Chapter 15
Optical Processes and Excitons

Dielectric Function $\varepsilon(\omega, \mathbf{K})$

- Electronic Band Structure & optical spectroscopy
- At IR, Visible and UV, **K** dependence is normally ignored
- Real and Imaginary part of $\varepsilon(\omega)$

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$$

- Derives $\varepsilon(\omega)$ from experimentally accessible measurements of $R(\omega)$, $n(\omega)$ and $K(\omega)$

Reflectance/Reflectivity

- Reflectivity Coefficient $r(\omega)$

$$r(\omega) \equiv \frac{E(refl)}{E(inc)} \equiv \rho(\omega)\exp[i\theta(\omega)] \qquad (1)$$

- $r(\omega)$ at normal incidence

$$r(\omega) = \frac{n(\omega)+iK(\omega)-1}{n(\omega)+iK(\omega)+1} \qquad (2)$$

- Complex Refractive Index: $N(\omega)$

$$\sqrt{\varepsilon(\omega)} \equiv n(\omega)+iK(\omega) \equiv N(\omega) \qquad (3)$$

- Reflectance: $R(\omega)$

$$R \equiv \frac{E^*(refl)E(refl)}{E^*(inc)E(inc)} \equiv r^* r \equiv \rho^2 \qquad (6)$$

Obtain Dielectric Function from Experimental measurements

- R can be measured,

$$R(\omega) \Rightarrow \rho(\omega) \bigcup \theta(\omega) \Rightarrow r(\omega) \Rightarrow n(\omega) \,\&\, K(\omega)$$

KK relations (1) (2)

- Obtain dielectric function from $n(\omega)$ and $K(\omega)$

$$\varepsilon'(\omega) = n^2 - K^2 \qquad \varepsilon''(\omega) = 2nK$$

- By Eq. (3)

Kramers-Kronig Relation

- The KK relations establish a link between the real and imaginary part of the ***frequency-dependent*** *complex* "response function" of a ***linear system***.

$$\alpha'(\omega) = \frac{2}{\pi} \mathrm{P} \int_0^\infty \frac{s\alpha''(s)}{s^2 - \omega^2} ds$$

$$\alpha''(\omega) = -\frac{2\omega}{\pi} \mathrm{P} \int_0^\infty \frac{\alpha'(s)}{s^2 - \omega^2} ds$$

- Take ln(ω) of $r(\omega)$

$$\ln r(\omega) = \ln R^{1/2}(\omega) + i\theta(\omega)$$

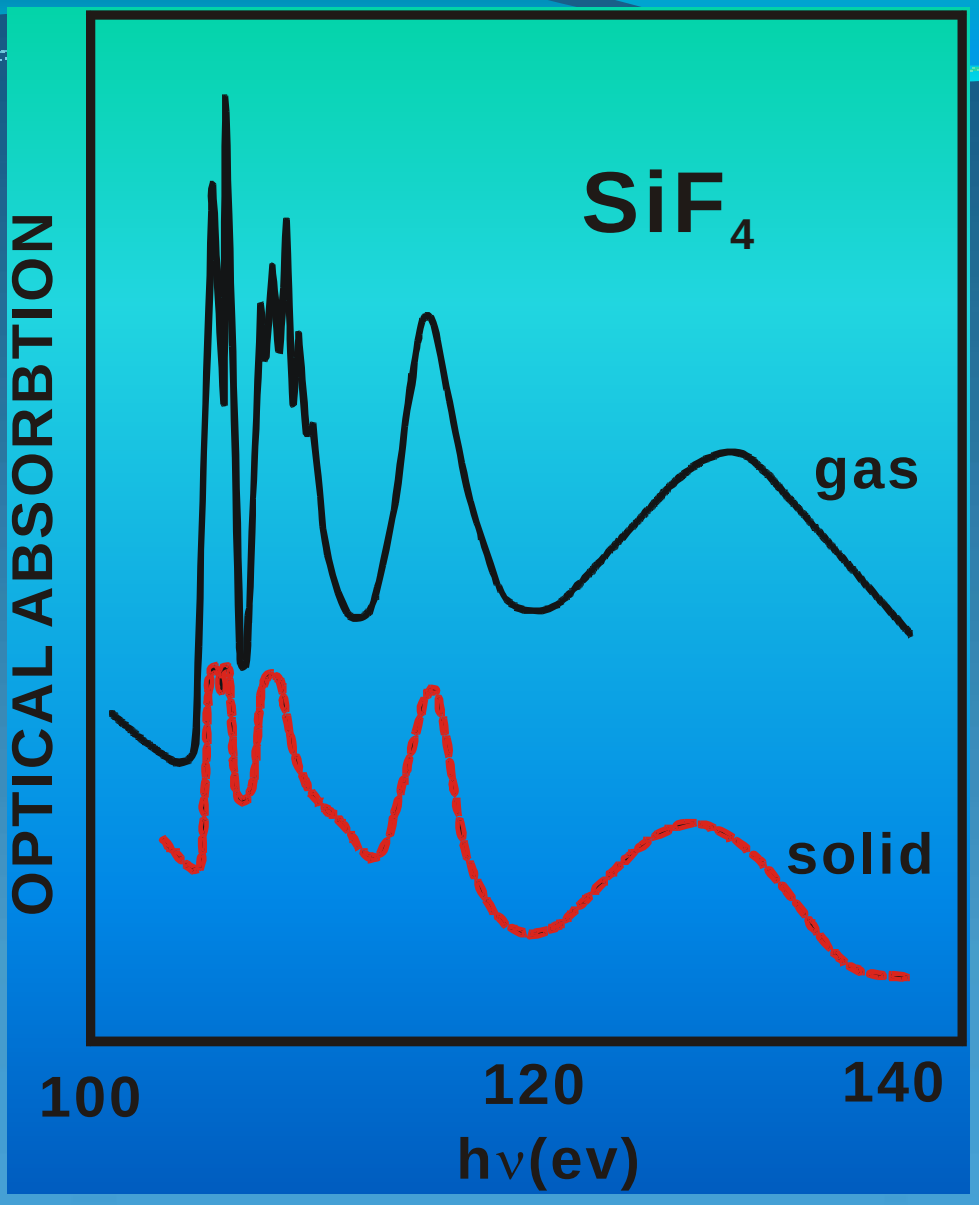
- Apply KK relations to obtain $\theta(\omega)$ from above equation:

