CHALMERS

Polarons, Excitons, and Defects in Scintillators

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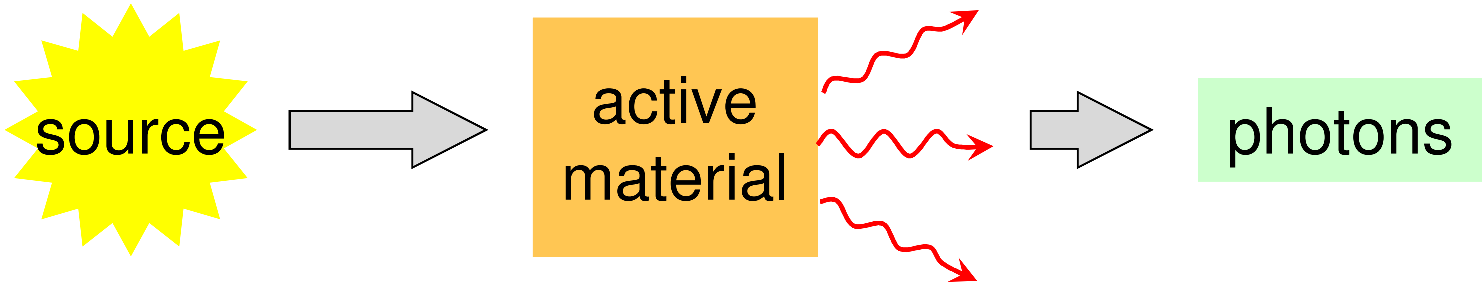
Overview

- **Basic scintillator physics**
- Resolution enhancement by Sr co-doping
- Polaron and exciton formation in NaI
- From excitons to defects

Phosphors and Scintillators

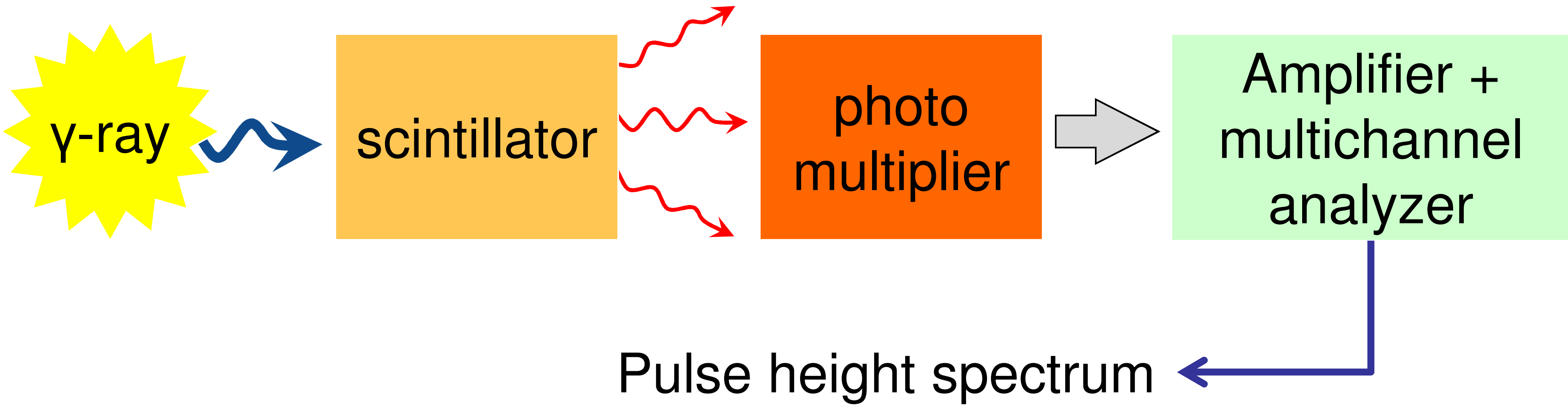


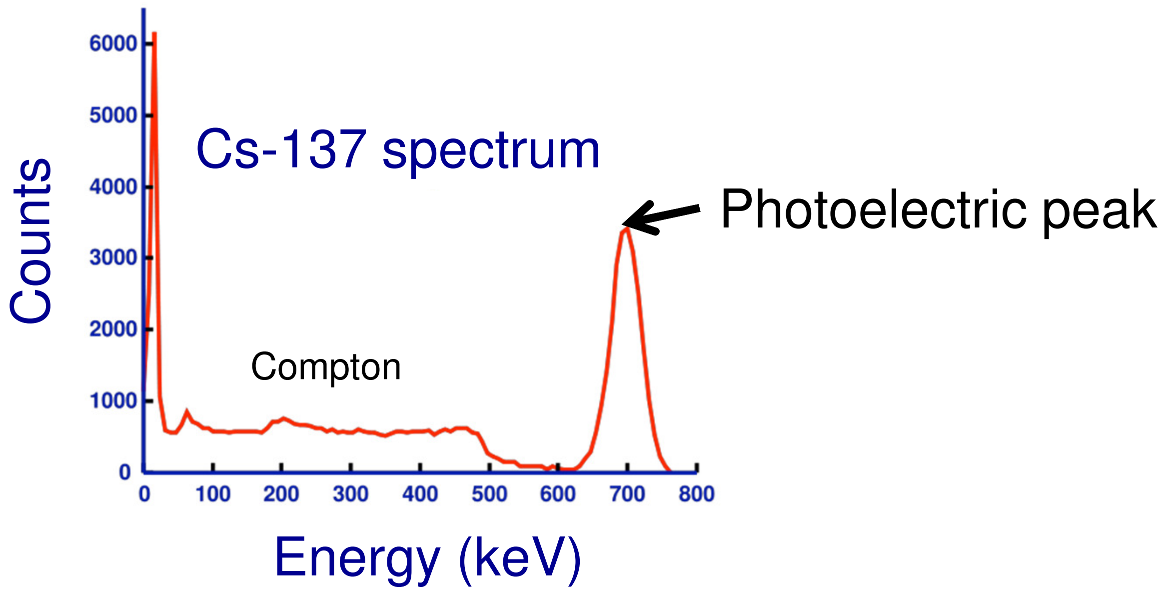
- Photons
- Neutrons
- Electrons
- α-particles
- γ-rays

- ZnS:Cu
- YAG:Ce
- NaI:Tl
- $LaBr_3$:Ce
- SrI_2:Eu

- Usually host material doped with activator e.g., Ce, Eu, other RE
- Solid state lighting
- Radiation detection (medical imaging, nonproliferation, …)

Energy resolved detection





Resolution $\frac{\Delta E_{\mathrm{FWHM}}}{h\nu_{\gamma}}$

Ideal scintillation pathway (simplified)

