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Theory of Recoil Effect in HAXPES and Its Prospect as a Tool for Material Research

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1. Introduction

   Recoil effect of atoms, molecules and solids

2. Core level X-ray photoemission in graphites

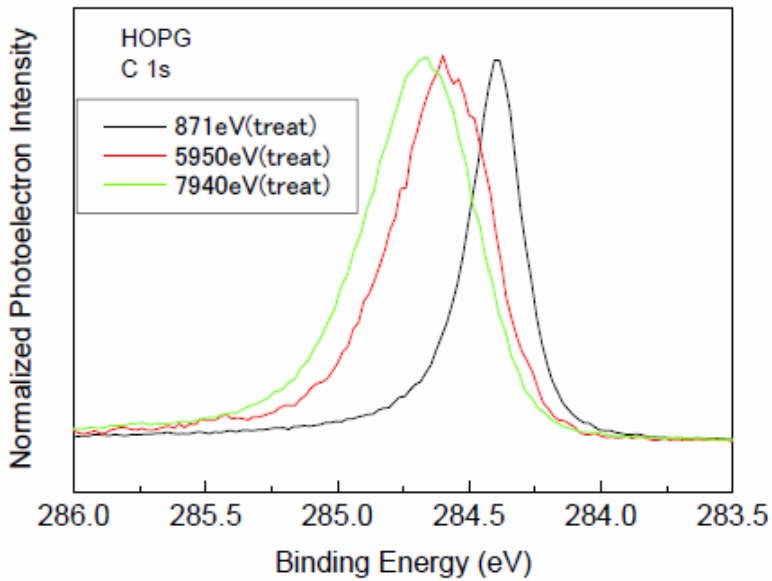
3. Valence band X-ray photoemission

4. Outlook

   Recoil spectroscopy?

Anomalies in HXPES for 1s core-level in graphite

Y. Takata et al.



Normal angle emission

RT

1. Shift of the binding energy
2. Anomalous broadening
3. Asymmetric line shape

} depend on X-ray energy

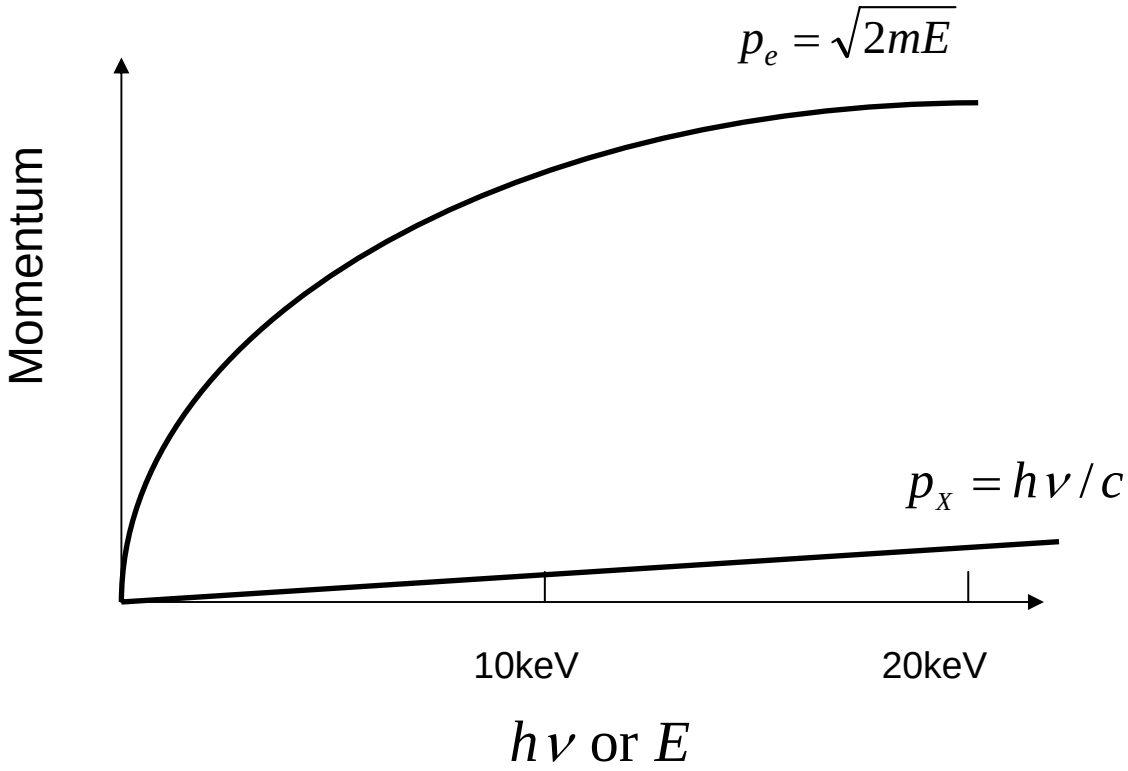
Recoil effect is observable！

$$\vec{P} = -\vec{p}$$

$$\Delta E = \frac{\vec{P}^2}{2M} = \frac{\vec{p}^2}{2m} \times \frac{m}{M} \qquad \frac{m}{M} = \frac{1}{22000}$$ (carbon atom)

$$\frac{\vec{p}^2}{2m} \approx 8\text{keV} \quad \Longrightarrow \quad \Delta E \approx 0.36\text{eV!}$$

