P#10: Raspršenje X-zraka i neutrona na kristalima

Fizika čvrstog stanja 1

predavanja 2021

Klasična teorija raspršenja X-zraka

$$\frac{d\sigma}{d\Omega} = C\,\frac{r'^2\langle|\vec{E}'|^2\rangle}{|\vec{E}|^2}\,, \qquad C = k/k'$$

Kvantna teorija

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{mc^2}\right)^2 \frac{1}{2}(1+\cos^2\theta)\, V S(\vec{q})$$

Statički strukturni faktor

$$S(\vec{q}) \equiv \langle n(0)\, n^*(0)\rangle_{\vec{q}} = \int_V d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} \langle n(\vec{r},t=0)\, n^*(0,t=0)\rangle$$

$$n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2 f(\varepsilon_i)$$

Udarni presjek razlučiv i po energiji

$$\frac{d\sigma}{d\Omega d\omega} = \left(\frac{e^2}{mc^2}\right)^2 \frac{1}{2}(1+\cos^2\theta)\, V\, S(\vec{q},\omega)$$

Dinamički strukturni faktor

$$S(\vec{q},\omega) = \langle n n^* \rangle_{\vec{q}\omega}$$

$$= \int_V d\vec{r} \int_{-\infty}^{\infty} dt\, e^{-i\vec{q}\vec{r}+i\omega t} \langle n(\vec{r},t)\, n^*(0,0)\rangle$$

Monoatomske rešetke - gustoća naboja elektrona

$$n(\vec{r}) = \sum_n n_a(\vec{r} - \vec{R}_n - \vec{u}_n)$$

$$n(\vec{q}) = \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}}\, n(\vec{r}), \qquad \vec{r}_n(t) = \vec{R}_n + \vec{u}_n(t)$$

"Atomski" predfaktor

$$n(\vec{q}) = \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} \sum_n n_a(\underbrace{\vec{r} - \vec{r}_n}_{\vec{s}})$$

$$= \sum_n e^{-i\vec{q}\cdot\vec{r}_n} \underbrace{\int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}}\, n_a(\vec{r})}_{\tilde{f}(\vec{q}) = f(\vec{q})/a(\vec{q})}$$

$$n(\vec{q}) = \tilde{f}(\vec{q}) \sum_n e^{-i\vec{q}\cdot(\vec{R}_n + \vec{u}_n)}$$

(Obična) korelacijska funkcija

$$\langle n(\vec{q},0)\, n^*(\vec{q}',0)\rangle = \int_V d\vec{r} \int_V d\vec{r}\,' \, e^{-i\vec{q}\cdot(\vec{r}-\vec{r}\,')} \langle n(\vec{r},0)\, n^*(\vec{r}\,',0)\rangle$$

$$= V \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} \langle n(\vec{r},0)\, n^*(0,0)\rangle = V \langle n n^* \rangle_{\vec{q}}$$

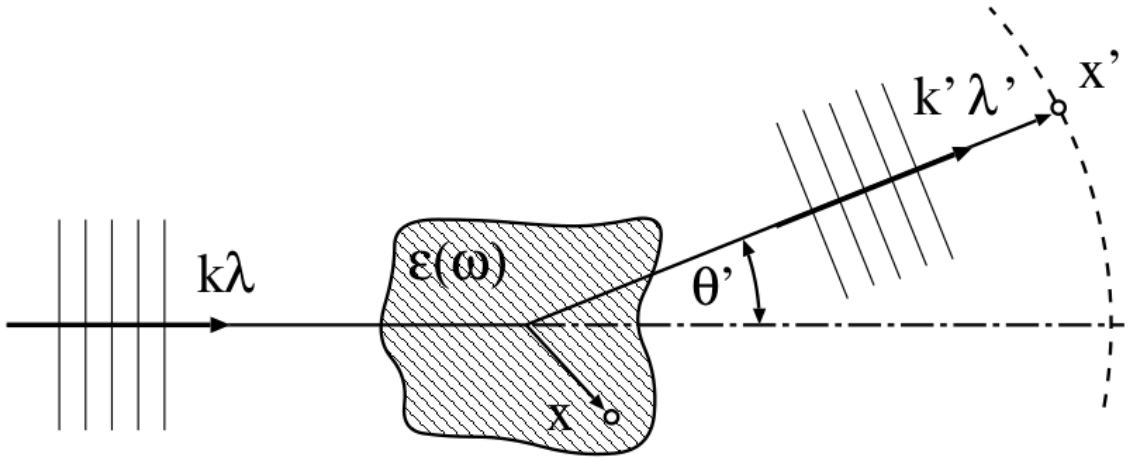
Statički strukturni faktor

$$V S(\vec{q}) = \langle n(\vec{q},0)\, n^*(\vec{q},0)\rangle \equiv \langle |n(\vec{q})|^2 \rangle$$

$$= |\tilde{f}(\vec{q})|^2 \underbrace{\left\langle \sum_{nn'} e^{i\vec{q}\cdot(\vec{r}_n - \vec{r}_{n'})} \right\rangle}_{\tilde{S}(\vec{q})}$$