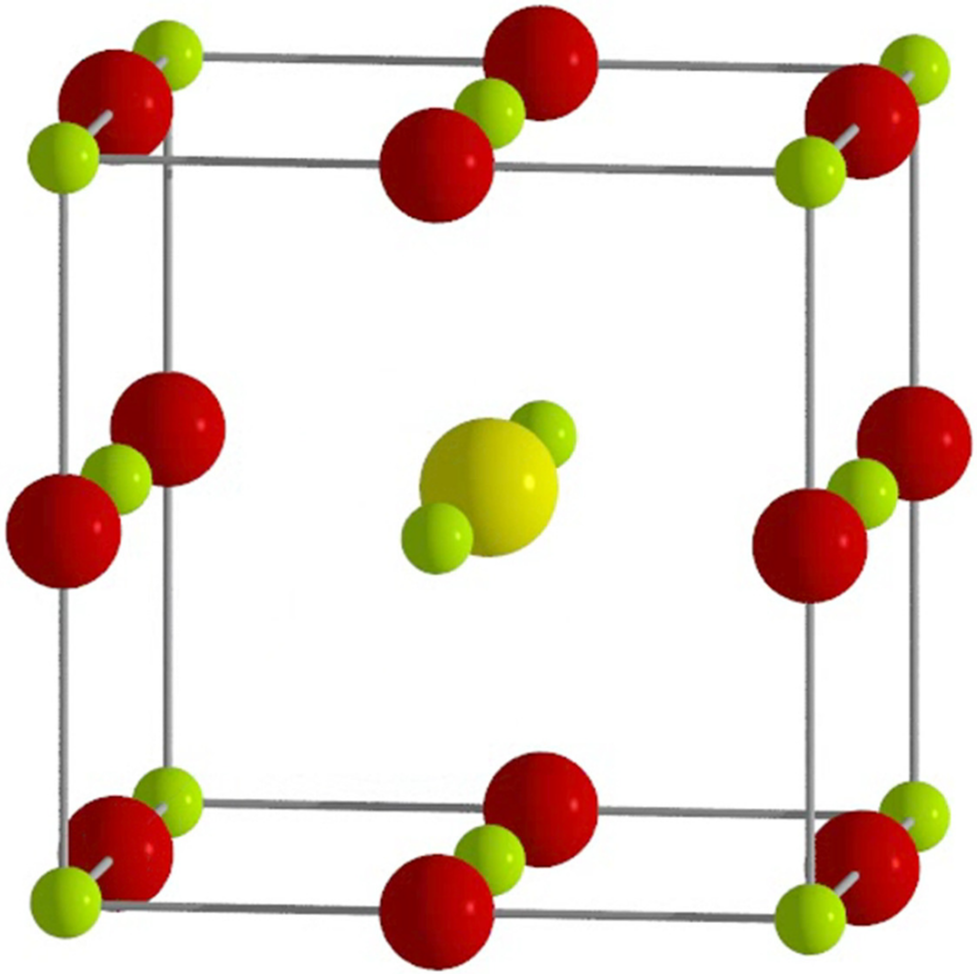
Incoming radiation

Hole trapping

Exciton formation

Energy to activator

Emission



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- Polaron and exciton formation in NaI
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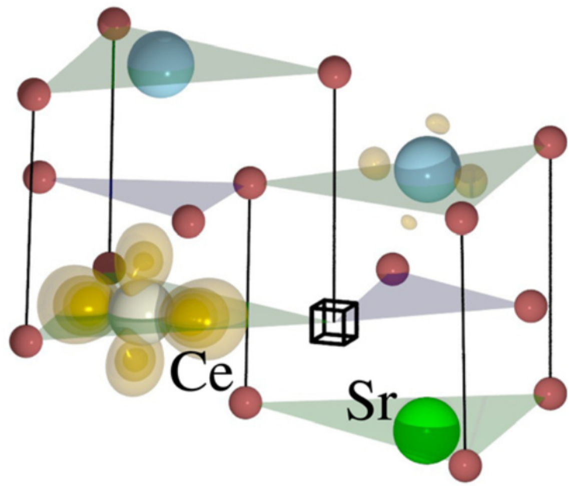
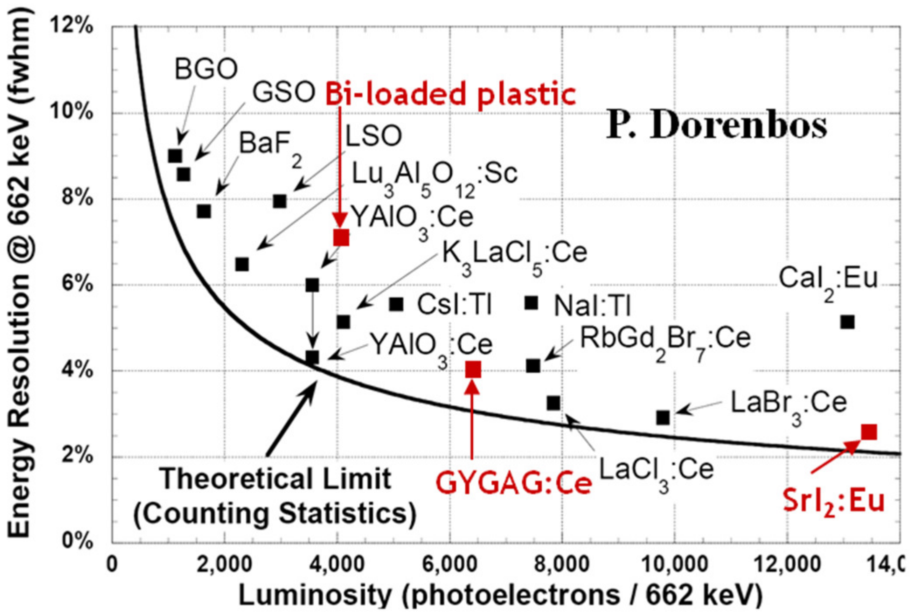
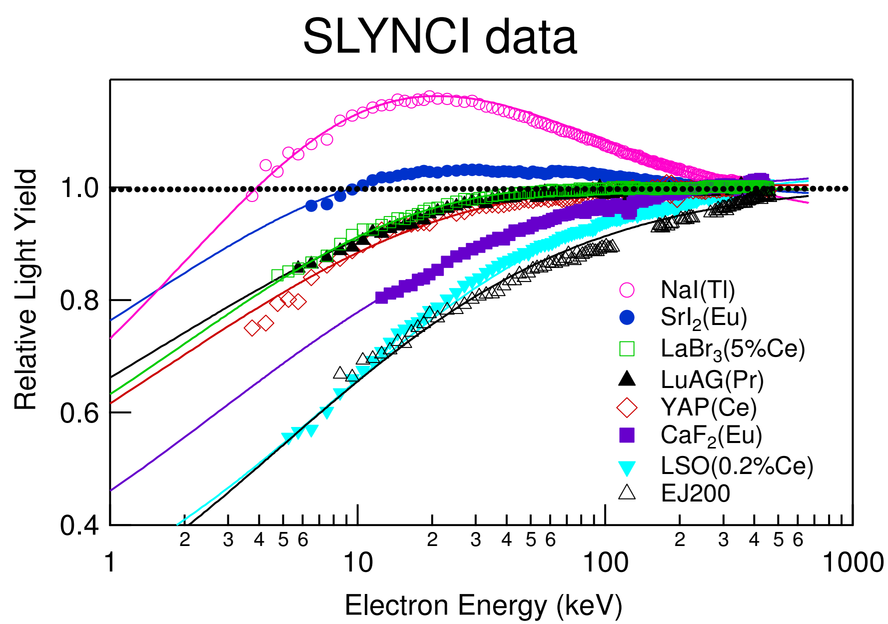


Limits on energy resolution

- Energy resolution of scintillator detectors is worse than suggested by counting statistics
- Problem linked to non-proportionality of light yield to energy of incoming radiation



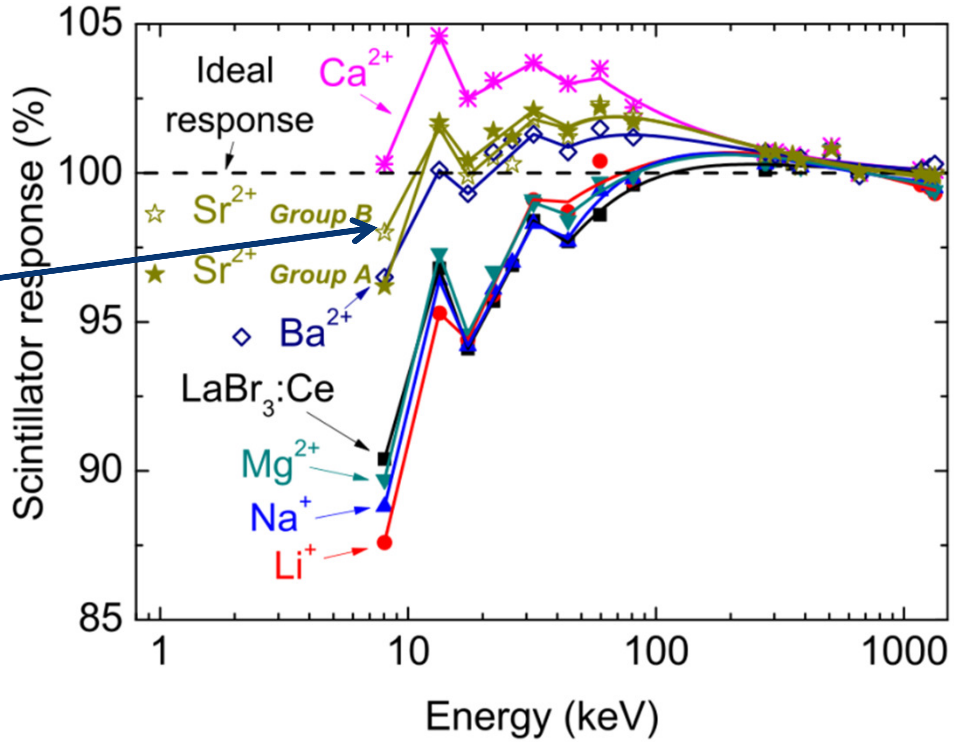


Resolution enhancement by Sr co-doping

- $LaBr_3$:Ce (3% = 30,000 ppm)
  Energy resolution **2.6%**
- $LaBr_3$:Ce + Sr (50–200 ppm)
  Energy resolution **2.0% [1]**
- Ca, Ba also work
- Mg and alkalis do not improve

How is this possible?

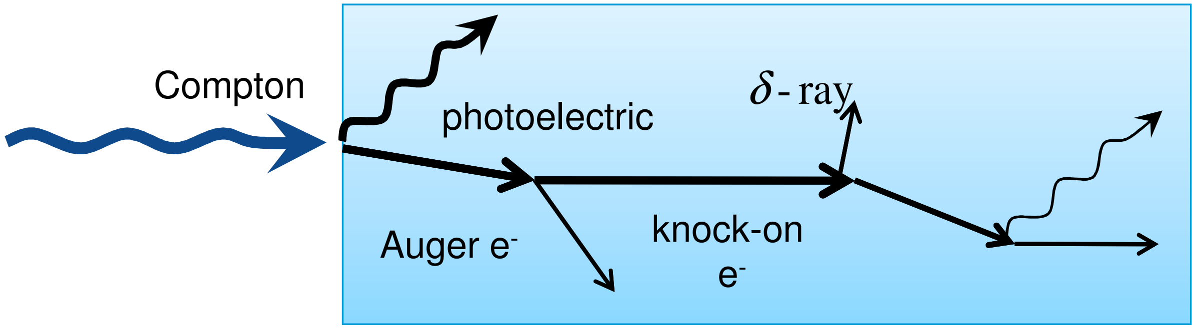
Scintillator response [2]



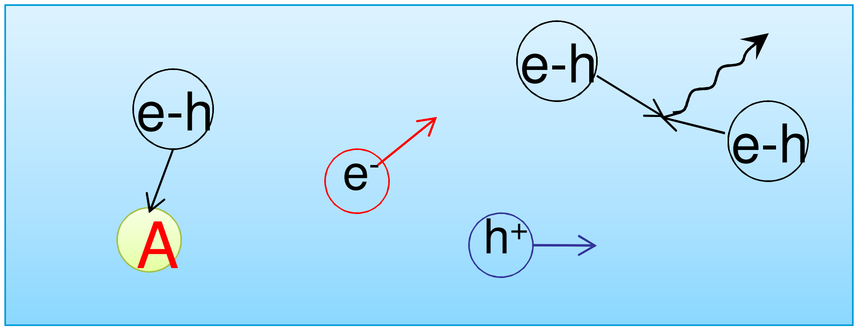
[1] Alekhin *et al.*, APL **102**, 161915 (2013)
[2] Alekhin *et al.*, JAP **113**, 224904 (2013)

