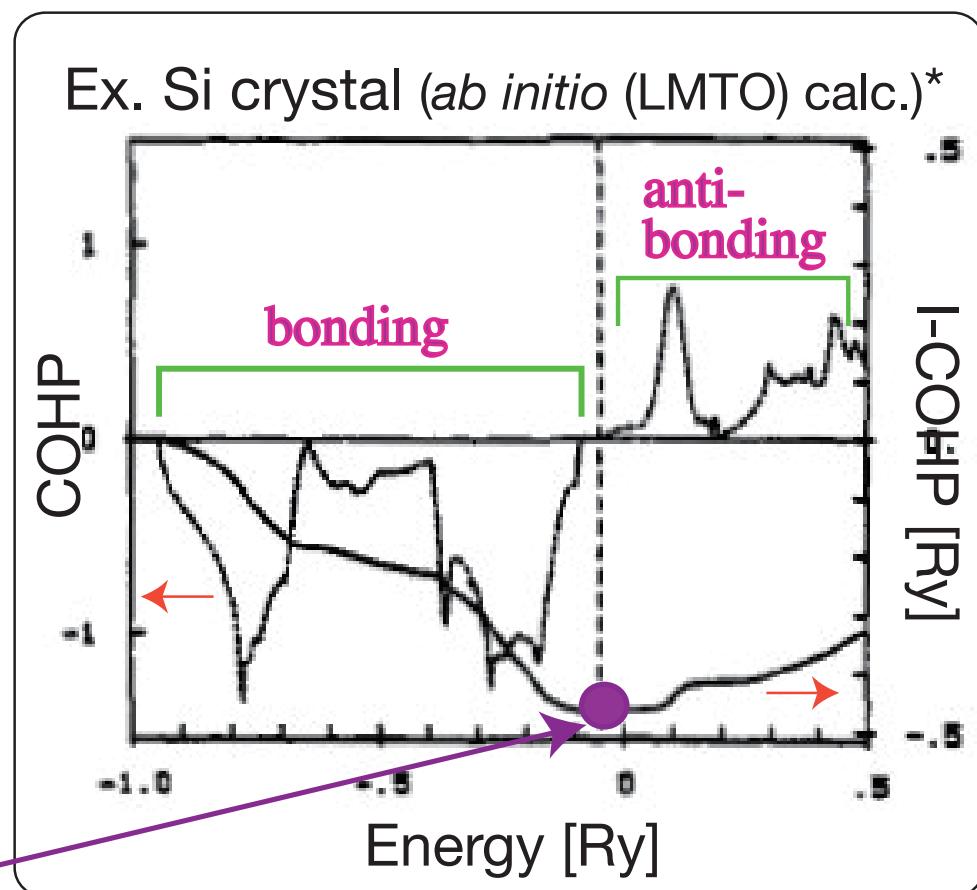
$C_{IJ}(\varepsilon) < 0$: Energy gain by bonding

$C_{IJ}(\varepsilon) > 0$: Energy loss by anti-bonding

(c) The sum of integrated COHP (ICOHP) gives the elec. struc. energy.

$$\begin{aligned} E_{\text{elec}} &\equiv \sum_i f_i \varepsilon_i \\ &= \sum_{IJ} \int^{\varepsilon_F} C_{IJ}(\varepsilon) d\varepsilon \end{aligned}$$

ICOHP at Fermi level



COHP analysis : Local bond-energy spectrum

COHP = Crystal Orbital Hamiltonian Populations*

*Dronskowski and Blochl: J. Phys. Chem. 97, 8617 (1993).

Note 1: Applicable to any material (metals and insulators)

Example of a metallic system:

Y Ishii and T. Fujiwara, J. Non-Cry. Sol. 334&335, (2004)

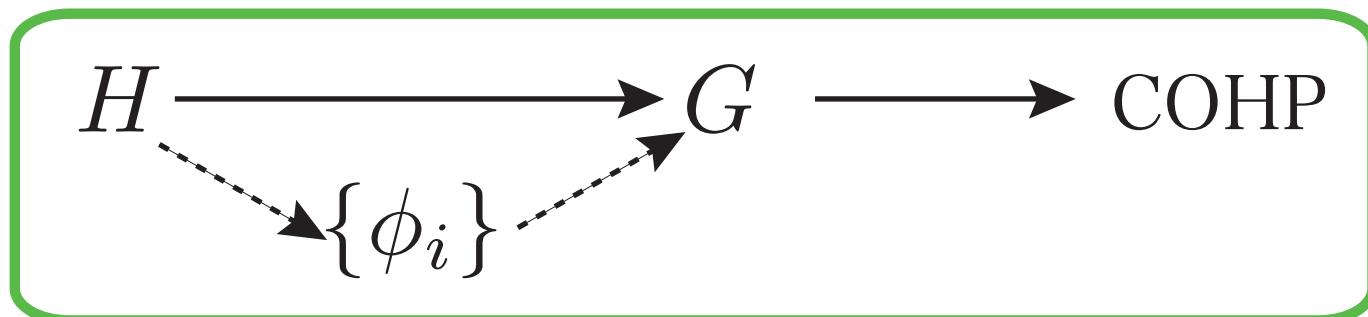
Cd-M (M=Yb and Ca) Quasi Crystals

→ covalent bonded clusters in metallic system

Note 2: Applicable to the order-N method with the Green's function

Takayama, Hoshi and Fujiwara, JPSJ 73, 1519 (2004);