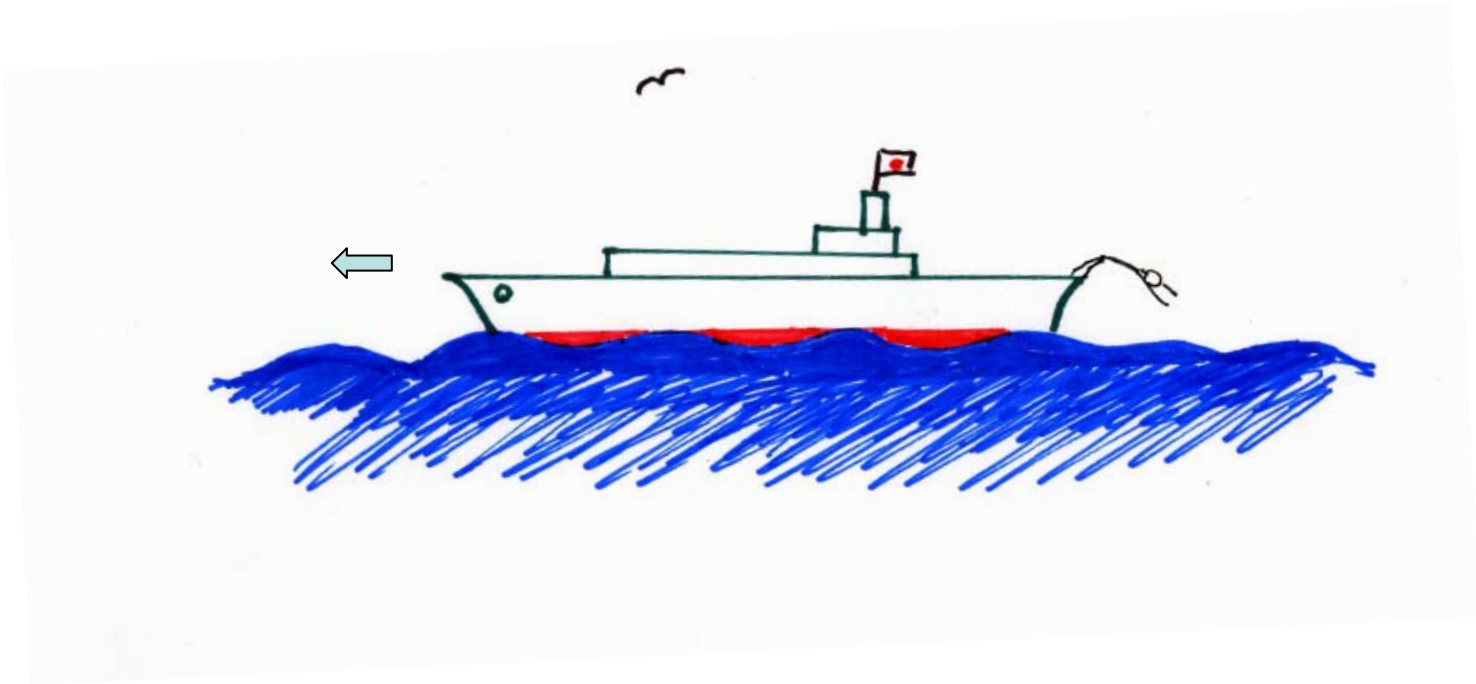
Energy momentum relation



at $h\nu = 10\text{keV},\ p_X / p_e \approx 0.1 \qquad \therefore\ \Delta E_X / \Delta E_e \approx 0.01$

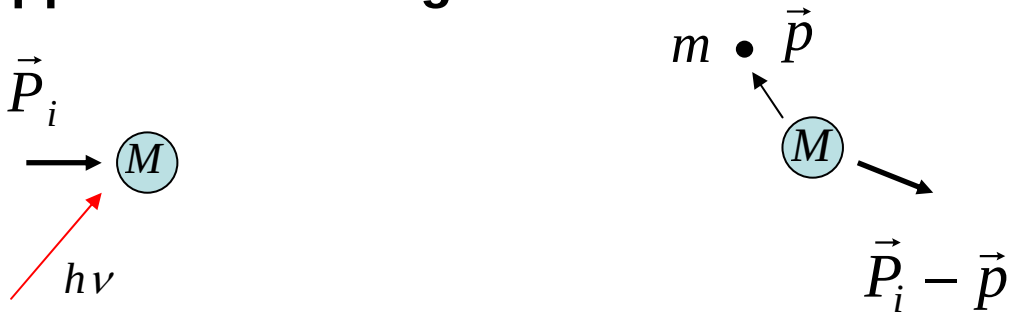
Momentum of photon is negligible.

But momentum of photoelectron is NOT.



A guy with weight 70kg dived from a ship of 1500t , and you observed the ship to move!

Doppler Broadening



Energy conservation

$$\varepsilon_c + h\nu + \frac{\vec{P}_i^{\,2}}{2M} = \frac{\vec{p}^{\,2}}{2m} + \frac{(\vec{P}_i - \vec{p})^2}{2M}$$

$$E_{obs} = \frac{\vec{p}^{\,2}}{2m} = \varepsilon_c + h\nu + \frac{\vec{P}_i^{\,2}}{2M} - \frac{(\vec{P}_i - \vec{p})^2}{2M}$$

$$= \varepsilon_c + h\nu - \frac{\vec{p}^{\,2}}{2M} + \frac{\vec{P}_i \cdot \vec{p}}{M}$$

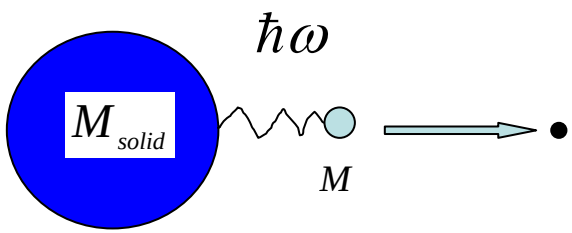
$$\frac{\vec{p}^{\,2}}{2M} = \Delta E$$

$$\left\langle \frac{\vec{P}_i \cdot \vec{p}}{M} \right\rangle = 0$$

$$\left\langle \left(E_{obs} - \langle E_{obs} \rangle \right)^2 \right\rangle = \frac{\left(\vec{P}_i \cdot \vec{p}\right)^2}{M^2} = \frac{\left\langle \vec{P}_i^{\,2} \right\rangle}{3M^2} \vec{p}^{\,2} = 2\Delta E \; k_B T$$

In crystal, $k_B T \rightarrow \hbar\omega$

We need quantum mechanics



$$\Delta E = \frac{p^2}{2M}$$

$$\boxed{S = \Delta E / \hbar\omega} \qquad e^{-S}$$

$S >> 1 \ (\Delta E >> \hbar\omega)$ ⇨ Observed peak shift $= \Delta E$

$S << 1 \ (\Delta E << \hbar\omega)$ ⇨ Observed peak shift $= 0$

Mossbauer Effect

Asymmetric line shape ⇦ **quantum effect of phonons**

Recoil effect comes out from only one assumption.

Initial state

Adiabatic approximation → $\langle \vec{r} | \psi_c \rangle = \psi_c(\vec{r} - \vec{R})$

Translational symmetry → Momentum conservation

Atomic position $\vec{R}$ is a dynamic variable.

Final state

$$\langle \vec{r} | \psi_k \rangle = \frac{1}{\sqrt{V}} \exp\left(i\vec{k} \cdot \vec{r}\right)$$

Fermi's golden rule

$$I(E) = \frac{\Gamma}{\pi} \left\langle \sum_f \frac{\left| \langle \Psi_f | H_I | \Psi_i \rangle \right|^2}{\left(E + \varepsilon_n - h\nu - \varepsilon_c - \varepsilon_m\right)^2 + \Gamma^2} \right\rangle$$

$$I(E) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-\Gamma|t|/\hbar - itE/\hbar} F(t)$$

$$F(t) \equiv \left\langle e^{iku(t)} e^{-iku} \right\rangle = \exp\left[G(t)\right]$$

$$G(t) = \sum_{q\lambda} \alpha_{q\lambda}^2 \left\{ \left(2n_{q\lambda} + 1\right)\left(\cos\omega_{q\lambda} t - 1\right) - i\sin\omega_{q\lambda} t \right\}$$

$$\alpha_{q\lambda}^2 = \left(\frac{\hbar}{2NM\omega_{q\lambda}}\right)\left|\vec{k}\cdot\eta_{q\lambda}\right|^2$$