Fundamental processes

- Sequence of events after high-energy radiation impact



Stage I:
- High-energy cascade
- Produces high-energy carriers and excitations

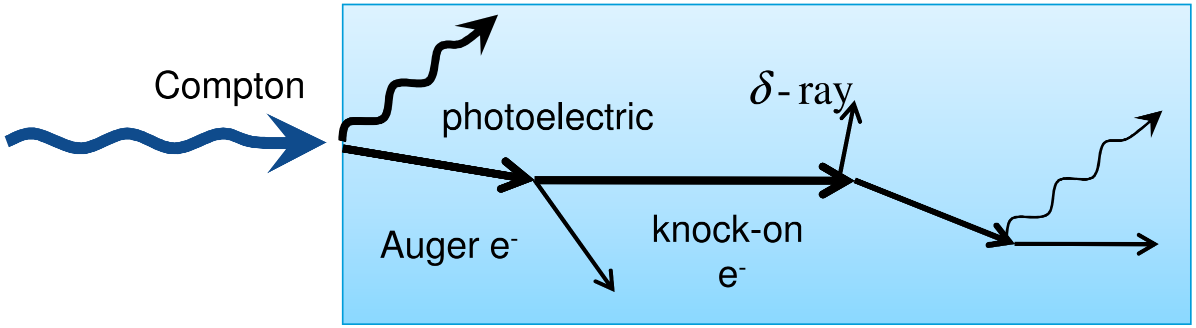


Stage II:
- Excitations diffuse to activators
- Can annihilate along the way via Auger

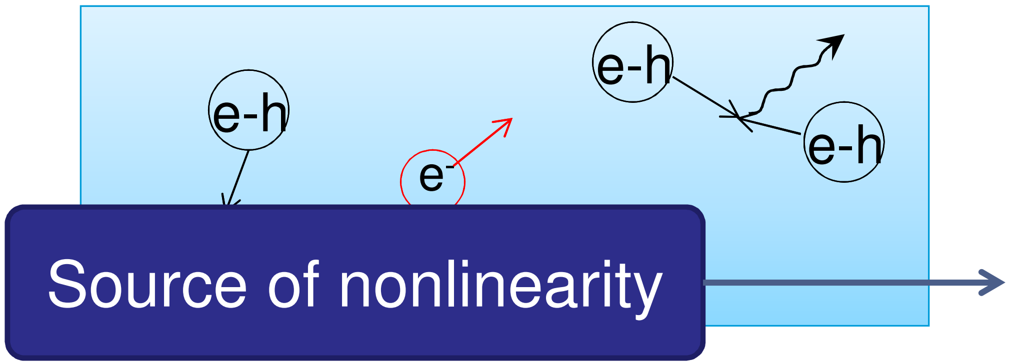
Stage III: Light output via recombination at activators

Fundamental processes

- Sequence of events after high-energy radiation impact



Stage I:
- High-energy cascade
- Produces low-energy carriers and excitations



Stage II:
- Excitations diffuse to activators
- **Can annihilate along the way via Auger**

Stage III: Light output via recombination at activators

Fundamental processes

- Nonlinearity in rate equation picture

$$\frac{\partial n}{\partial t} = \sum_{j\neq i} \alpha_{j\rightarrow i} n_j(t) - \sum_{j\neq i} \alpha_{i\rightarrow j} n_i(t)$$

"unimolecular"

$$+ \sum_{j\neq i, k\neq i} \beta_{jk\rightarrow i}(t) n_j(t) n_k(t) + \sum_{j\neq i, k\neq i} \beta_{ik\rightarrow i}(t) n_i(t) n_k(t)$$

"bimolecular"

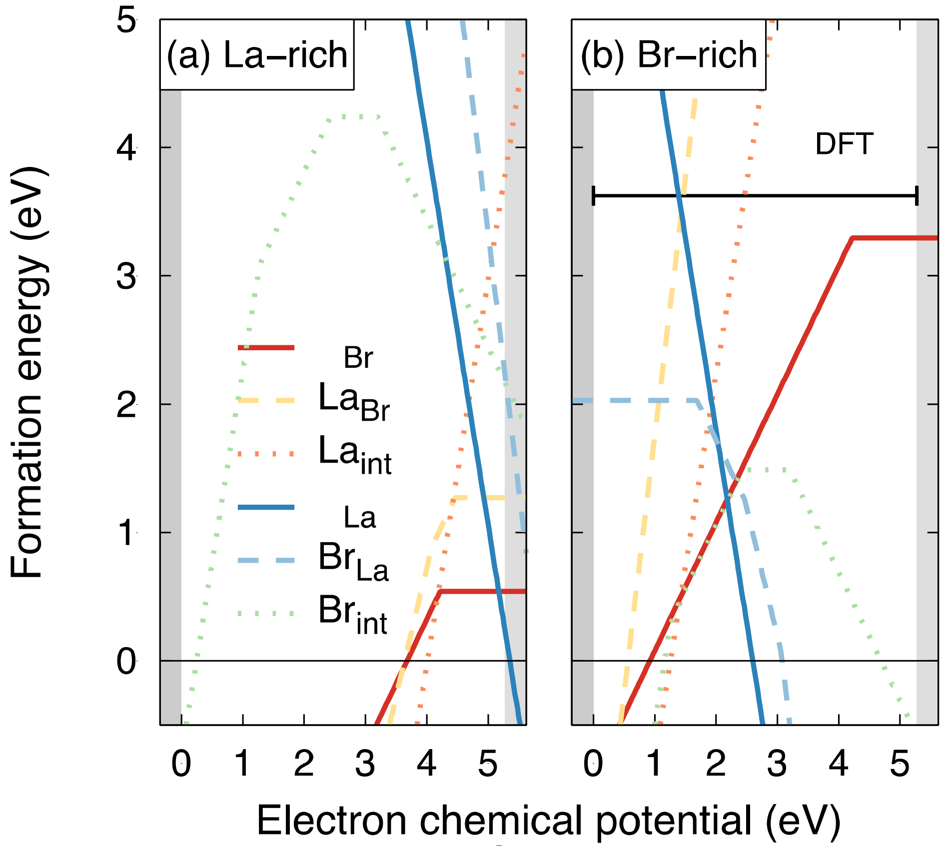
Nonlinear terms

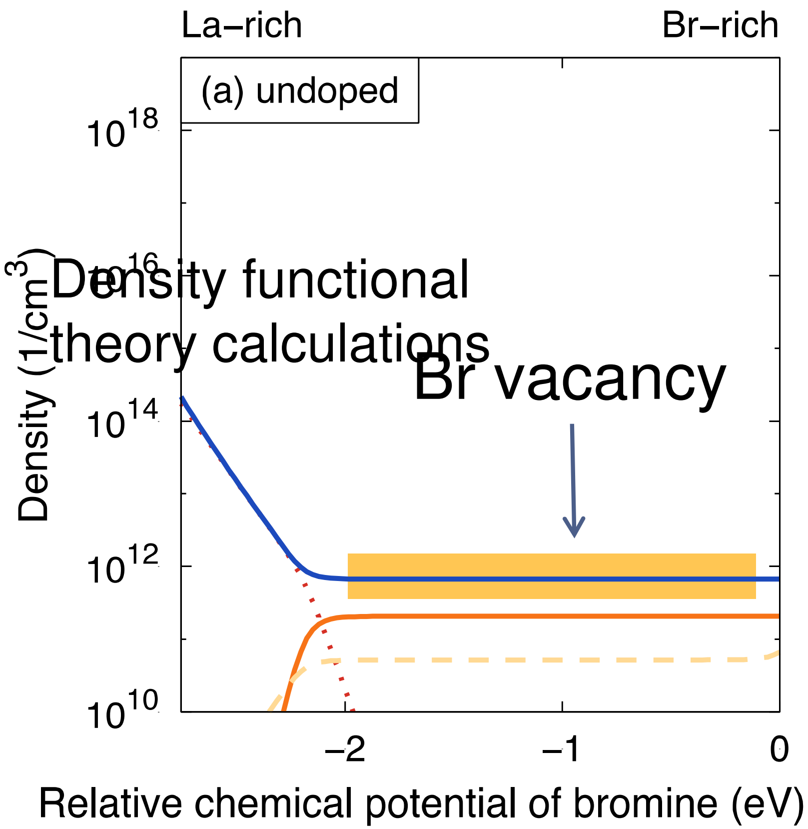
Electronic excitations
- Electrons
- Holes
- Excitons
- …