Takayama, Hoshi, Sogabe, Zhang, Fujiwara, PRB73, 165108 (2006)



σ - and π -COHP: a theoretical extention of COHP

→ interaction-decomposed components

$$C_{IJ}(\varepsilon) = C_{IJ}^{(\sigma)}(\varepsilon) + C_{IJ}^{(\pi)}(\varepsilon)$$

σCOHP πCOHP

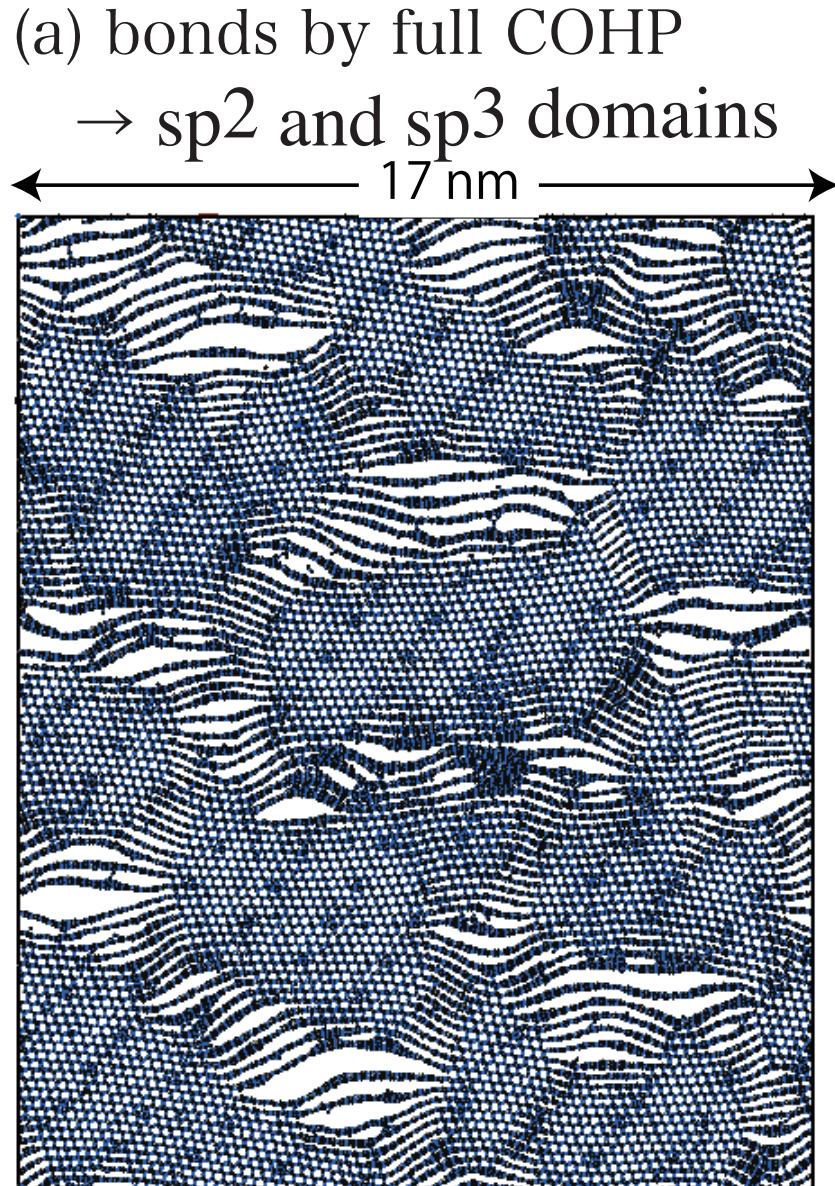
Derivation

$$H_{I\alpha;J\beta} = H_{I\alpha;J\beta}^{(\sigma)} + H_{I\alpha;J\beta}^{(\pi)}$$

$$\begin{aligned} C_{IJ}(\varepsilon) &\equiv \frac{-1}{\pi} \sum_{\alpha\beta} \text{Im} [G_{I\alpha;J\beta}(\varepsilon)] H_{J\beta;I\alpha} \\ &= \frac{-1}{\pi} \sum_{\alpha\beta} \text{Im} [G_{I\alpha;J\beta}(\varepsilon)] H_{J\beta;I\alpha}^{(\sigma)} \quad \sigma\text{COHP} \\ &\quad + \frac{-1}{\pi} \sum_{\alpha\beta} \text{Im} [G_{I\alpha;J\beta}(\varepsilon)] H_{J\beta;I\alpha}^{(\pi)} \quad \pi\text{COHP} \end{aligned}$$