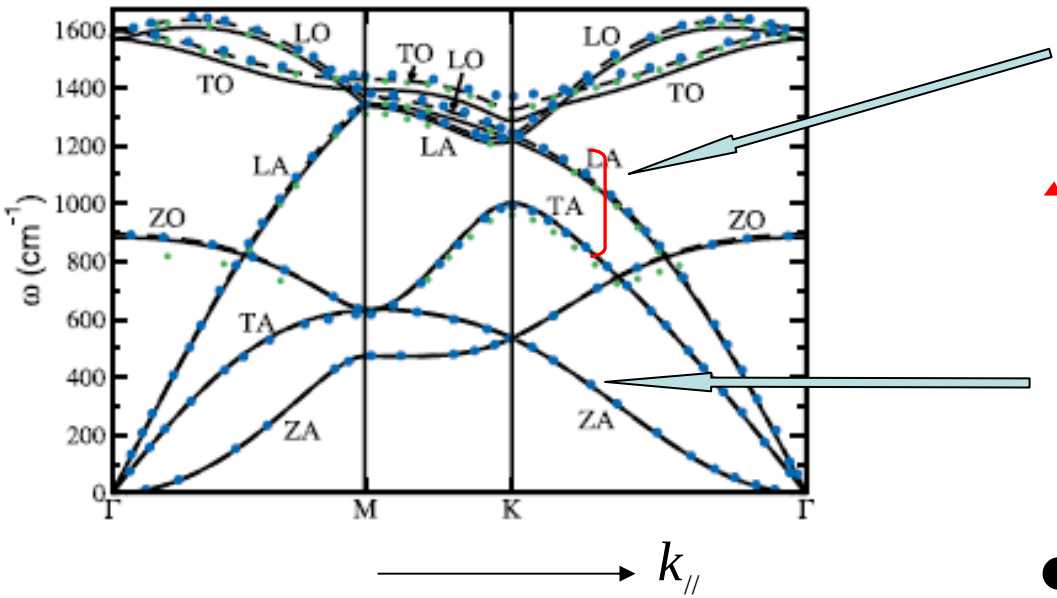
Displacement vector of atom

Wave vector of electron

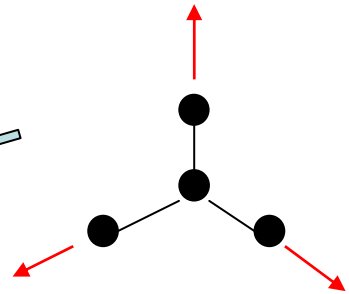
Atomic mass

Phonon dispersion of graphite

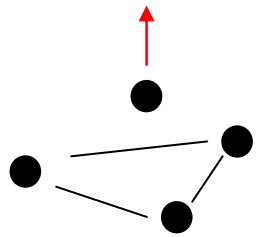
L. Wirtz and A. Rubio, Solid State Commn., 131,141 (2004)

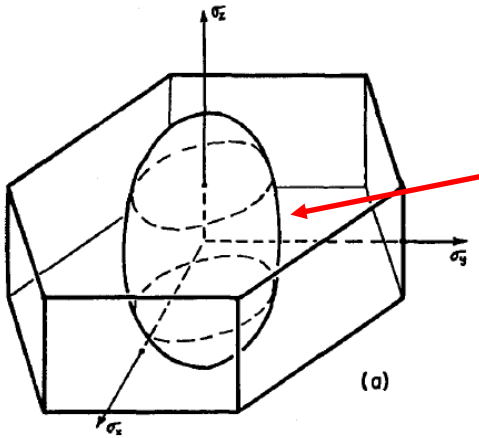


stretching



bending

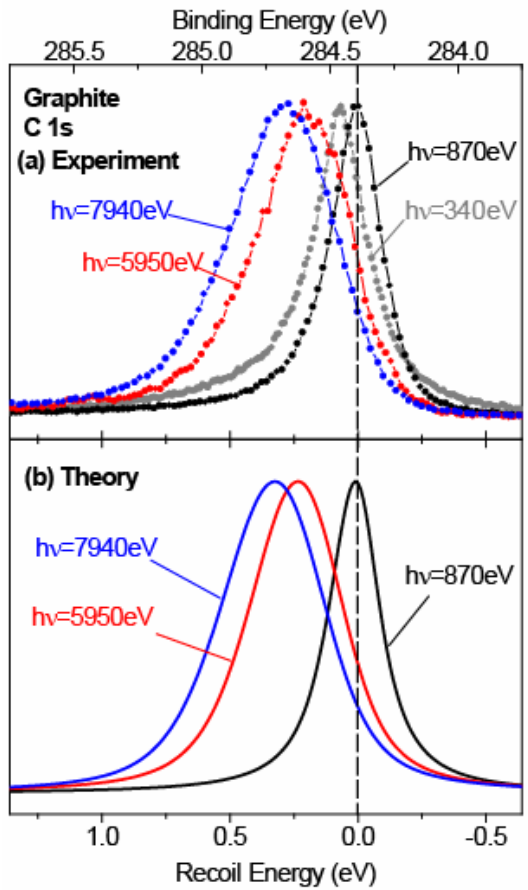




Equi-frequency surface

Anisotropic Debye Model

Excitation energy dependence （normal emission）

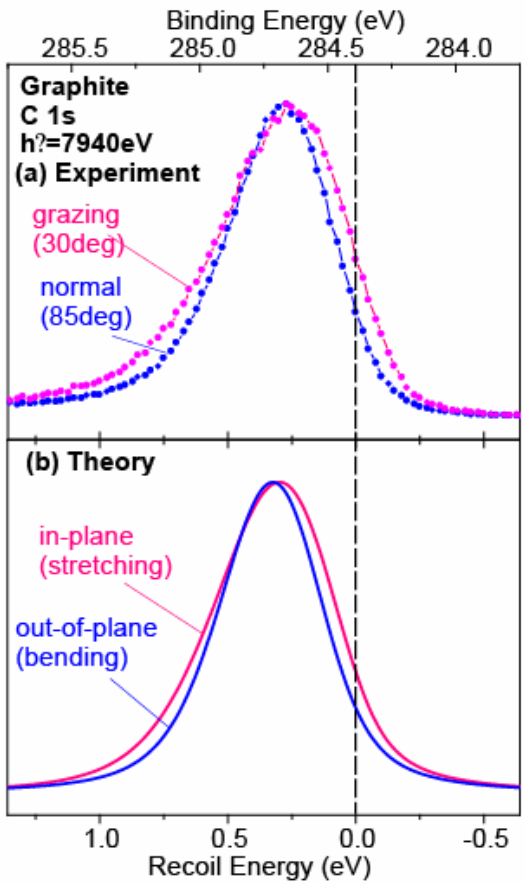


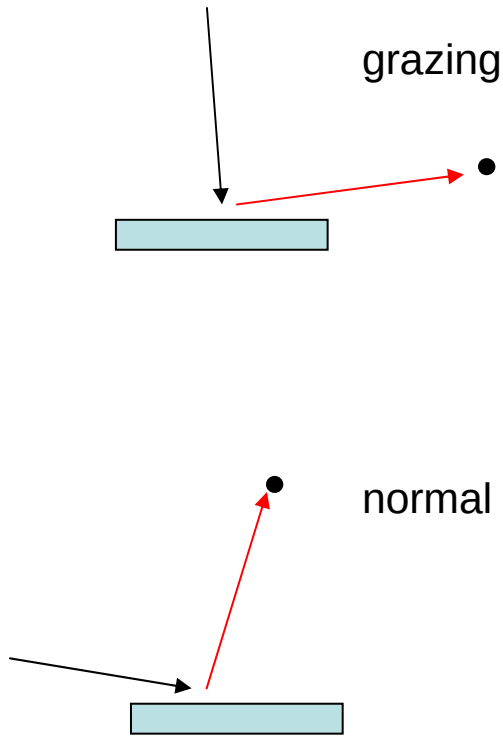
$$\Gamma = 80\text{meV(HWHM)}$$

$$\text{Experimental resolution} = 120\text{meV(FWHM)}$$

Y. Takata et al. Phys. Rev. B **75**, 233404 (2007).

Emission angle dependence（7940eV, RT）





Y. Takata et al. Phys. Rev. B **75**, 233404 (2007).

Why?