Udarni presjek

$$\frac{d\sigma}{d\Omega} \propto \tilde{S}(\vec{q}), \quad \vec{q} = \vec{k} - \vec{k}'$$



Udarni presjek razlučiv i po energiji

$$\frac{d\sigma}{d\Omega d\omega} = \left(\frac{e^2}{mc^2}\right)^2 \frac{1}{2}(1+\cos^2\theta) V S(\vec{q},\omega)$$

Unutarnja energija fononskog podsustava

$$\Delta U^{ph} = \sum_{\vec{k}\lambda} \hbar\omega_{\vec{k}\lambda}\left[\langle n_{\vec{k}\lambda}\rangle + \frac{1}{2}\right]$$

kvantno statistički prosjek od H^{ph}

$$\Delta U^{ph} = \langle H^{ph}\rangle = \sum_{\vec{k}\lambda}\left(\frac{1}{2M}\langle|\vec{P}_{\vec{k}\lambda}|^2\rangle + \frac{M}{2}\omega_{\vec{k}\lambda}^2\langle|U_{\vec{k}\lambda}|^2\rangle\right)$$

Amplituda titranja moda $\vec{k}\lambda$

$$M\omega_{\vec{k}\lambda}^2\langle|U_{\vec{k}\lambda}|^2\rangle = \hbar\omega_{\vec{k}\lambda}\left(\langle n_{\vec{k}\lambda}\rangle + \frac{1}{2}\right)$$

$$\langle|U_{\vec{k}\lambda}|^2\rangle = \frac{\hbar}{M\omega_{\vec{k}\lambda}}\left(\langle n_{\vec{k}\lambda}\rangle + \frac{1}{2}\right)$$

Realna amplituda pomaka

$$\vec{u}_n(t) = \sum_{\vec{k}} \frac{1}{2}\left[\vec{u}_{\vec{k}}(t) e^{i\vec{k}\cdot\vec{R}_n} + \vec{u}^{\,*}_{\vec{k}}(t) e^{-i\vec{k}\cdot\vec{R}_n}\right]$$

$$= \sum_{\vec{k}\lambda} u_{\vec{k}\lambda} \vec{\epsilon}_{\vec{k}\lambda} e^{i(\vec{k}\cdot\vec{R}_n - \omega_{\vec{k}\lambda} t)}$$

10.2 Raspršenje X-zraka

10.2.1 Laueova formula

Rešetka koja miruje ($\vec{r}_n = \vec{R}_n$)

$$\tilde{S}(\vec{q}) = \left\langle \sum_{nn'} e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_{n'})} \right\rangle = \underbrace{\sum_{n'}}_{N} \underbrace{\sum_{n} e^{i\vec{q}\cdot\vec{R}_n}}_{N\,\delta_{\vec{q},\vec{K}_m}}$$

Laueova formula

$$\vec{q} = \vec{k} - \vec{k}' = \vec{K}_m$$

10.2.2 Razvoj po malim pomacima

$$\tilde{S}(\vec{q}) = \left\langle \sum_{nn'} e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_{n'})} e^{i\vec{q}\cdot(\vec{u}_n - \vec{u}_{n'})} \right\rangle$$

$$= \left\langle \sum_{nn'} e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_{n'})} \right\rangle + \left\langle \sum_{nn'} e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_{n'})} i\vec{q}\cdot(\vec{u}_n - \vec{u}_{n'}) \right\rangle$$

$$+ \left\langle \sum_{nn'} e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_{n'})} \frac{1}{2}\left[i\vec{q}\cdot(\vec{u}_n - \vec{u}_{n'})\right]^2 \right\rangle + \dots$$

$$\left\langle \sum_{nn'} e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_{n'})} i\vec{q}\cdot(\vec{u}_n - \vec{u}_{n'}) \right\rangle = N^2 \delta_{\vec{q},\vec{k}_m} i\vec{q}\cdot\left\langle \vec{u}_{\vec{k}_m} - \vec{u}^{*}_{\vec{k}_m} \right\rangle$$

$$= 0$$

Kvadratni doprinosi

$$-\frac{1}{2}\left\langle\left(\sum_n e^{i\vec{g}\cdot\vec{R}_n}(\vec{g}\cdot\vec{u}_n)\underbrace{\sum_{n'} e^{-i\vec{g}\cdot\vec{R}_{n'}}}_{\hookrightarrow N\delta_{\vec{g},\vec{k}_m}}+\text{c.c.}\right)\right\rangle$$