Bimolecular terms relatively less important at lower densities

(1) Effect of Sr on defect equilibria

Pure material





Density functional theory calculations

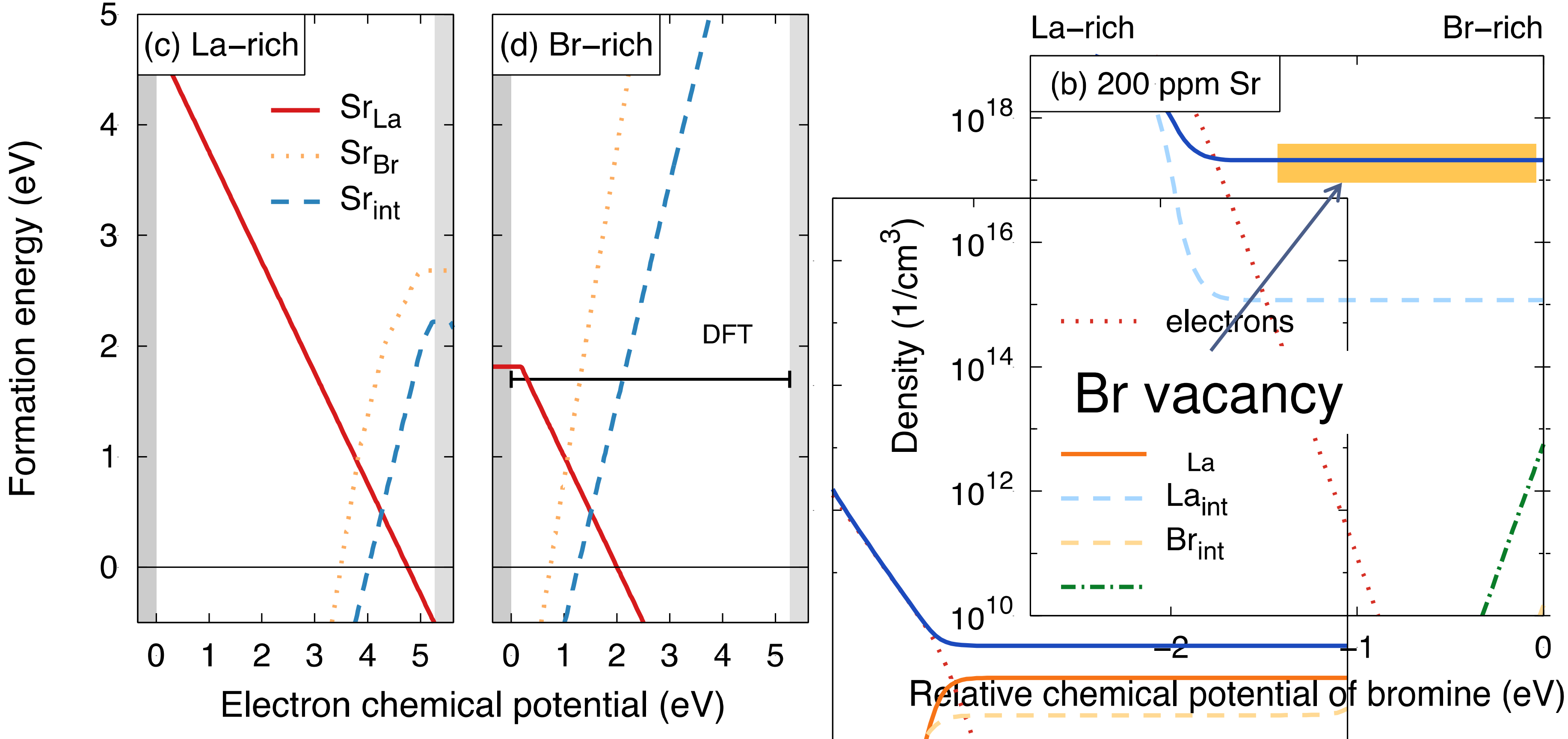
Br vacancy

Charge neutrality condition

(I) Pure material → Br vacancy most important defect

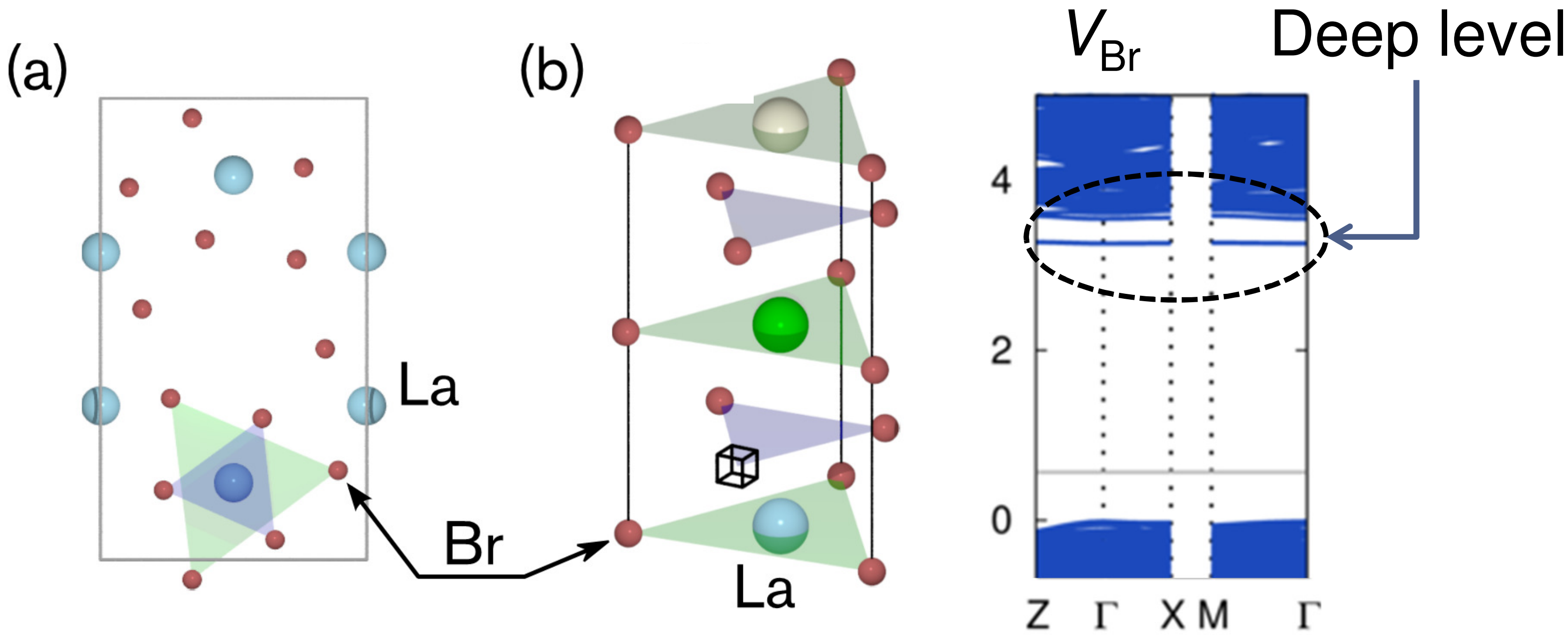
(1) Effect of Sr on defect equilibria

Sr-doping



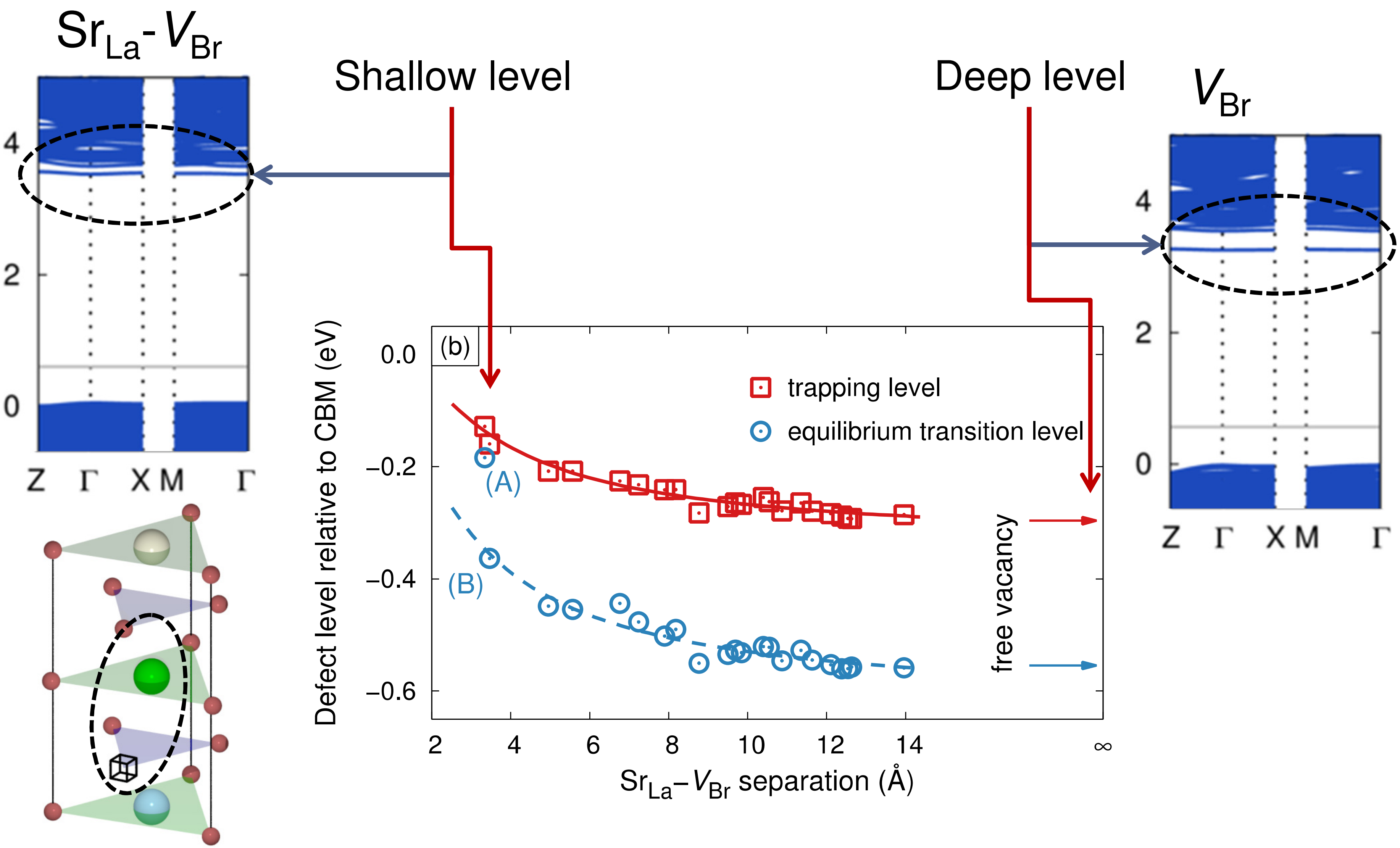
(II) Sr-doping → V_{Br} concentration up by >10^4