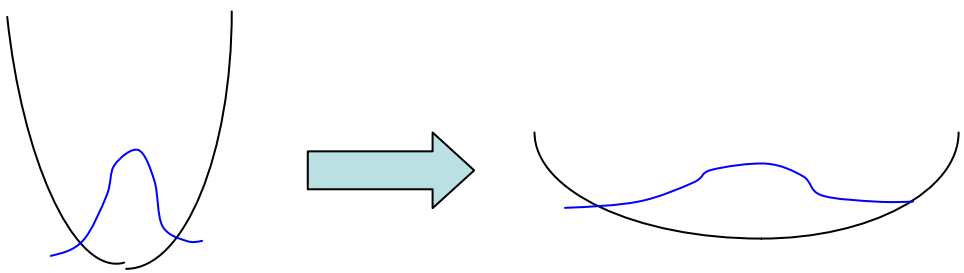
$$S_\lambda = \frac{\Delta E}{\hbar\omega_{\lambda,D}}$$ Effective electron-phonon coupling const.

if $S_\lambda >> 1$

Peak shift = $S_\lambda \hbar\omega_{\lambda,D} = \Delta E$

Width = $\sqrt{S_{\lambda,D}}\hbar\omega_{\lambda,D} = \sqrt{\Delta E \hbar\omega_{\lambda,D}} \propto \sqrt{\omega_{\lambda,D}}$

Doppler broadening is larger for high ω



coordinate space **Momentum space**

Recoil effect is universal

Neutron scatterings

Electron scatterings

HX photoelectron emission

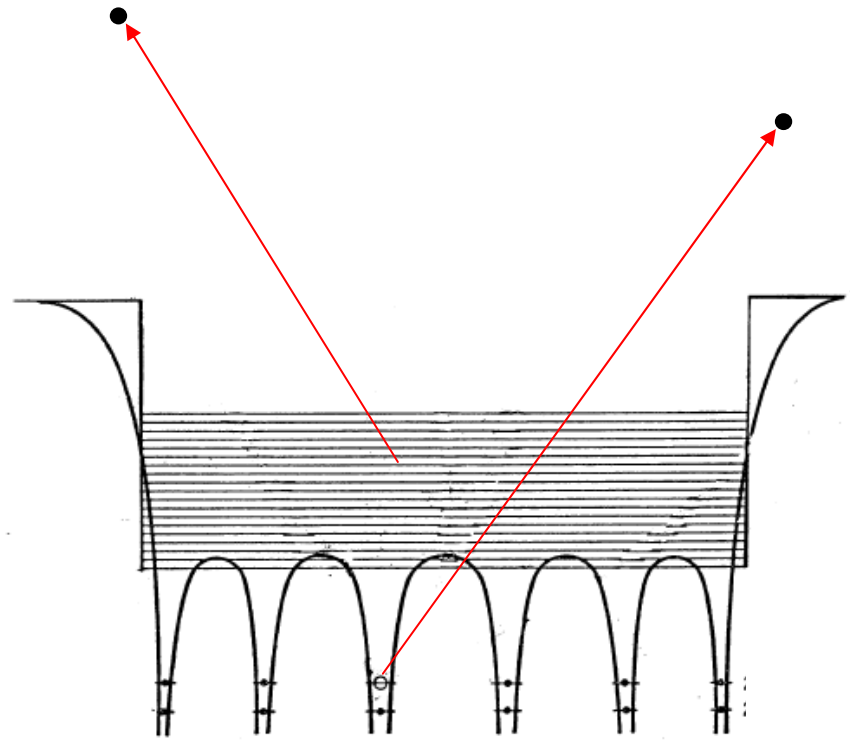
....etc

But,

the photoelectron carries also information on the electronic state it has occupied initially.

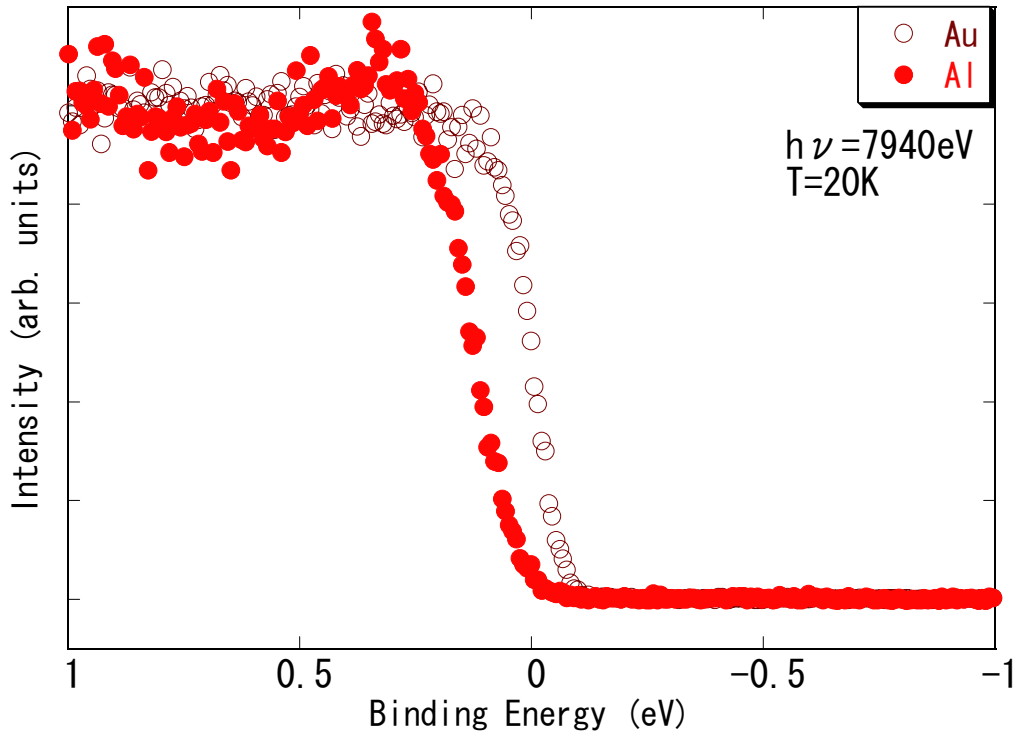
→ The recoil effect in valence level XPS will be much more interesting !

Recoil effect in Bloch electrons?



Which atom(s) receives the recoil momentum?

Striking recoil shift does exist!