$$\sum_n \underbrace{e^{i\vec{k}_m\cdot\vec{R}_n}}_{=1}(\vec{k}_m\cdot\vec{u}_n)^2 = \sum_{\vec{k}\lambda}\sum_{\vec{k}'\lambda'}\underbrace{\sum_n e^{i(\vec{k}+\vec{k}')\cdot\vec{R}_n}}_{N\delta_{\vec{k},-\vec{k}'}}(\vec{k}_m\cdot\vec{\epsilon}_{\vec{k}\lambda})$$

$$\times(\vec{k}_m\cdot\vec{\epsilon}_{\vec{k}'\lambda'})\,u_{\vec{k}\lambda}u_{\vec{k}'\lambda'}$$

$$= N\sum_{\vec{k}\lambda\lambda'}(\vec{k}_m\cdot\vec{\epsilon}_{\vec{k}\lambda})(\vec{k}_m\cdot\vec{\epsilon}_{-\vec{k}\lambda'})\,u_{\vec{k}\lambda}u_{-\vec{k}\lambda'}$$

Bilinearni doprinos

$$\sum_n e^{i\vec{q}\cdot\vec{R}_n}\, \vec{q}\cdot\vec{u}_n = \sum_{k\lambda} \underbrace{\sum_n e^{i\vec{q}\cdot\vec{R}_n} e^{i\vec{k}\cdot\vec{R}_n}}_{\hookrightarrow\ N\,\delta_{\vec{q},-\vec{k}}} (\vec{q}\cdot\vec{\epsilon}_{k\lambda})\, u_{k\lambda}$$

$$= N \sum_\lambda (\vec{q}\cdot\vec{\epsilon}_{-\vec{q}\lambda})\, u_{-\vec{q}\lambda}$$

Harmonička aproksimacija

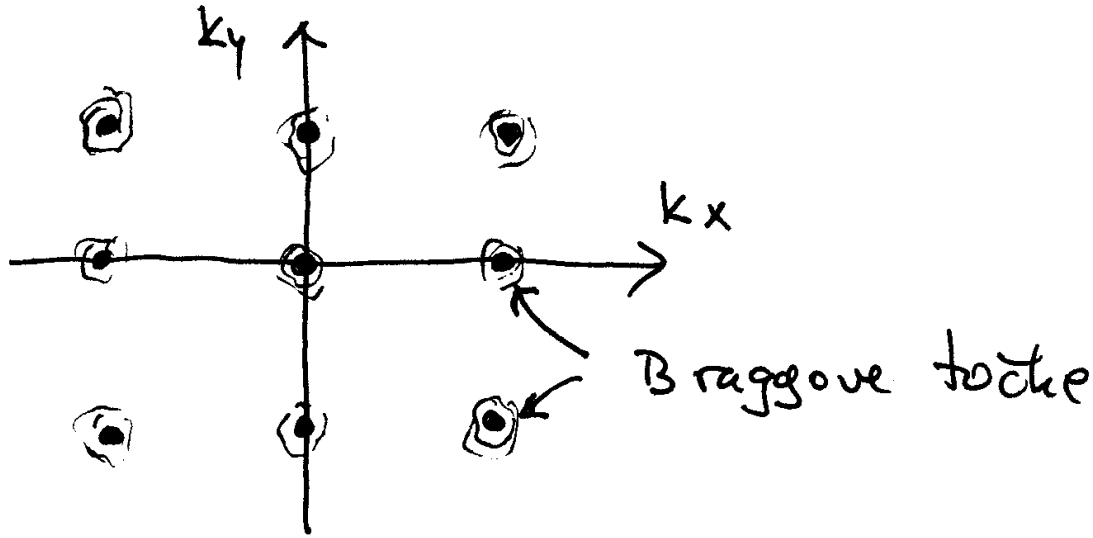
$$\langle u_{k\lambda}\, u_{-k\lambda'}\rangle = \delta_{\lambda,\lambda'} \quad \langle |u_{k\lambda}|^2\rangle$$

Ukupni rezultat

$$\tilde{S}(\vec{q}) = N^2 S_{\vec{q},\vec{K}_m}\left(1 - \sum_{\vec{k}\lambda\lambda'} (\vec{q}\cdot\vec{\epsilon}_{\vec{k}\lambda})(\vec{q}\cdot\vec{\epsilon}_{-\vec{k}\lambda'}) \langle U_{\vec{k}\lambda} U_{-\vec{k}\lambda'}\rangle\right)$$

$$+ N^2 \sum_{\lambda\lambda'} (\vec{q}\cdot\vec{\epsilon}_{\vec{q}\lambda})(\vec{q}\cdot\vec{\epsilon}_{-\vec{q}\lambda'}) \langle U_{\vec{q}\lambda} U_{-\vec{q}\lambda'}\rangle + \cdots$$