(2) Electronic structure of free vacancy

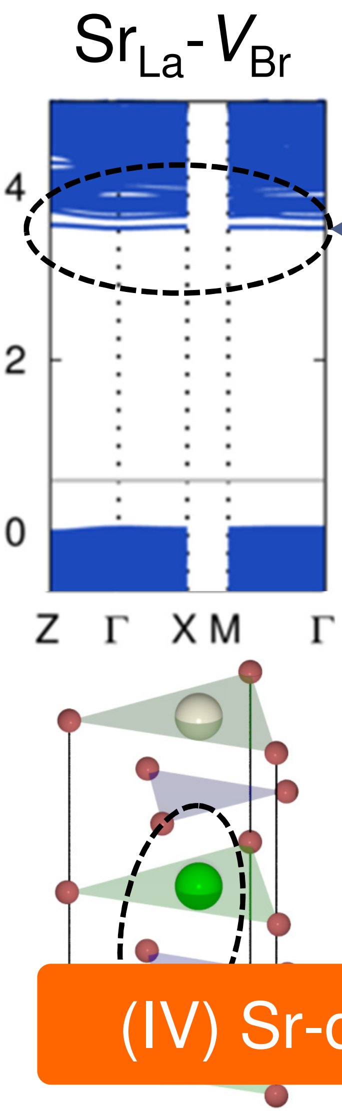


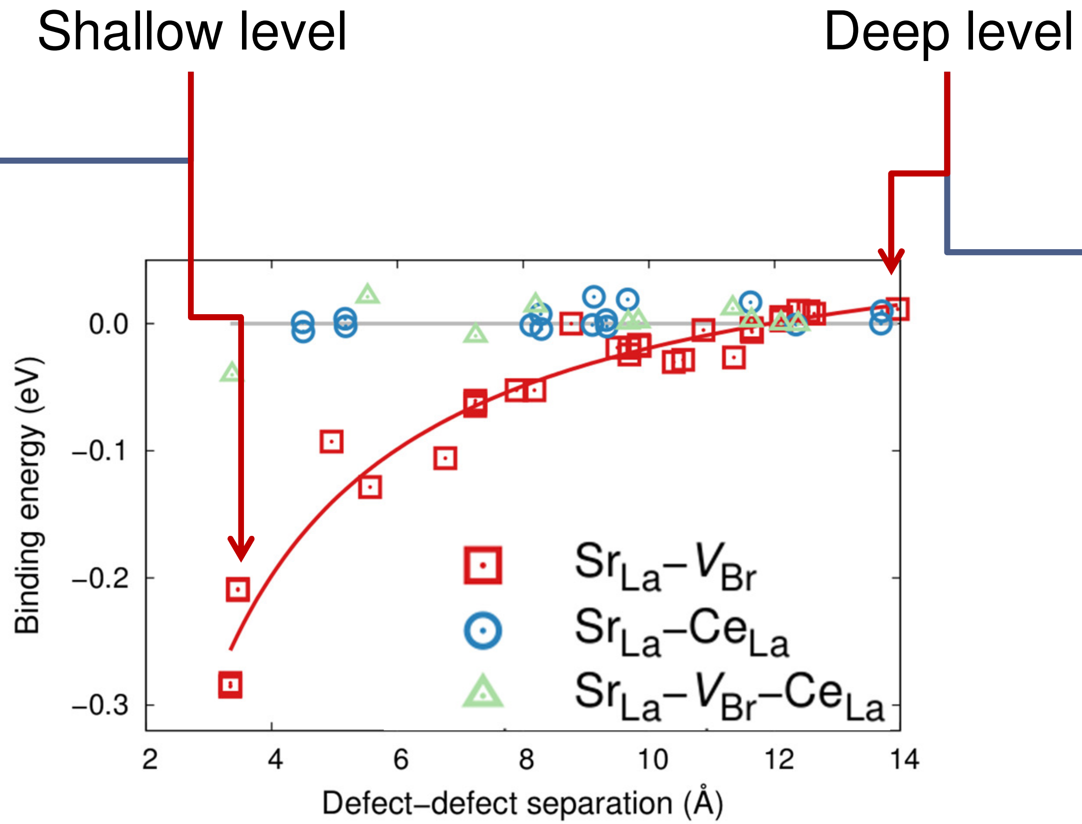
(III) Free V_{Br} → deep electron trapping level

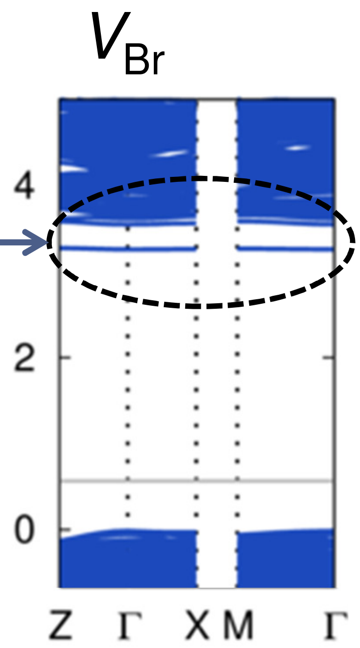
(3) Effect of Sr on Br vacancy



(3) Effect of Sr on Br vacancy

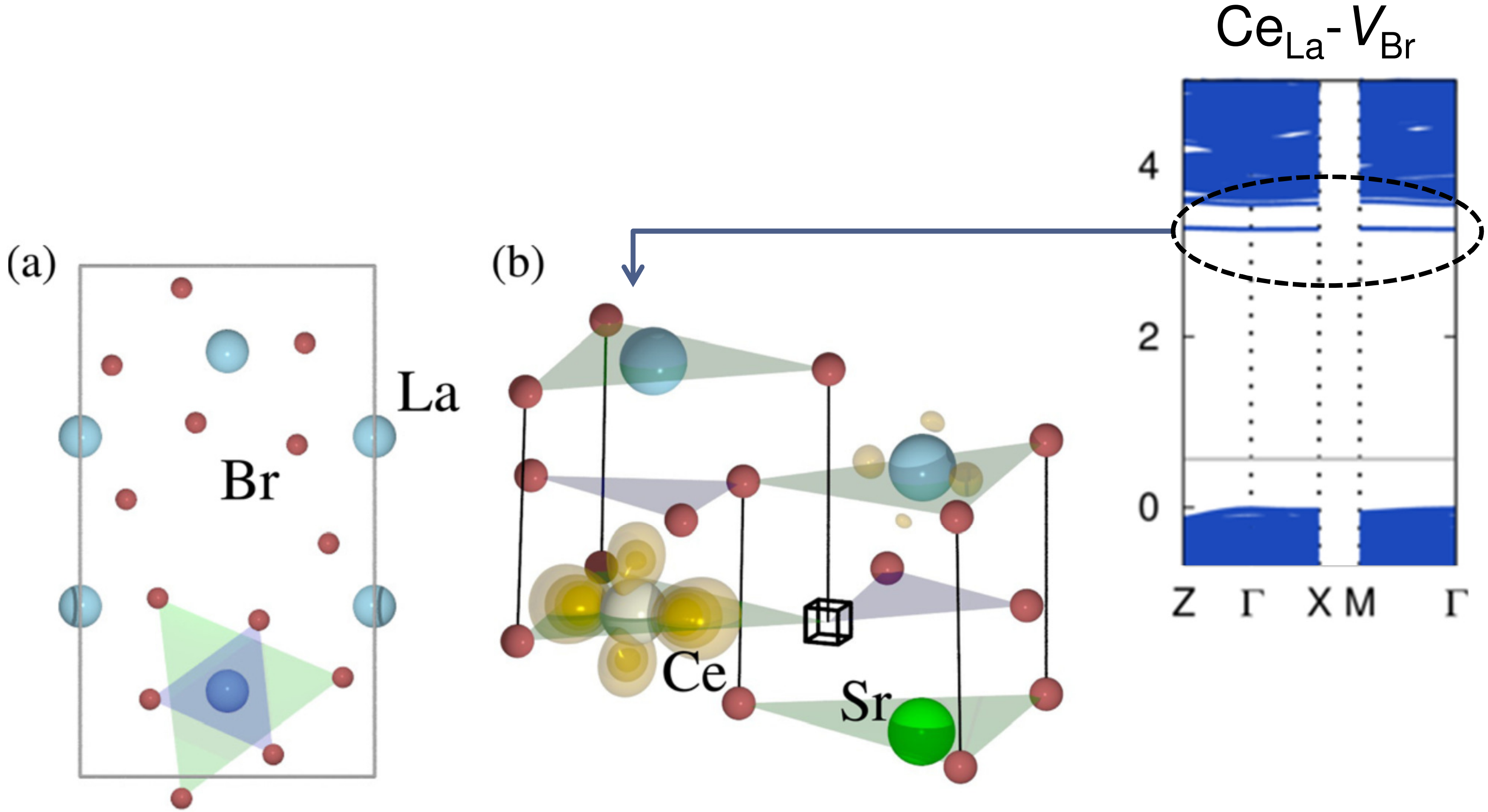






(IV) Sr-doping → moves V_{Br} trapping level closer to CBM

(4) Coupling between V_{Br} and Ce



(V) Vacancy level localizes on Ce!!

What do we know?

I.	Pure material	→ Br vacancy most important defect
II.	Sr-doping	→ V_{Br} concentration up by >10^4
III.	Free V_{Br}	→ deep electron trapping level
IV.	Sr-doping	→ moves V_{Br} trapping level closer to CBM
V.	Ce_{La}-V_{Br}	→ vacancy level localizes on Ce

Model

- Initial electrons trapped during stage I/II
  → Not available for annihilation processes (scales n^3)
- Allows Ce to catch larger fraction of (slower) holes
  Ce^{3+} + h → Ce^{4+}
- Followed by electron transfer
  Ce^{4+} + e' → Ce^{3+*} (and emission)