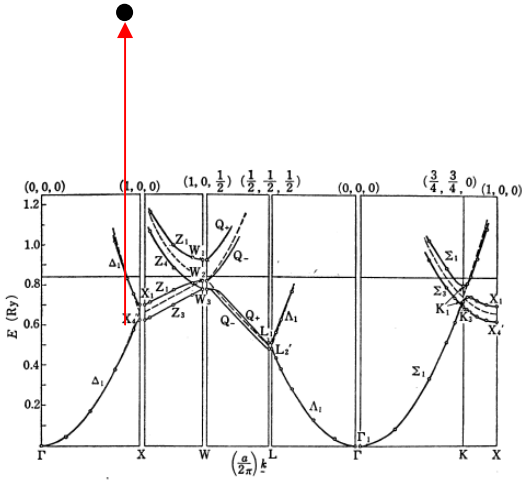


Au=197

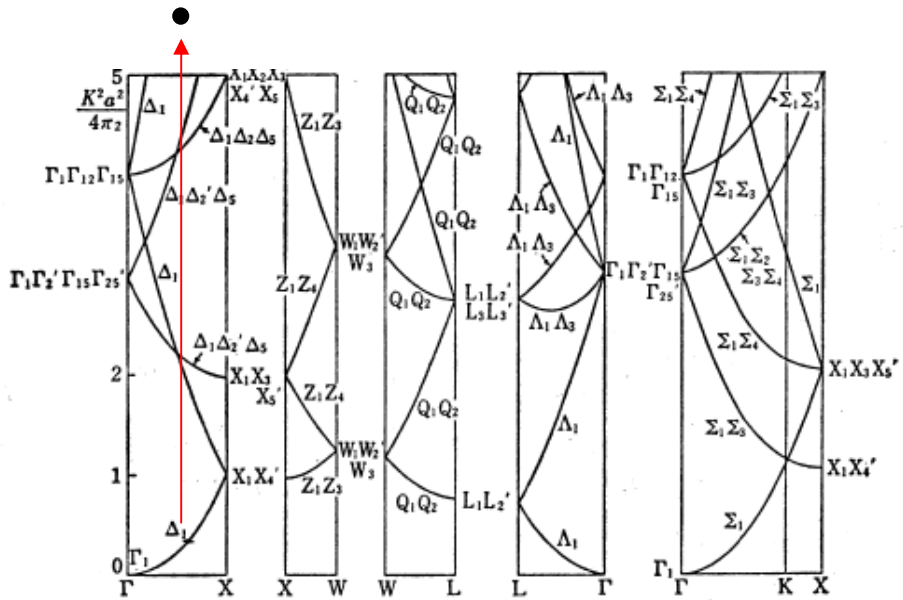
Al=27

Y. Takata et al.

Even nearly free electrons see lattice structure!



Al (pseudopotential)



Free electron (FCC)

$$\frac{p_{photoelectron}}{p_{Fermi}} = \sqrt{\frac{8\times10^3\,\mathrm{eV}}{11\,\mathrm{eV}}} \approx 27$$

Momentum is not conserved.

existence of HX photoemission ➡ existence of Umklapp process

➡ electrons see lattice

Recoil Effect of Bloch Electrons

$$H_e = \sum_{i,j} t(\vec{R}_i - \vec{R}_j) a_i^+ a_j$$

Wannier function

$$\varphi_i(\vec{r}) \equiv \langle \vec{r} | a_i^+ | 0 \rangle = \varphi(\vec{r} - \vec{R}_i) \qquad \vec{R}_i = \vec{R}_i^{\,0} + \vec{u}_i$$

$$H_L = \sum_j \frac{\vec{P}_j}{2M} + \sum_{i \neq j} V(\vec{R}_i - \vec{R}_j) \quad \Rightarrow \quad H_L = \sum_{q,\lambda} \hbar\omega_{q,\lambda} \left(b_{q,\lambda}^+ b_{q,\lambda} + \frac{1}{2} \right)$$

$$|\psi_k\rangle = \sum_i c_i a_i^+ |0\rangle$$

$$\psi_k(\vec{r}) = \sum_i e^{ikR_i^0} \varphi(\vec{r} - \vec{R}_i) \qquad c_i = \frac{1}{\sqrt{N}} e^{ikR_i^0}$$

Bloch function

$$I\left(\vec{k},\vec{K}\right)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dte^{-\Gamma|t|/\hbar-i\left(E-h\nu-\varepsilon_{\vec{k}}\right)t/\hbar}\sum_{j}e^{i\left(\vec{K}-\vec{k}\right)\cdot\vec{R}_j^0}F_j(t)$$

$$F_j(t)=\left\langle e^{i\vec{K}\cdot\vec{u}_j(t)}e^{-\vec{K}\cdot\vec{u}_0}\right\rangle$$

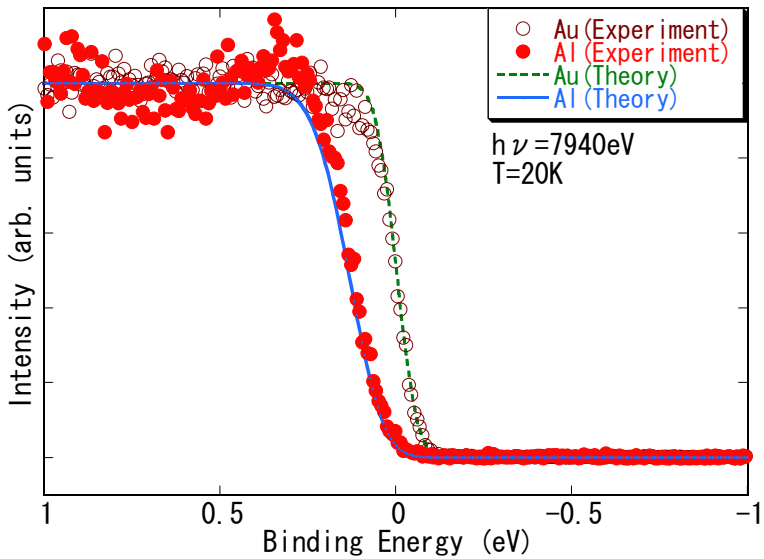
dynamical structure factor

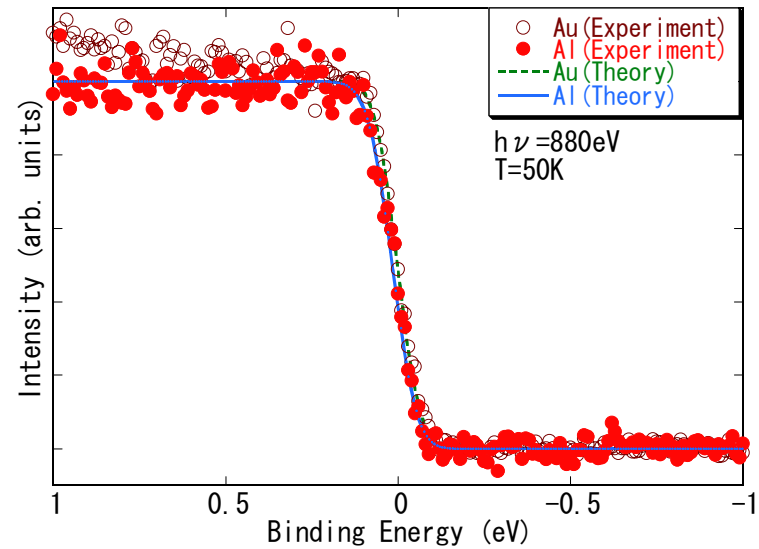
Off diagonal terms are negligible.

$$I\left(\varepsilon_{\vec{k}},E_{\vec{K}}\right)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dte^{-\Gamma|t|/\hbar-i\left(E-h\nu-\varepsilon_{\vec{k}}\right)t/\hbar}F_0(t)$$

It seems that a single atom receives the recoil momentum.