$$\theta(\omega) = -\frac{\omega}{\pi} \mathrm{P} \int_0^\infty \frac{\ln R(s)}{s^2 - \omega^2} ds$$

$$\theta(\omega) = -\frac{1}{2\pi} \int_0^\infty \ln \left| \frac{s+\omega}{s-\omega} \right| \frac{d \ln R(s)}{ds} ds$$

Electronic Interband Transitions

$$\hbar\omega = E_c(\mathbf{k}) - E_v(\mathbf{k})$$


SiF4
gas
solid
OPTICAL ABSORBTION
100
120
140
hν(ev)

- Band structure

$$E_e = E_e(\mathbf{k})$$

- Density of states (DOS)

$$DOS = \frac{dN_e}{dE_e}$$

- Energy-dependent DOS

$$DOS(E_e) \propto \int \frac{dS_{E_e}}{\left|\nabla_{\mathbf{k}} E_e(\mathbf{k})\right|}$$

- The number of transitions contributing to the absorption coefficient at photon eneryg $h\nu$,

$$\varepsilon''(\omega) \propto DOS(E_b + \hbar\omega)$$

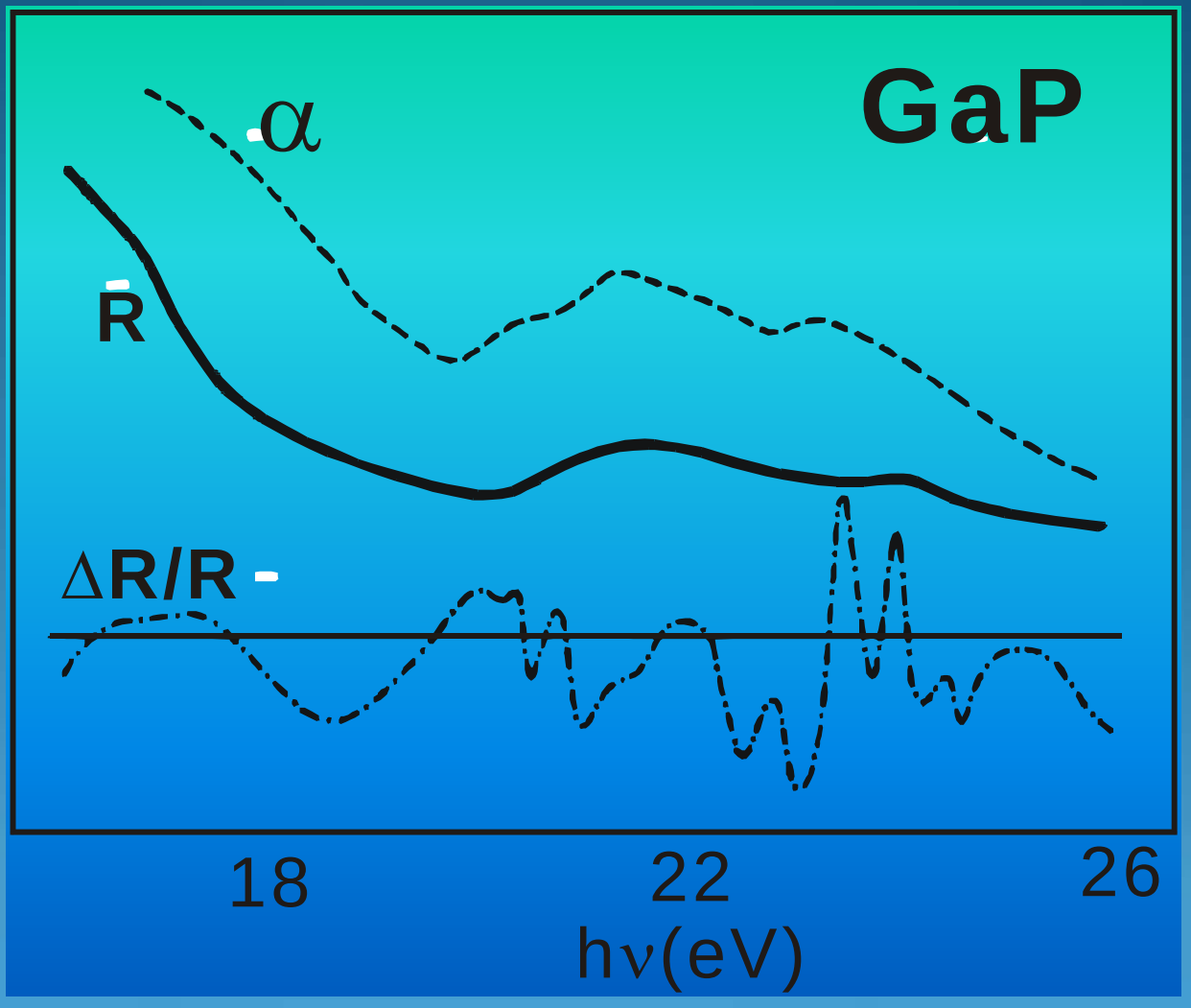
Electronic Interband Transitions

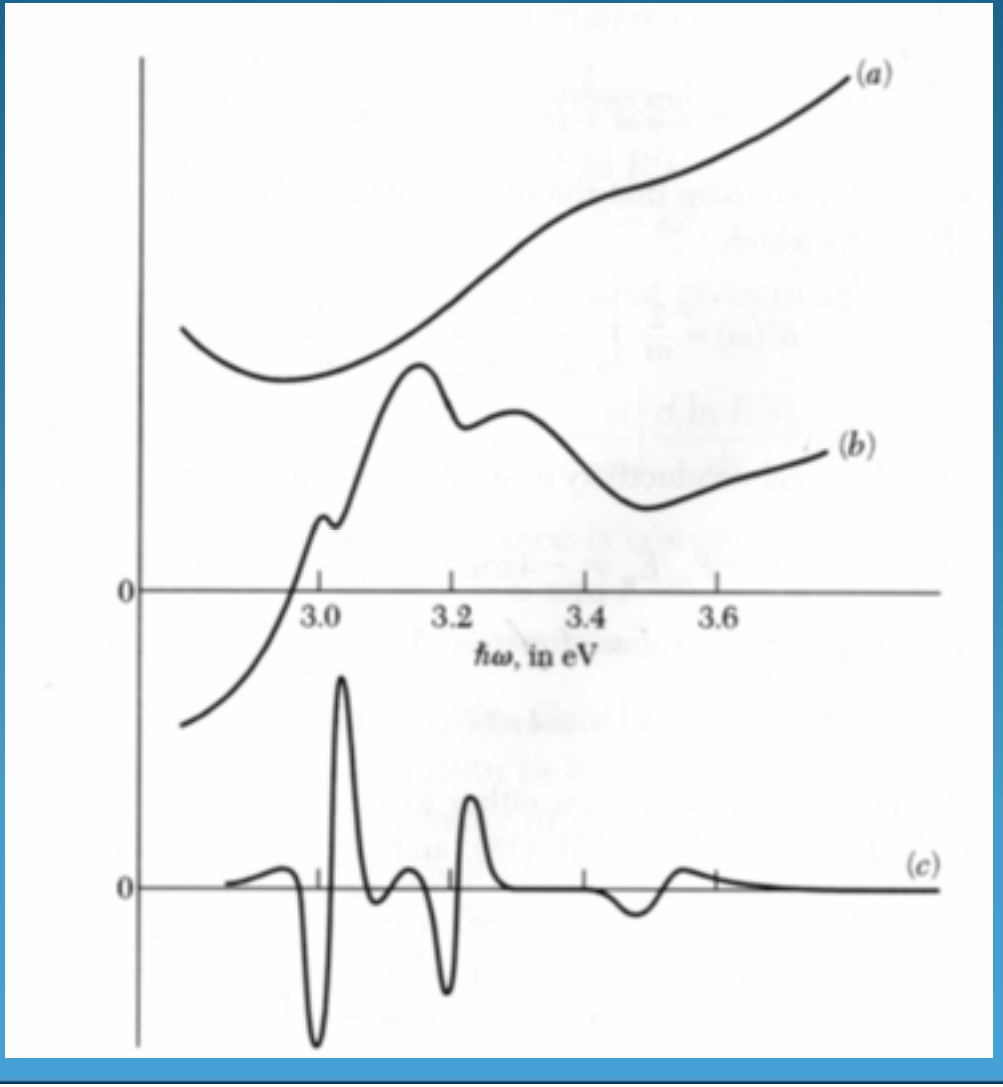
- Modulation Spectroscopy—derivatives of the reflectance with respect to wavelength, electric field, temperature, presure, or uniaxial stress, etc.
- Singular/critical points