Preraspodjela intenziteta Braggovih točaka



QM identitet

$$\langle e^A e^B \rangle = e^{1/2 \langle A^2 + 2AB + B^2 \rangle}$$

A i B linearni u $\vec{u}_n$ i/ili $\vec{P}_n$, u harmoničkoj aproksimaciji

Statički strukturni faktor

$$\tilde{S}(\vec{q}) = \sum_{nn'} e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_{n'})} \langle e^{i\vec{q}\cdot(\vec{u}_n - \vec{u}_{n'})} \rangle$$

$$\langle e^{i\vec{q}\cdot(\vec{u}_n - \vec{u}_{n'})} \rangle = \exp\left\{ -\frac{1}{2} \left[\langle (\vec{q}\cdot\vec{u}_n)^2 \rangle + \langle (\vec{q}\cdot\vec{u}_{n'})^2 \rangle - 2\langle (\vec{q}\cdot\vec{u}_n)(\vec{q}\cdot\vec{u}_{n'}) \rangle \right] \right\}$$

$$\left\langle e^{i\vec{g}\cdot(\vec{u}_n-\vec{u}_{n'})}\right\rangle = \exp\left\{-\frac{1}{2}\left[\left\langle(\vec{g}\cdot\vec{u}_n)^2\right\rangle + \left\langle(\vec{g}\cdot\vec{u}_{n'})^2\right\rangle - 2\left\langle(\vec{g}\cdot\vec{u}_n)(\vec{g}\cdot\vec{u}_{n'})\right\rangle\right]\right\}$$

$$= 1 - \frac{1}{2}\left[\left\langle(\vec{g}\cdot\vec{u}_n)^2\right\rangle + \left\langle(\vec{g}\cdot\vec{u}_{n'})^2\right\rangle\right] + \left\langle(\vec{g}\cdot\vec{u}_n)(\vec{g}\cdot\vec{u}_{n'})\right\rangle + \dots$$

Translacijska invarijantnost (u prostoru)

$$\left\langle(\vec{g}\cdot\vec{u}_n)^2\right\rangle = \left\langle(\vec{g}\cdot\vec{u}_{n'})^2\right\rangle = \left\langle(\vec{g}\cdot\vec{u}_0)^2\right\rangle = 2W(\vec{g})$$

$$\tilde{S}(\vec{g}) = e^{-2W(\vec{g})} \sum_{nn'} e^{i\vec{g}\cdot(\vec{R}_n-\vec{R}_{n'})} \exp\left\{\left\langle(\vec{g}\cdot\vec{u}_n)(\vec{g}\cdot\vec{u}_{n'})\right\rangle\right\}$$

$\sim$ Debye-Wallerov faktor

$$\equiv N e^{-2W(\vec{g})} \sum_n e^{i\vec{g}\cdot\vec{R}_n} \exp\left\{\left\langle(\vec{g}\cdot\vec{u}_n)(\vec{g}\cdot\vec{u}_0)\right\rangle\right\}$$

10.3.1 Intenzitet Braggovih točaka

Elastični signal (Braggove točke)

$$\tilde{S}_{(0)}(\vec{g}) = e^{-2W(\vec{g})} N^2 S_{\vec{g},\vec{k}_m}$$

Koliko je redukcija intenziteta

$$1 - \sum_{\vec{k}\lambda} [\vec{g}\cdot\vec{\epsilon}_{\vec{k}\lambda}]^2 \langle |u_{\vec{k}\lambda}|^2 \rangle + \cdots = e^{-2W(\vec{g})}$$

Dinamički strukturni faktor

$$\tilde{S}(\vec{q},\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} \left\langle \sum_{nn'} e^{i\vec{q}\cdot(\vec{r}_n(t) - \vec{r}_{n'}(0))} \right\rangle$$

$$= \int_{-\infty}^{\infty} dt\, e^{i\omega t} \sum_{nn'} e^{i\vec{q}(\vec{R}_n - \vec{R}_{n'})} \left\langle e^{i\vec{q}\cdot(\vec{u}_n(t) - \vec{u}_{n'}(0))} \right\rangle$$

Translacijska invarijantnost (u $\vec{r}$ i t)

$$\tilde{S}(\vec{q},\omega) = N \sum_n e^{i\vec{q}\cdot\vec{R}_n} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \left\langle e^{i\vec{q}\cdot(\vec{u}_n(t) - \vec{u}_0(0))} \right\rangle$$

$$= e^{-2W(\vec{q})} N \sum_n e^{i\vec{q}\cdot\vec{R}_n} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \exp\left\{ \left\langle (\vec{q}\cdot\vec{u}_n(t))(\vec{q}\cdot\vec{u}_0) \right\rangle \right\}$$