⇨ Shrinkage of the wave function by the measurement?





Recoil effect of photoelectrons in the Fermi edge of simple metals
Y. Takata et al., Phys. Rev. Lett, **101, 137601(2008)**

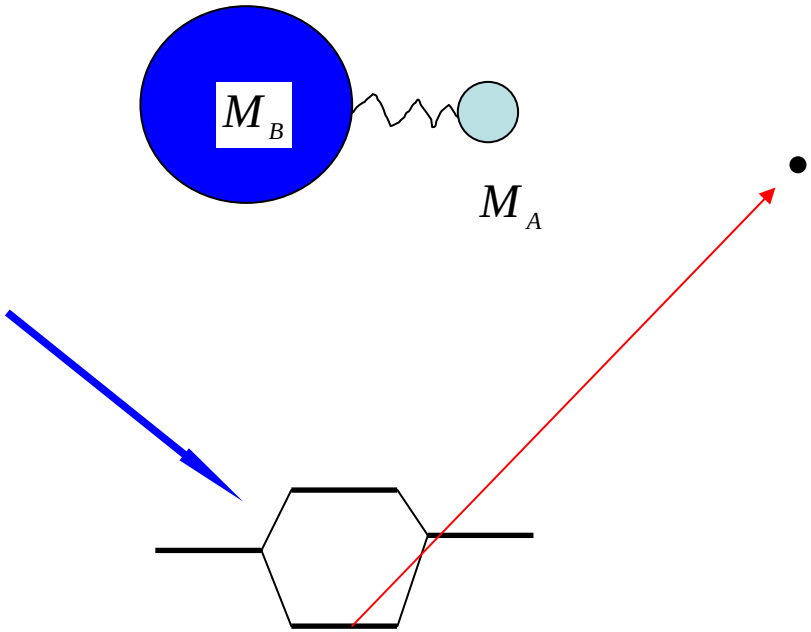
Origins of broadening

1. **Temperature (Fermi distribution)**
2. **Resolution (Gaussian broadening)**
3. **Recoil effect (New!)**

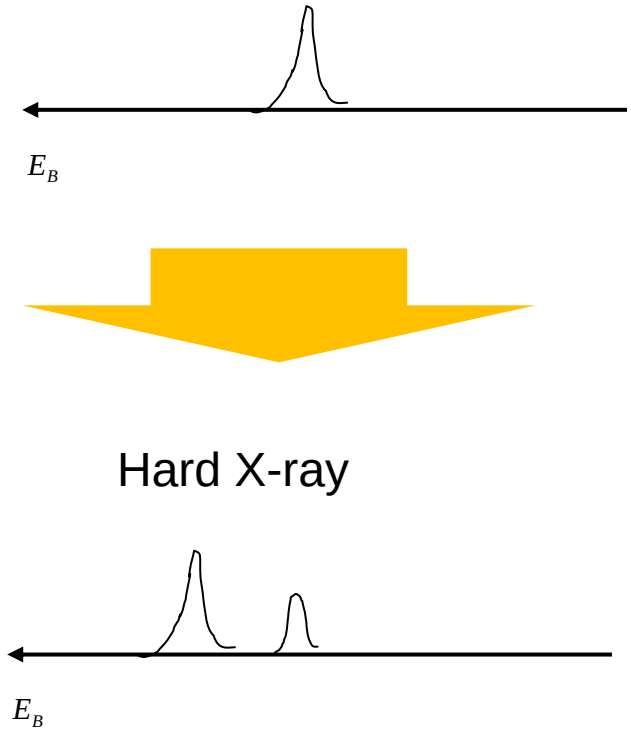
Next Target

How is it in compounds?

Recoil splitting ?

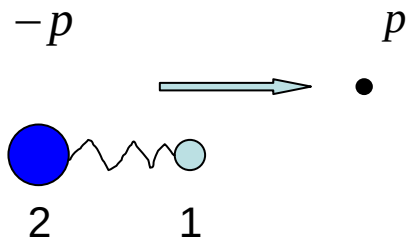


Soft X-ray

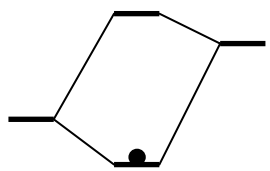


Hard X-ray

Model 1 diatomic molecule



a



b

$$H = H_e + H_a$$

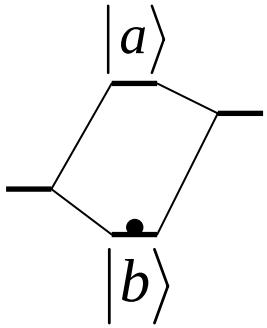
$$H_e = \varepsilon_1 |1\rangle\langle 1| + \varepsilon_2 |2\rangle\langle 2| + \Delta\left(|1\rangle\langle 2| + |2\rangle\langle 1|\right)$$

$$H_a = \frac{P_1^{\,2}}{2M_1} + \frac{P_2^{\,2}}{2M_2} + V\left(|X_1 - X_2|\right)$$

$$H_I = p\left(A + A^+\right), \quad p = -i\hbar\frac{d}{dx}$$

$$\varphi_1(x) \equiv \langle x|1\rangle = \varphi_1(x - X_1)$$

$$\varphi_2(x) \equiv \langle x|2\rangle = \varphi_2(x - X_2)$$



$$\varphi_1(x) \equiv \langle x|1\rangle = \varphi_1(x - X_1)$$
$$\varphi_2(x) \equiv \langle x|2\rangle = \varphi_2(x - X_2)$$

Adiabatic approx.

$$|a\rangle = -\beta|1\rangle + \alpha|2\rangle$$
$$|b\rangle = \alpha|1\rangle + \beta|2\rangle$$

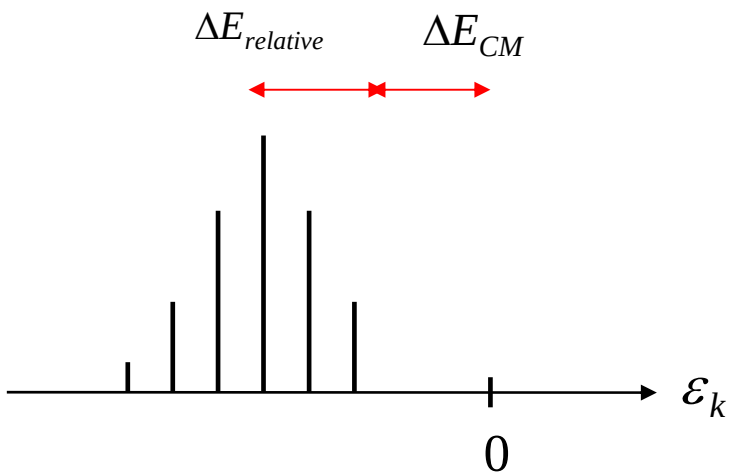
$$|\Psi_i\rangle = |h\nu\rangle \otimes |b\rangle \otimes |g\rangle \otimes |0\rangle$$

$$|\Psi_f\rangle = |vac\rangle \otimes |k\rangle \otimes |K\rangle \otimes |m\rangle$$

$$I(\varepsilon_k) = \sum_m \sum_K \left|\langle m, K, k|p|0, g, b\rangle\right|^2 \delta(h\nu + \varepsilon_b - \varepsilon_k - E_K - \varepsilon_m)$$