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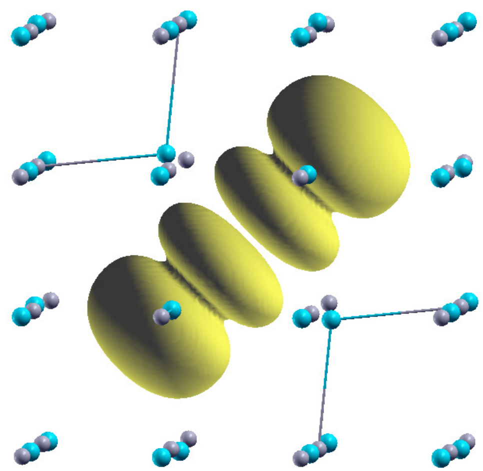
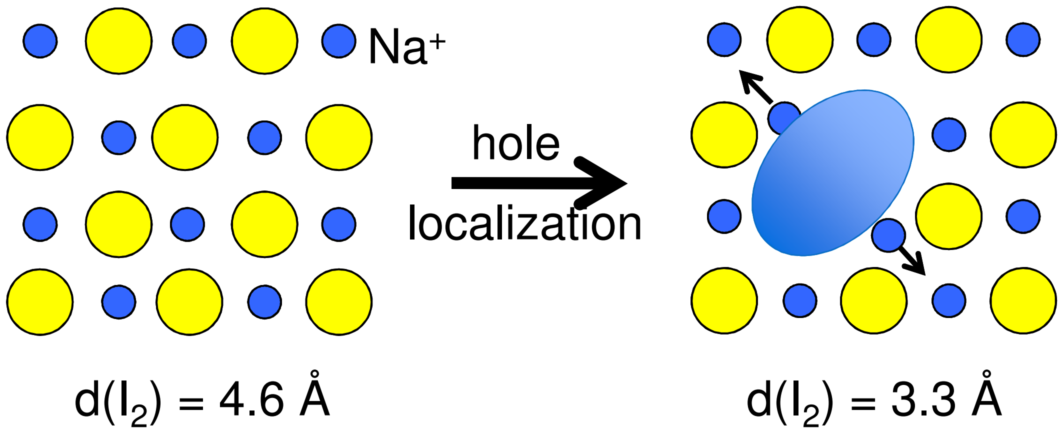
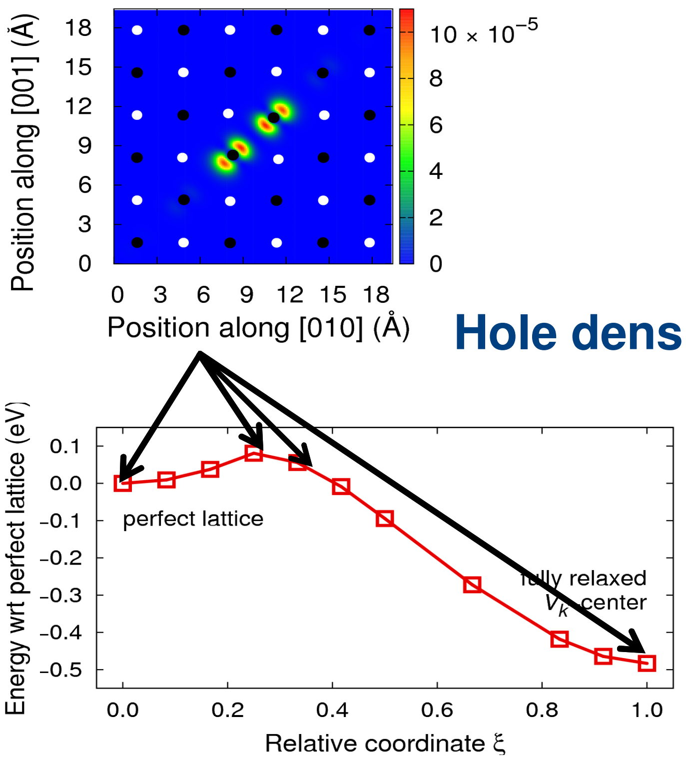


Dynamics of STH/STE Formation in NaI

V_k-center closely resembles an $\mathbf{I_2^-}$ dimer

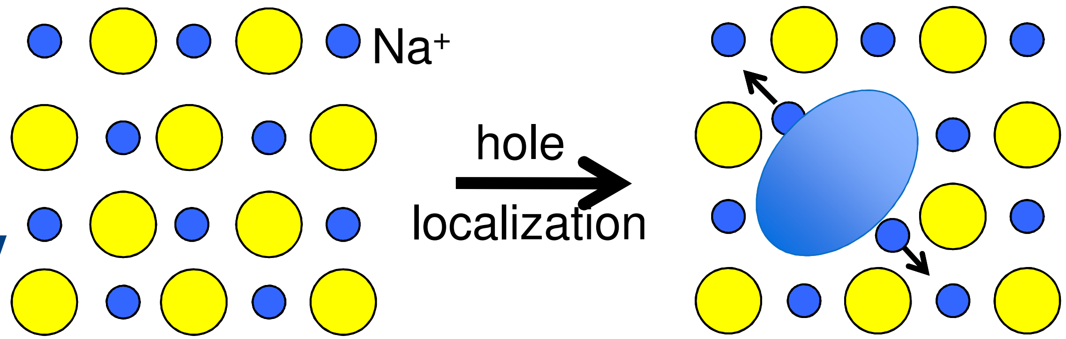


Dynamics of STH/STE Formation in NaI



Hole density

V_k-center closely resembles an $\mathbf{I_2^-}$ dimer

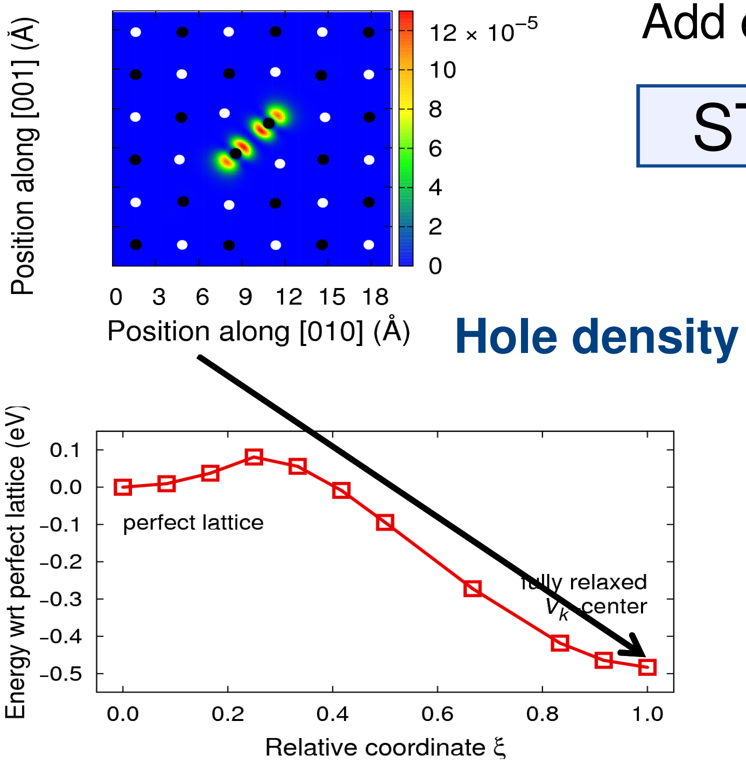


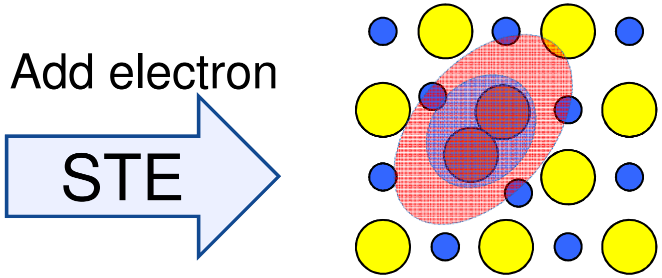
$d(I_2)$ = 4.6 Å

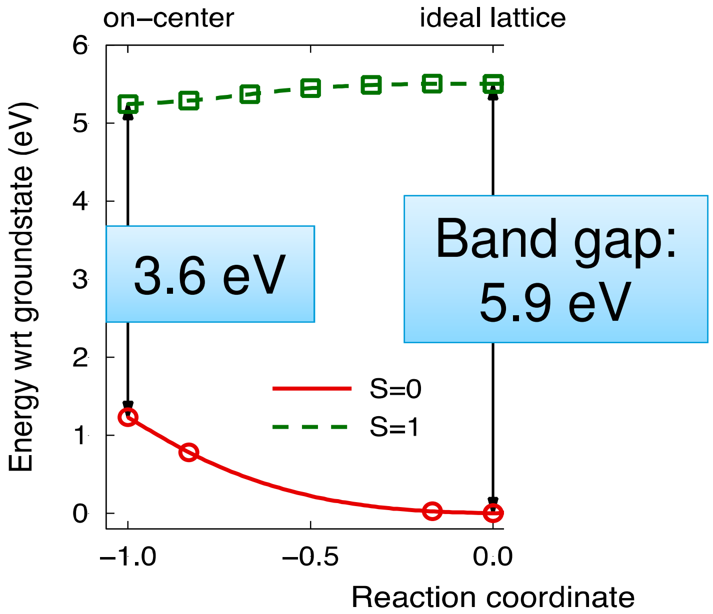
$d(I_2)$ = 3.3 Å

The localization of the hole leads to a significant energy gain of about 0.4 eV.

Dynamics of STH/STE Formation in NaI







Exp. Luminescence energy: 4.2 eV

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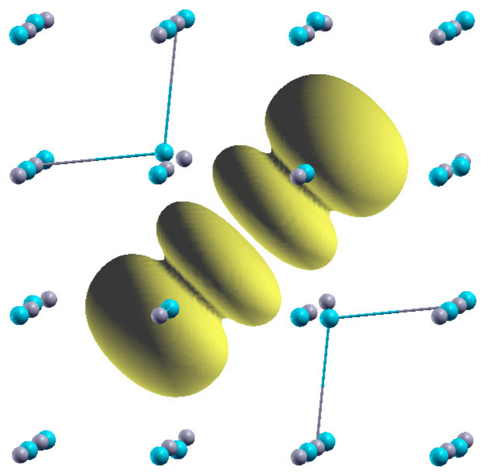
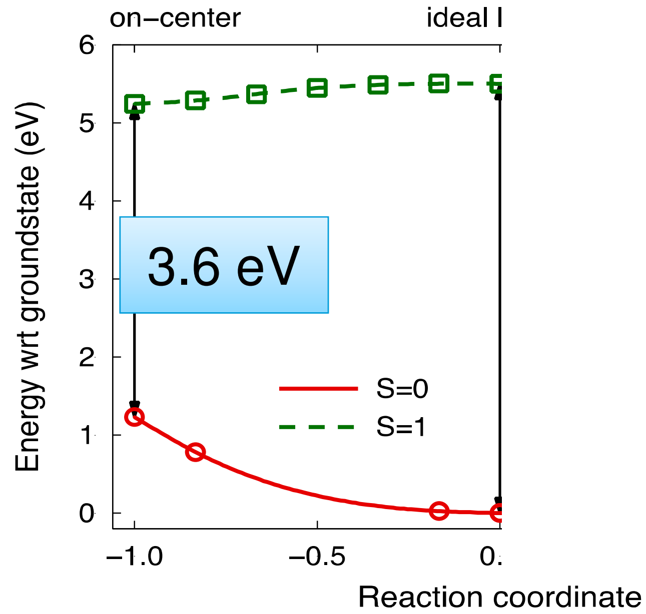