10.4.1 Elastični doprinos

Elastični doprinos

$$\tilde{S}_{(0)}(\vec{q},\omega) = e^{-2W(\vec{q})} N^2 \delta_{\vec{q},\vec{K}_m} 2\pi\delta(\omega)$$

$$\tilde{S}_{(0)}(\vec{q}) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \tilde{S}_{(0)}(\vec{q},\omega) = e^{-2W(\vec{q})} N^2 \delta_{\vec{q},\vec{K}_m}$$

10.4.2 Apsorpcija i emisija jednog fonona

Apsorpcija / emisija fonona

$$\tilde{S}_{(1)}(\vec{\kappa},\omega) = e^{-2W(\vec{\kappa})} N \sum_n e^{i\vec{\kappa}\cdot\vec{R}_n} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle (\vec{\kappa}\cdot\vec{u}_n(t))(\vec{\kappa}\cdot\vec{u}_0)\rangle$$

↳ kako izračunati

Statička granica

$$\tilde{S}_{(1)}(\vec{\kappa}) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \tilde{S}_{(1)}(\vec{\kappa},\omega)$$

$$= \sum_\lambda N^2 [\vec{\kappa}\cdot\epsilon_{\vec{\kappa}\lambda}]^2 \frac{\hbar}{2M\omega_{\vec{\kappa}\lambda}} (2\langle n_{\vec{\kappa}\lambda}\rangle + 1)\, e^{-2W(\vec{\kappa})}$$

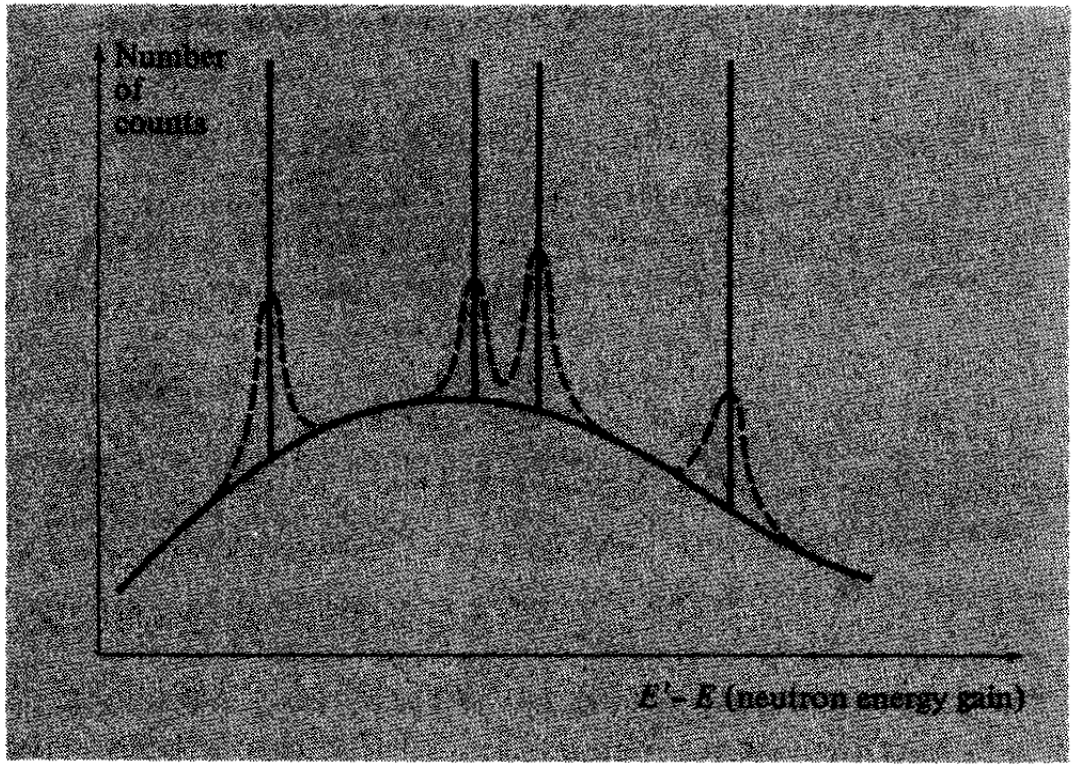
$$\tilde{S}_{(1)}(\vec{g},\omega) = e^{-2W(\vec{g})} N^2 \sum_{\lambda} [\vec{g}\cdot\epsilon_{\vec{g}\lambda}]^2 \frac{\pi}{2M\omega_{\vec{g}\lambda}} \Big[(\langle n_{\vec{g}\lambda}\rangle + 1) \times \delta(\omega + \omega_{\vec{g}\lambda}) + \langle n_{\vec{g}\lambda}\rangle 2\pi\delta(\omega - \omega_{\vec{g}\lambda}) \Big]$$