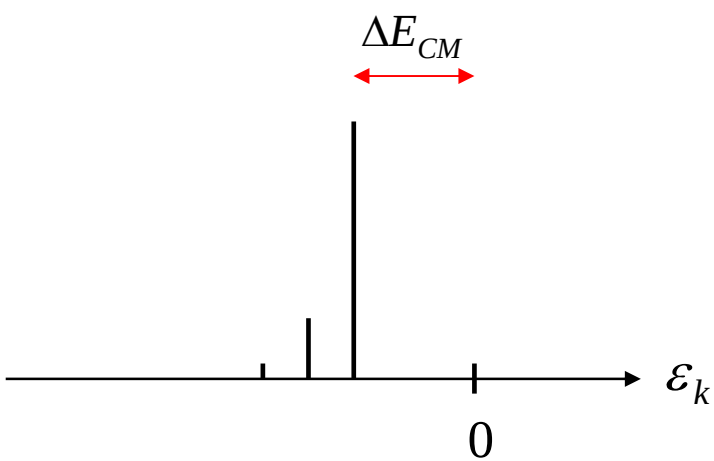
$$I(\varepsilon_k) = \alpha^2 |\varsigma_1|^2 I_1(\varepsilon_k) + \beta^2 |\varsigma_2|^2 I_2(\varepsilon_k) + \text{cross terms}$$

$$\varsigma_i = \int dx\, e^{-ikx} \left(-i \frac{d}{dx} \right) \varphi_i(x)$$



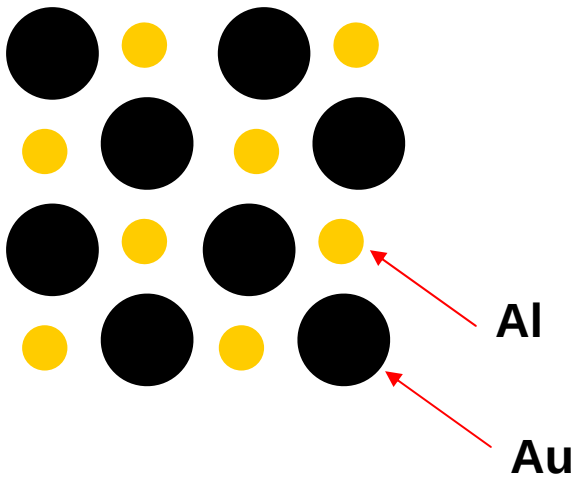
$$\times \alpha^2 |\varsigma_1|^2$$

$$+$$



$$\times \beta^2 |\varsigma_2|^2$$

Model 2 composite metal



Heavy atom and light atom

In a unit cell

Bloch function

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{N}} \sum_j \left\{ C_A(\vec{k}) w_1\left(\vec{r} - \underline{\vec{R}_j}^{\,A}\right) + C_B(\vec{k}) w_2\left(\vec{r} - \underline{\vec{R}_j}^{\,B}\right) \right\} e^{i\vec{k}\cdot\vec{R}^0{}_j}$$

Atomic positions are dynamic variables (not parameters).

Local DOS

$$D(\varepsilon) = D_A(\varepsilon) + D_B(\varepsilon)$$

Contribution from A site

$$I_A(E,\varepsilon) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i(E-h\nu-\varepsilon)t/\hbar} F_A(t)$$

$$F_A(t) = \exp\left[\sum_{q\lambda}\left|\alpha_{q\lambda}^{A}\right|^2 \left\{(2n_{q\lambda}+1)(\cos\omega_{q\lambda}t - 1) - i\sin\omega_{q\lambda}t\right\}\right]$$

$$\left|\alpha_{q\lambda}^{A}\right|^2 = \left(\frac{\hbar}{2N\underline{M_A}\omega_{q\lambda}}\right)\left|\vec{k}\cdot\eta_{q\lambda}\right|^2$$

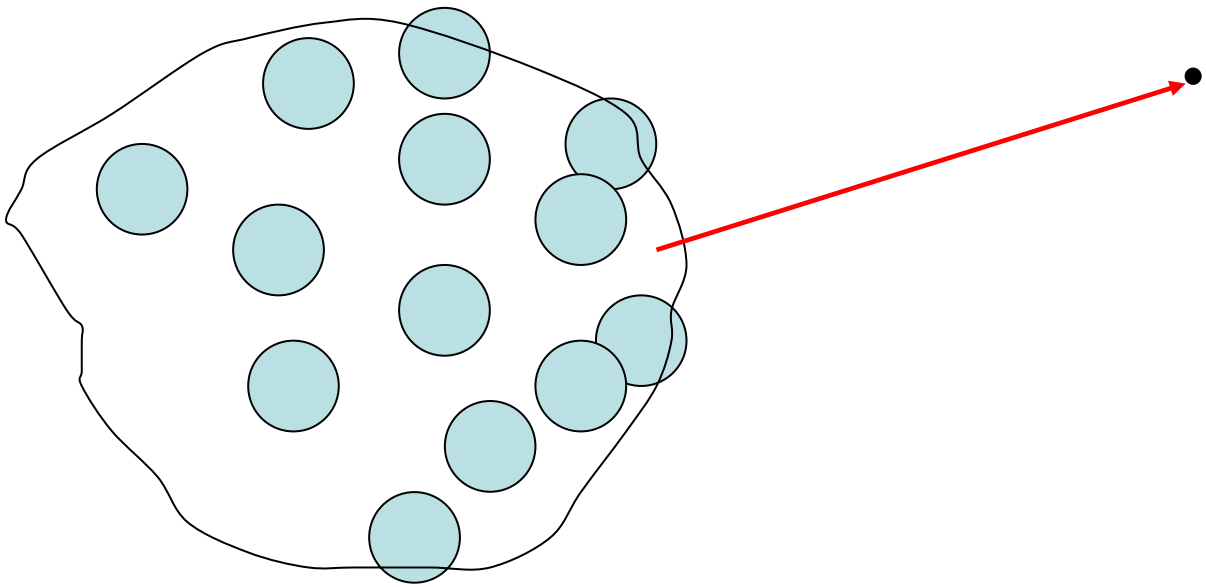
Contribution from B site $A \rightarrow B$

$$I(E) = \int_{-\infty}^{\infty} d\varepsilon\, f(\varepsilon)\left\{\left|\varsigma_A\right|^2 D_A(\varepsilon) I_A(E,\varepsilon) + \left|\varsigma_B\right|^2 D_B(\varepsilon) I_B(E,\varepsilon)\right\}$$

Valence band PES may split due to recoil effect!