π COHP analysis for the sp₂ and sp₃ nano-domain composite

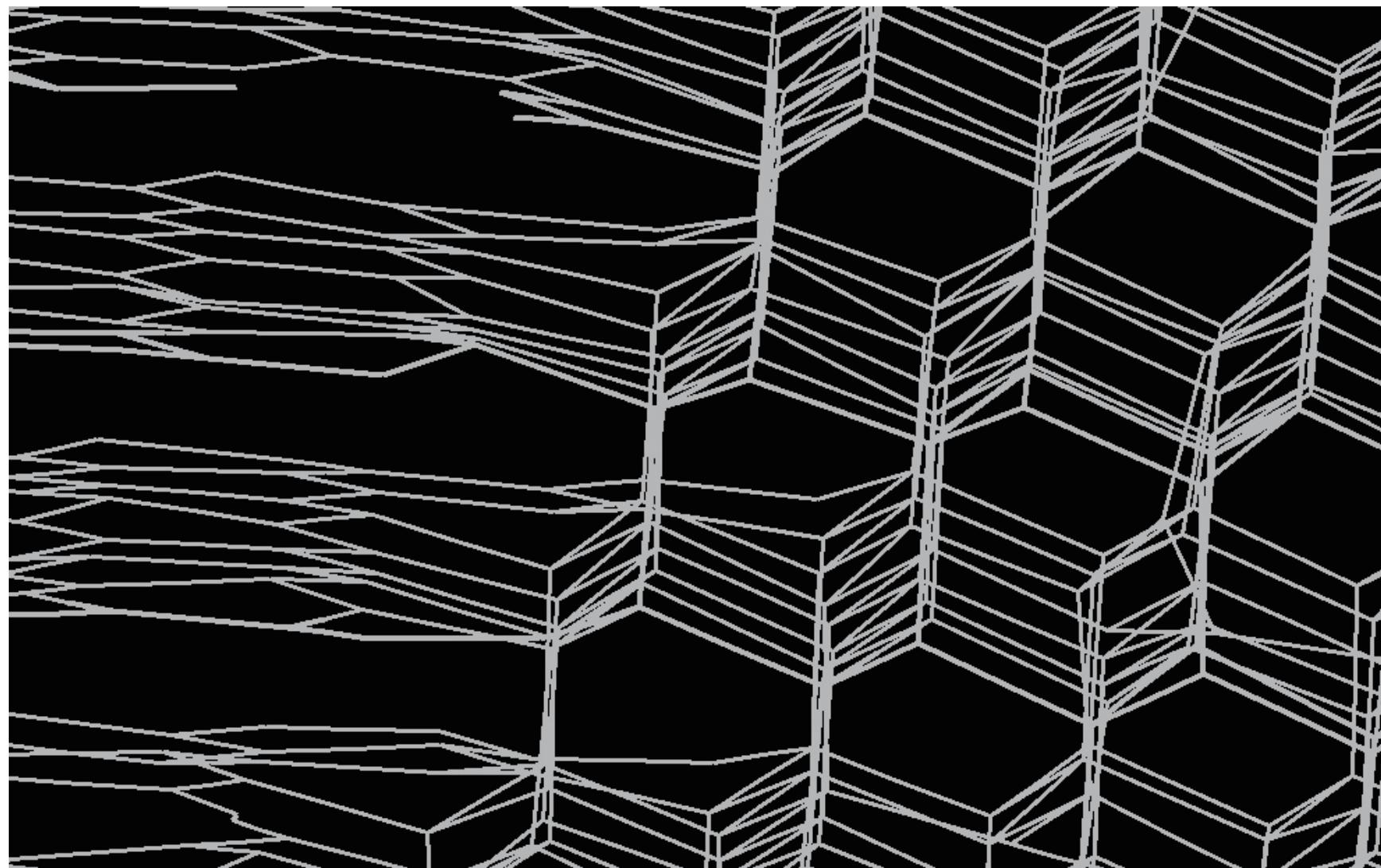
by our original visualization tool ‘VisBAR’



(b) bonds by π COHP
→ sp₂ domain only



Close-up of a boundary between sp2-like and sp3-like domains



Summary

(1) COHP (= Crystal Orbital Hamiltonian Populations)

→ Local bond-energy spectrum with rigorous mathematical foundation

$$C_{IJ}(\varepsilon) = -\frac{1}{\pi} \sum_{\alpha\beta} \text{Im} [G_{I\alpha;J\beta}(\varepsilon)] H_{J\beta;I\alpha} \quad I, J : \text{atom , } \alpha, \beta : \text{orbital}$$

(2) σ - and π -COHP → analysis of π states

$$C_{IJ}(\varepsilon) = \underbrace{C_{IJ}^{(\sigma)}(\varepsilon)}_{\sigma\text{COHP}} + \underbrace{C_{IJ}^{(\pi)}(\varepsilon)}_{\pi\text{COHP}}$$

(3) Application in large-scale (order-N) electronic structure calculation

→ an sp₂ and sp₃ nano-domain composite
that appears in the research of nano-crystalline diamond

Note: visualized by our original visualization tool ‘VisBAR’