$\delta(\omega + \omega_{\vec{g}\lambda})$ → absorpcija jednog fonona

$\delta(\omega - \omega_{\vec{g}\lambda})$ → emisija jednog fonona

Dopriuri višeg reda

$\tilde{S}_{(2)}(\vec{\kappa}, \omega)$ – kontinuum signala poništenjem od $\hbar\omega_{\vec{k}} \pm \hbar\omega_{\vec{\kappa}-\vec{k}}$, $\vec{k}$ u IBZ



Kinetička energija neutrona

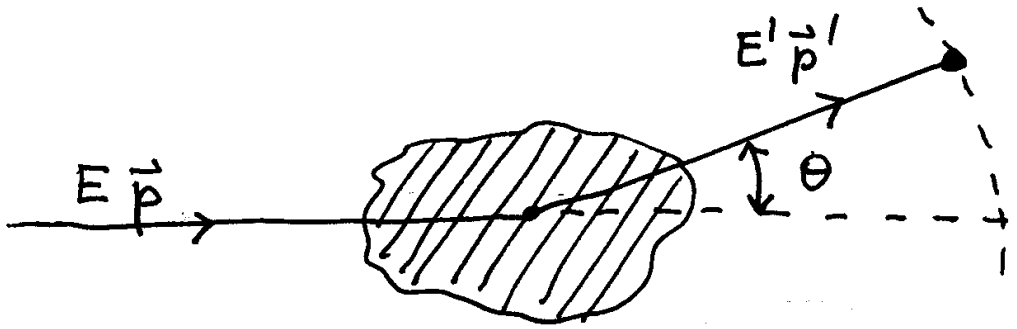
$(M_n/m \sim 1000)$ $\quad E_n = 2.1\,(Q[\text{Å}^{-1}])^2$ meV

Zakoni sačuvanja

energije $\quad E' - E = -\sum_{\vec{k}\lambda} \hbar\omega_{\vec{k}\lambda}\,\Delta n_{\vec{k}\lambda}$

$$\Delta n_{\vec{k}\lambda} = n'_{\vec{k}\lambda} - n_{\vec{k}\lambda}$$

impulsa $\quad \vec{p}' - \vec{p} = \underbrace{-\sum_{\vec{k}\lambda} \hbar\vec{k}\,\Delta n_{\vec{k}\lambda}}_{\text{kristalnog impulsa}} - \hbar\vec{K}_m$