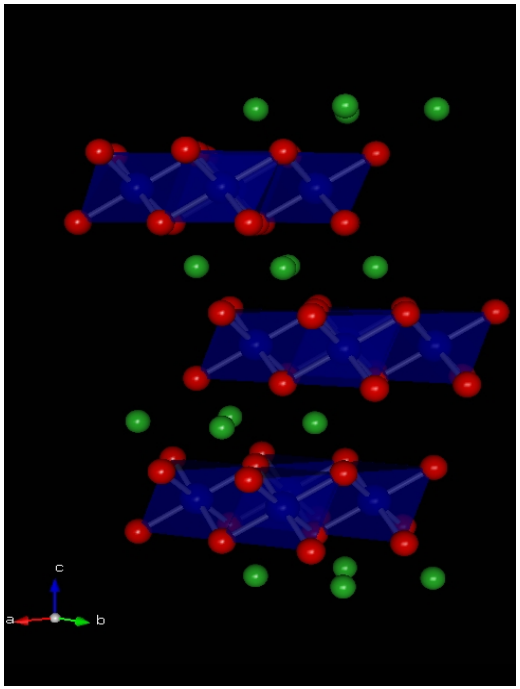
How about amorphous materials?

Which atom(s) receive recoil momentum?



Recoil effect as a probe of local atomic environment

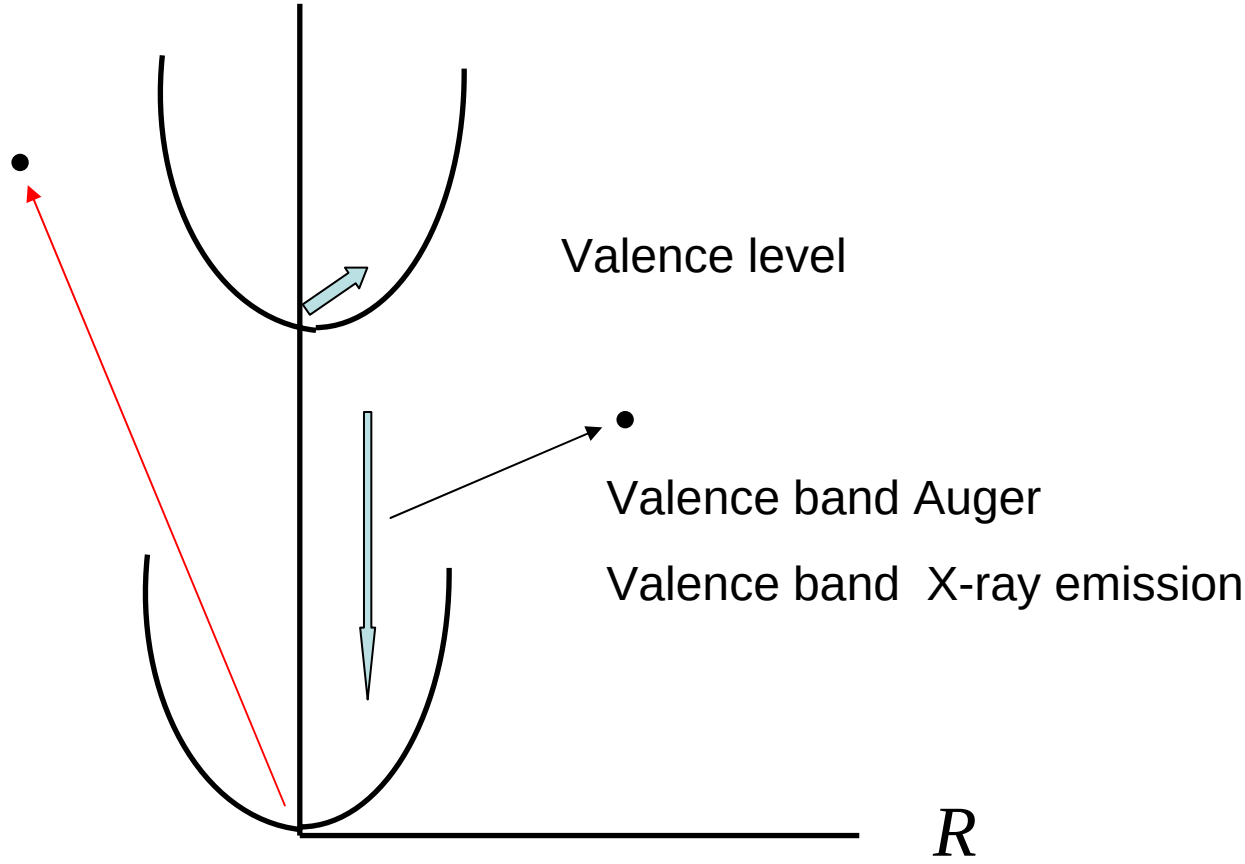
$LiCoO_2$



Yokohama CU, Yamada Lab.

Lithium ion battery

Second Order Effect of Recoil

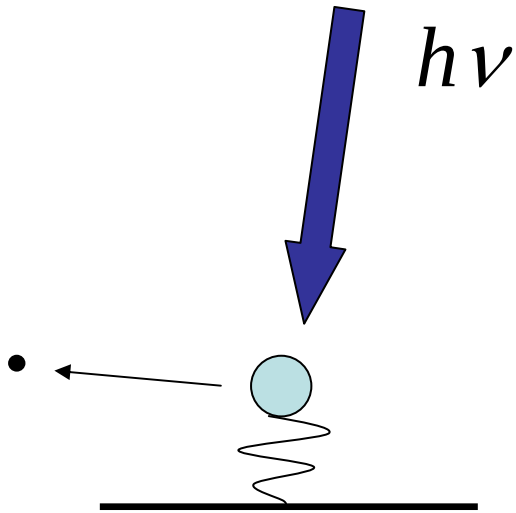


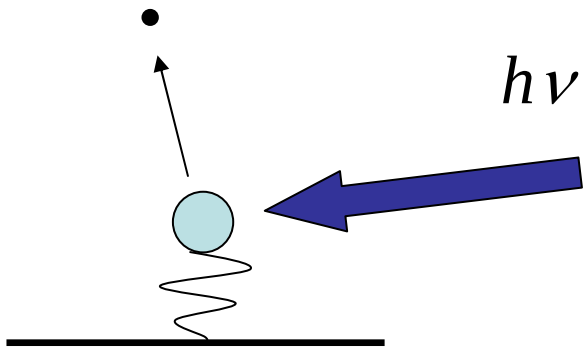
Recoil Spectroscopy of Local Vibration

site selective

angle selective

level selective





Message of this work

1. Recoil effect in x-ray photoemission is a purely kinematic effect.

   Only the adiabatic approximation is needed theoretically.

2. Line shape in core level recoil spectra carries information of the

   rigidity of the atomic environment. (Doppler broadening)

3. Even Bloch electrons show recoil effect. (From which atom was it ejected?)

4. Valence spectra may split due to recoil effect.

→ Recoil Spectroscopy, a new tool?