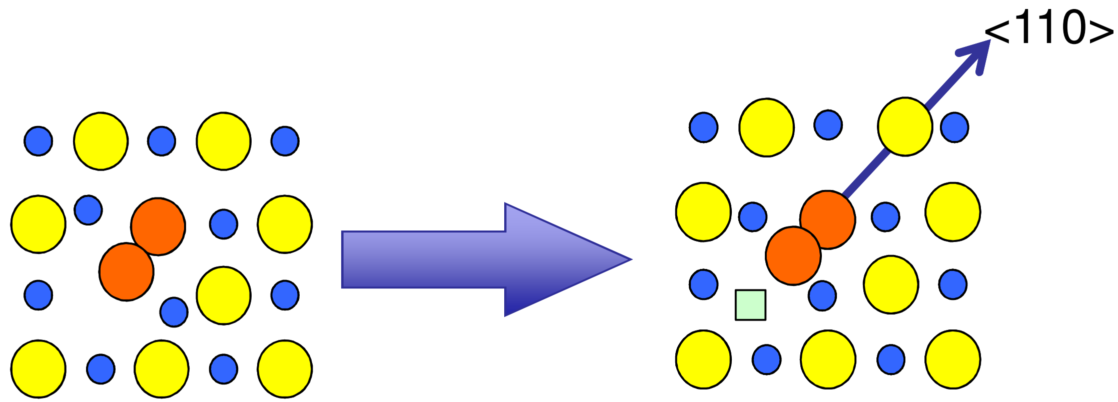
On-center vs Off-center STE

- Low densities (ρ_{STE}<0.5%)
  → **on-center STE**



- Large densities (ρ_{STE}>1%) such as along the track of an incident gamma-ray
  → **off-center STE**

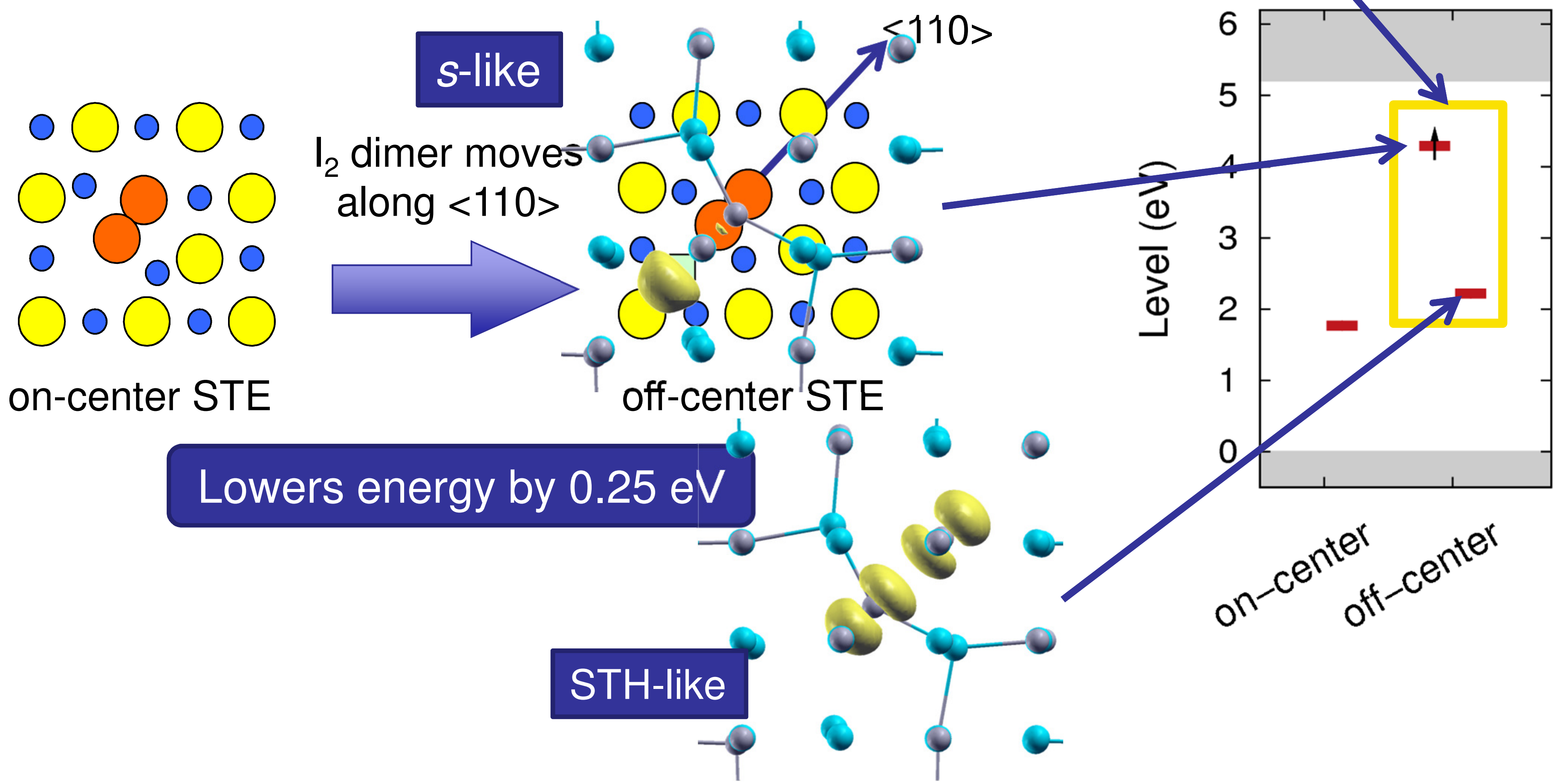
On-center is the stable configuration in most experiments



on-center STE off-center STE

Self-trapped exciton formation

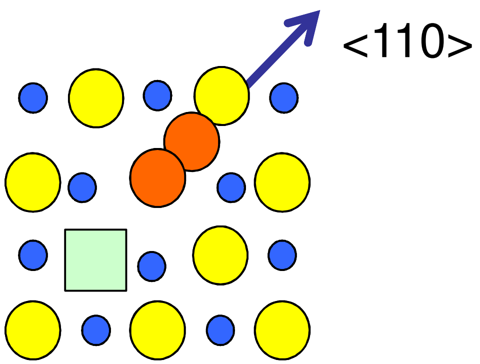
- Relaxation to off-center STE at high ρ_{STE}



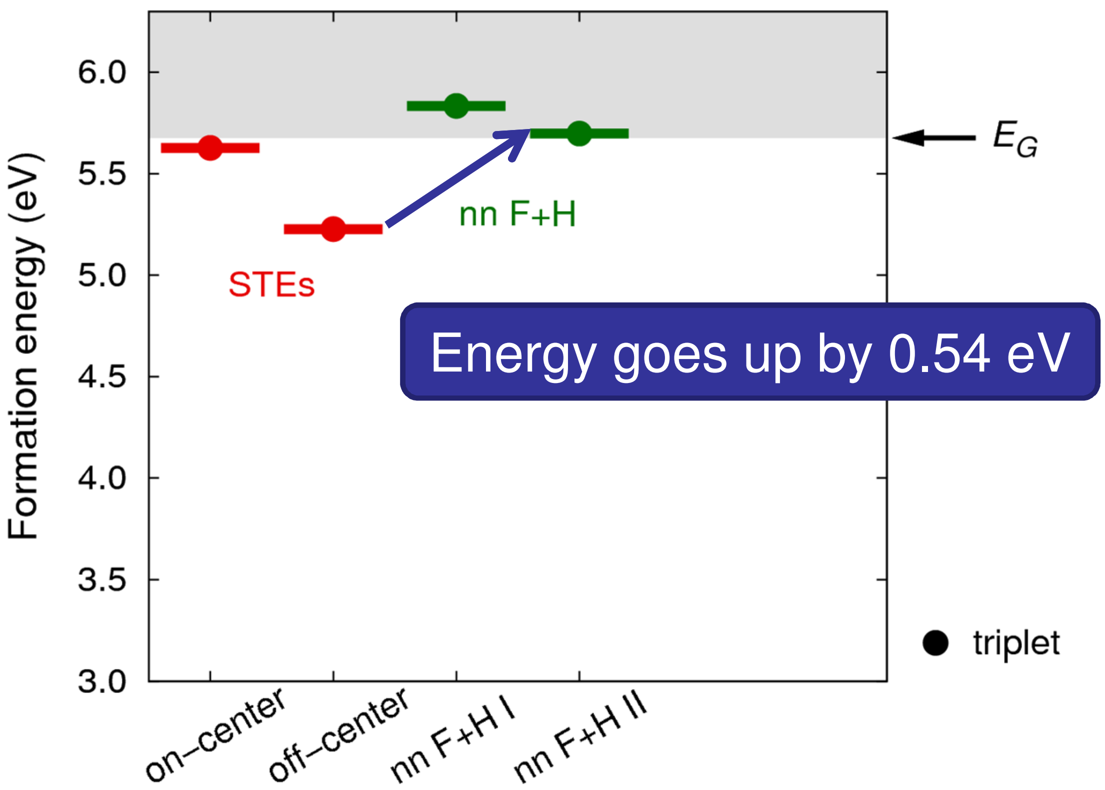
From STEs to F+H pairs

What happens if we continue moving along <110>?

- Nearest neighbor F+H pairs (Frenkel pairs)
  F = neutral vacancy (V_i^x)
  H = neutral interstitial (I_{int}^x)
- Type I: in-plane
- Type II:
  dimer tilted out-of-plane



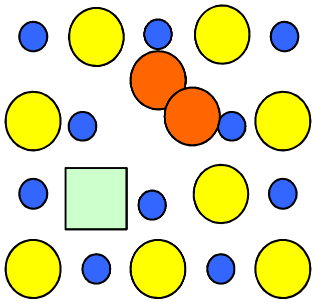
nn F+H



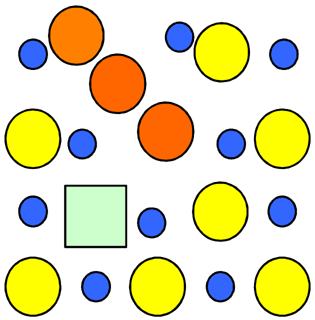
From STEs to F+H pairs

Are there other configurations of interest?