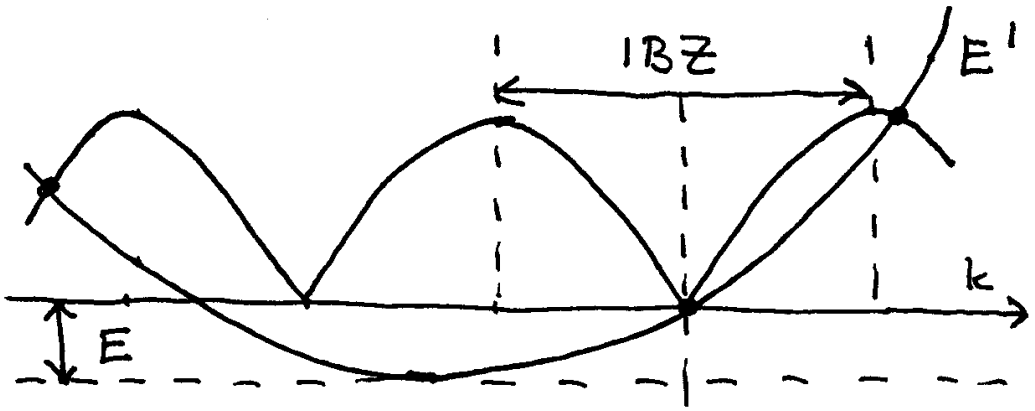


$$\vec{p} - \vec{p}' = \hbar \vec{q}$$

Apsorpcija / emisija jednog fonona

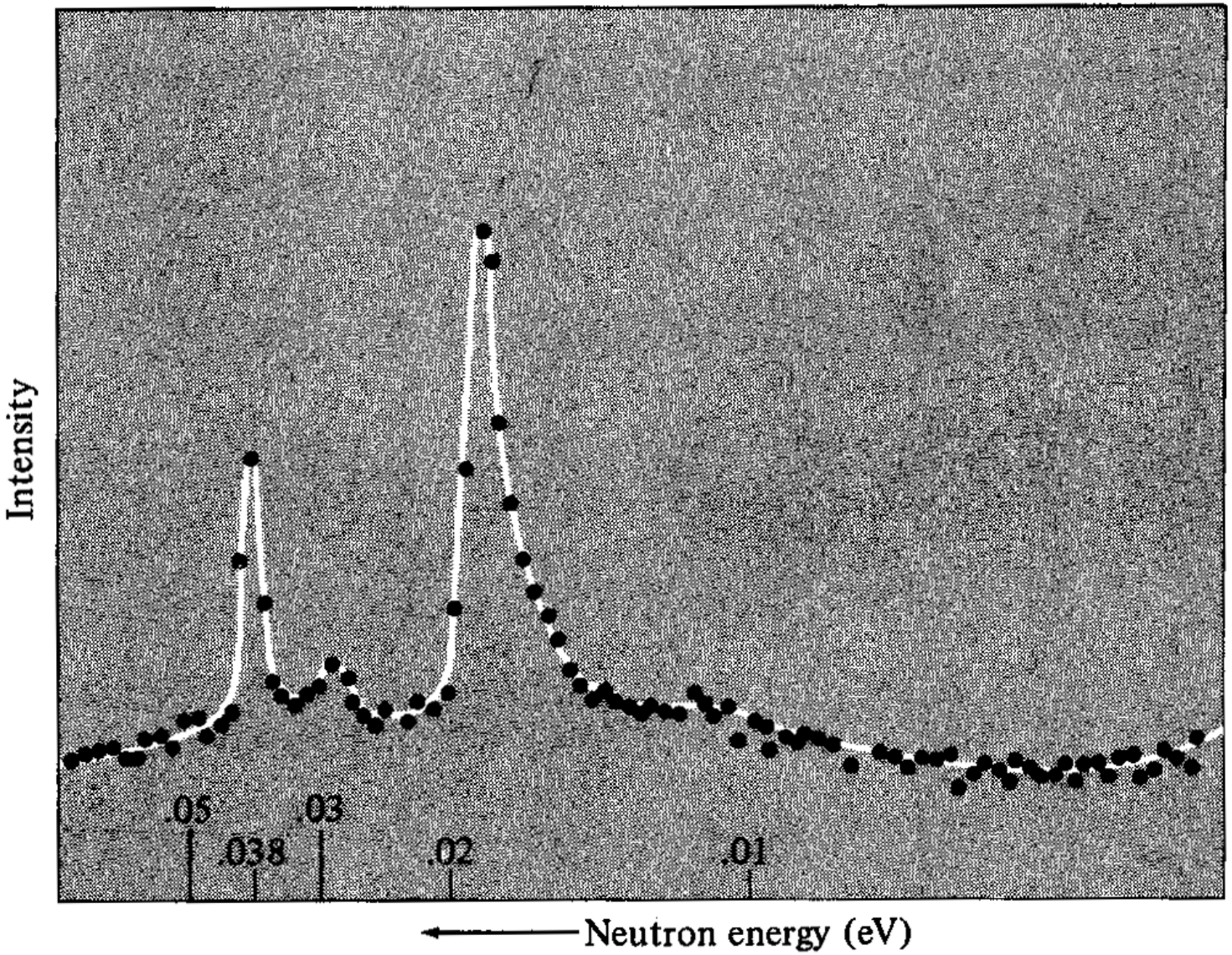
$$E' - E = \frac{p'^2}{2M_n} - \frac{p^2}{2M_n} = \pm \hbar \omega_{\vec{q}\lambda}$$

$$\vec{p} - \vec{p}' = \hbar \vec{q} = \hbar(\vec{k} + \vec{K}_m)$$

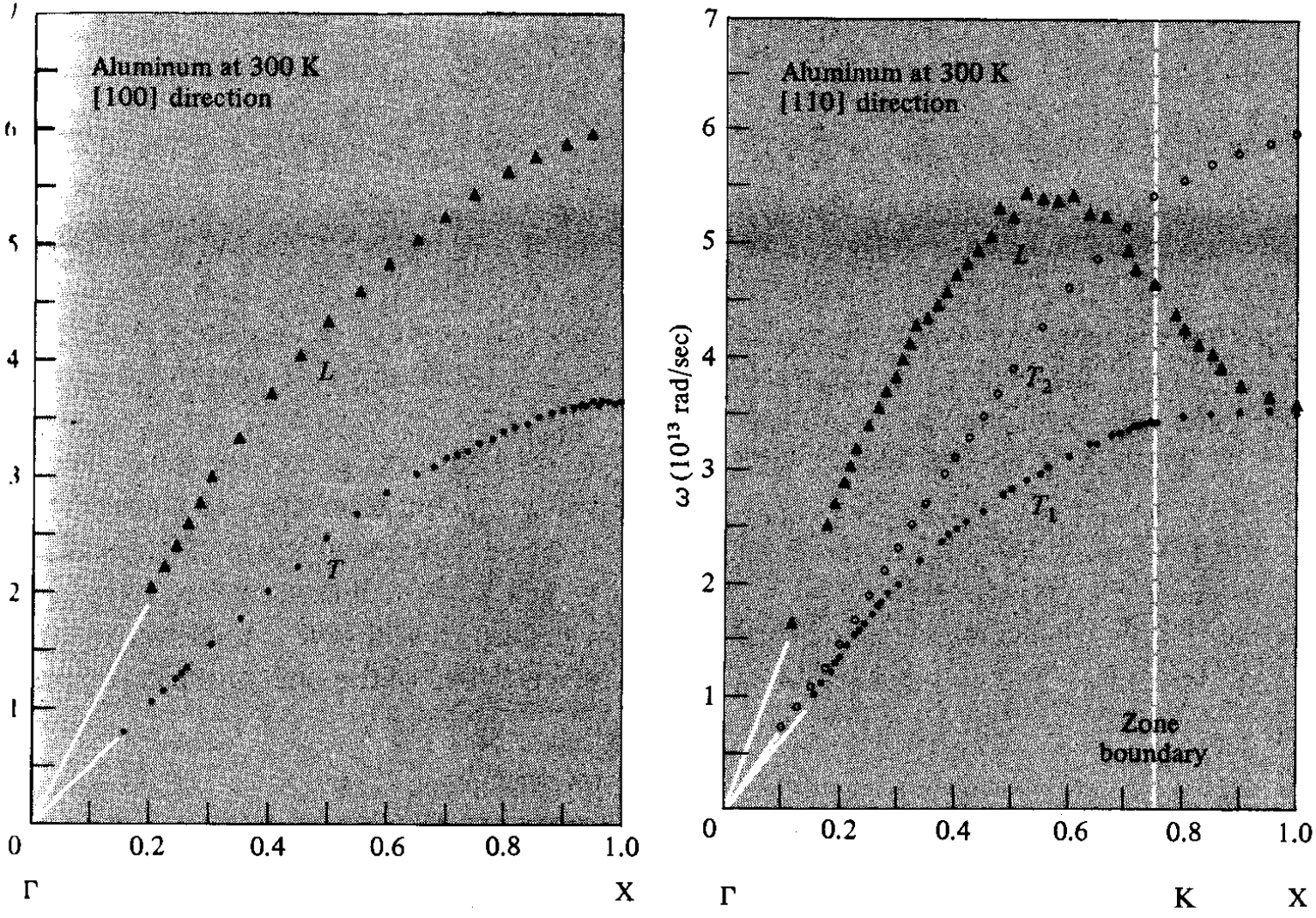


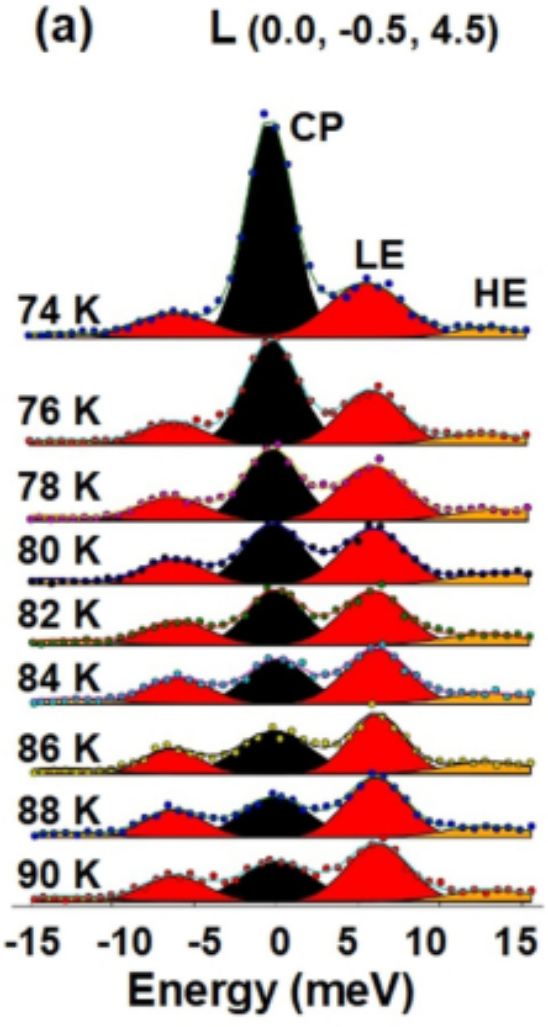
$$\hbar \omega_{k+\vec{K}_m \lambda} = \hbar \omega_{k\lambda}$$

Neelastično raspršenje neutrona



Neelastično raspršenje neutrona




(a)
L (0.0, -0.5, 4.5)
CP
LE
HE
74 K
76 K
78 K
80 K
82 K
84 K
86 K
88 K
90 K
-15
-10
-5
0
5
10
15
Energy (meV)

Literatura

1) Ziman, *Principles of the Theory of Solids*, §§ 2.7 - 2.9
2) Ashcroft & Mermin, *Solid State Physics*, §§ 24.U, 24.1, App. N
3) [Kupčić, *Elektrodinamika kontinuuma*, Pog. 13]