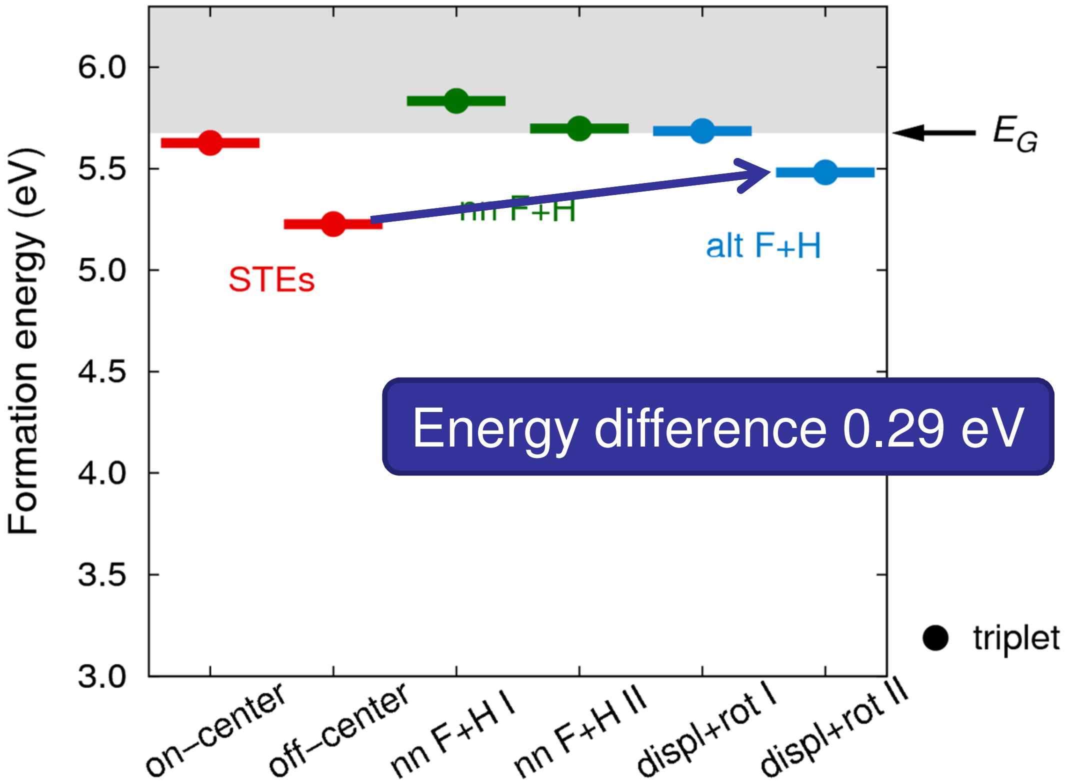
- Nearest neighbor F+H pairs (Frenkel pairs)
  F = neutral vacancy (V_i^x)
  H = neutral interstitial (I_{int}^x)



displ+rot I



displ+rot II



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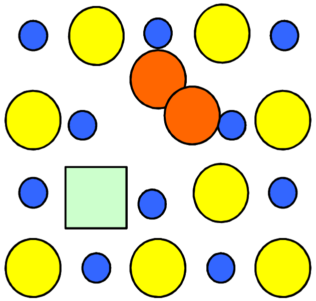

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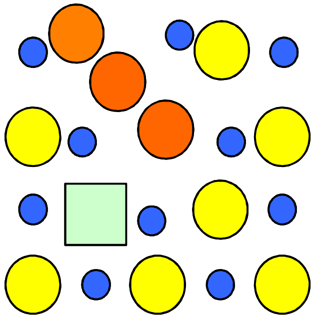
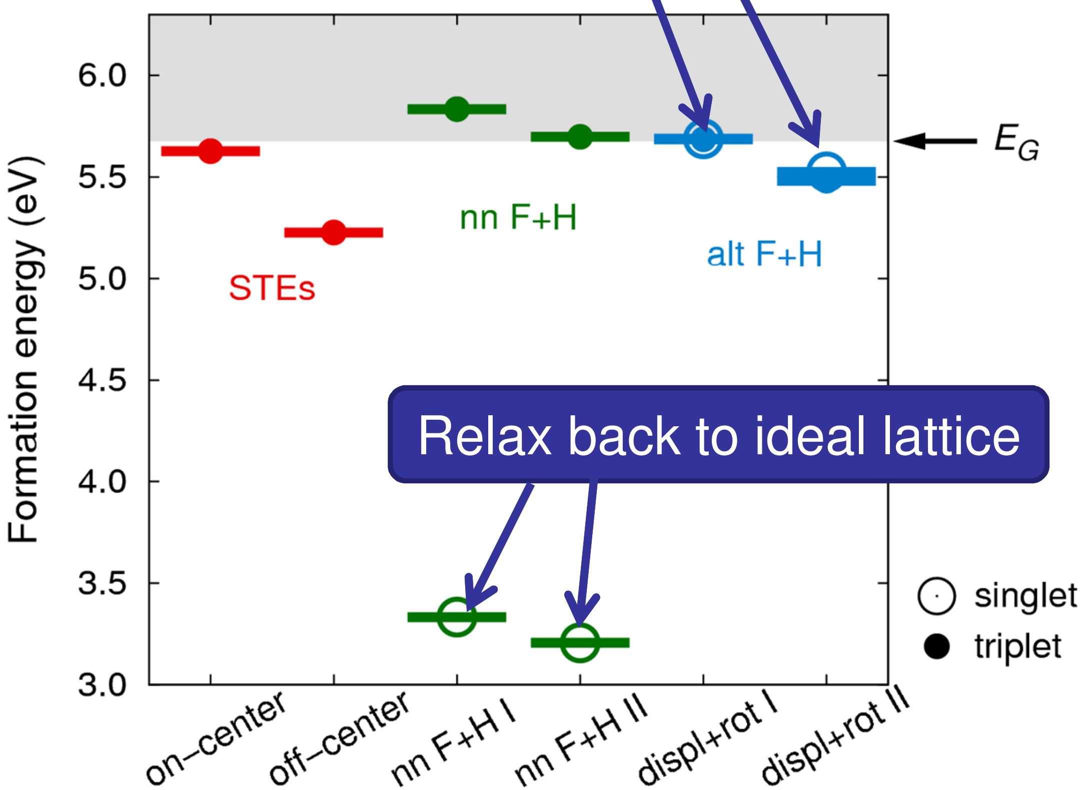


displ+rot II

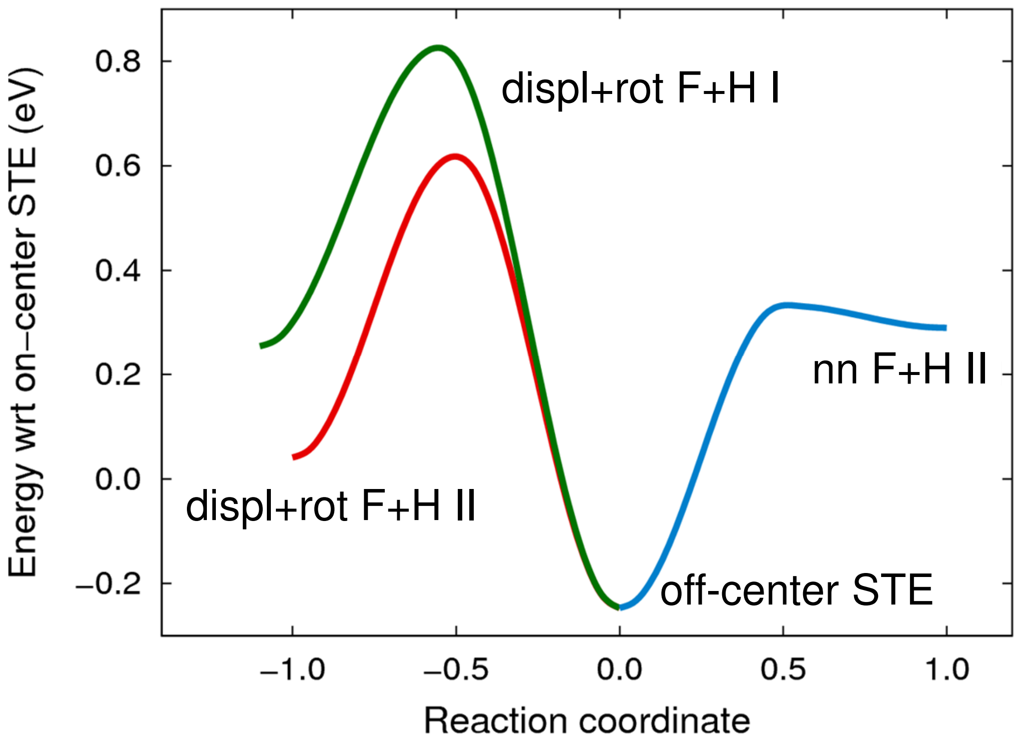


From STEs to F+H pairs

Transition from STE to defect pairs

- Flat energy landscape along <110>
- Barriers for rotation much higher

$V_I^{\bullet} + I_{int}' \leftarrow \text{STE} \rightarrow \text{F+H} \ (V_I^{x} + I_{int}^{x})$



- Unlikely path for NaI but possibly viable for other AHCs (→ KCl, RbI?) which show more defect production and are also less proportional

Summary

- Polaron and exciton formation in halides coupled to large lattice distortion
- Density dependence of exciton configuration provides nucleus for defect formation

- Model for resolution enhancement by co-doping:
  - Initial electrons trapped during stage I/II
    → Not available for annihilation processes (scales n^3)
  - Allows Ce to catch larger fraction of (slower) holes
    $Ce^{3+} + h^{\bullet} \rightarrow Ce^{4+}$
  - Followed by electron transfer
    $Ce^{4+} + e' \rightarrow Ce^{3+*}$ (and emission)

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