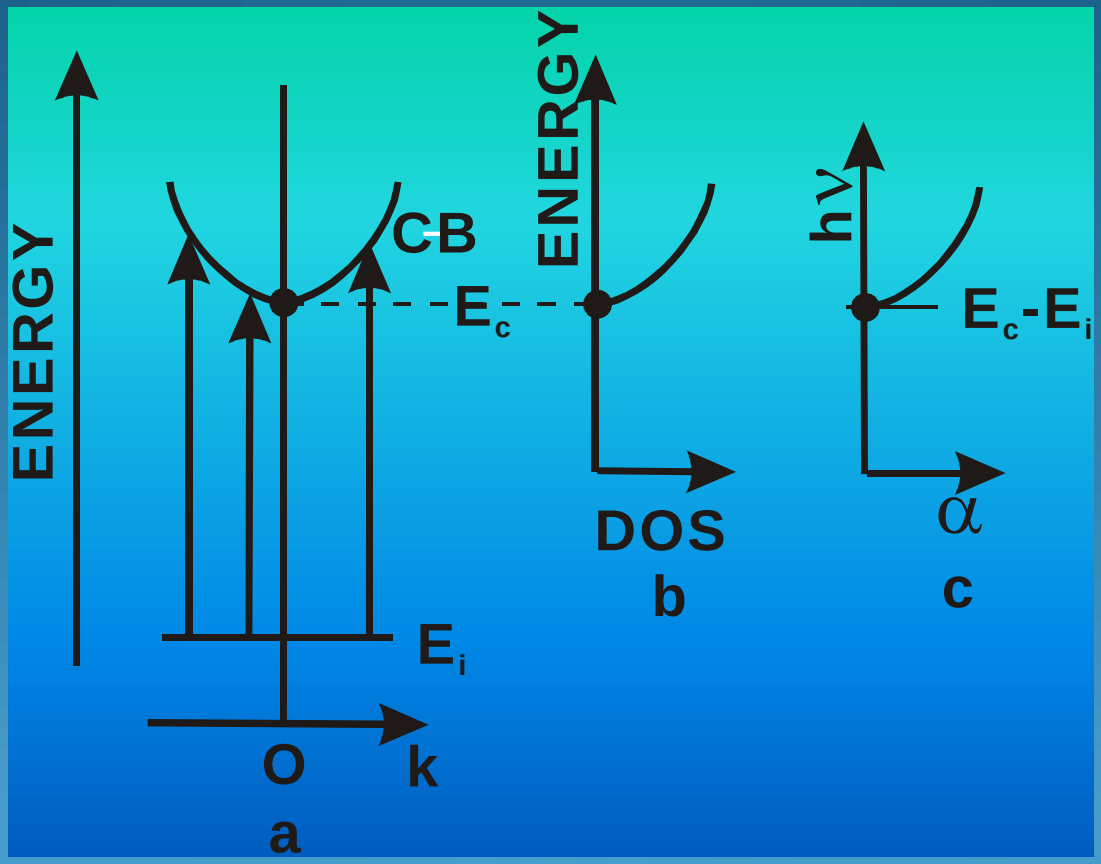
$$\nabla_{\mathbf{k}}[E_c(\mathbf{k}) - E_v(\mathbf{k})] = 0$$

$$DOS(E_e) \propto \int \frac{dS_{E_e, E_c, \hbar\omega}}{\left|\nabla_{\mathbf{k}} E_e(\mathbf{k}) - E_c(\mathbf{k})\right|}$$

- Pseuopotential calculation of band structure and band-band energy difference


GaP
α
R
ΔR/R
18
22
26
hν(eV)


(a)
(b)
0
3.0
3.2
3.4
3.6
ħω, in eV
0
(c)


ENERGY
CB
E_c
E_i
O
k
a
ENERGY
DOS
b
hν
E_c-E_i
α
c

Excitons

- Frenkel—tightly bound
- Mott Wannier
- Both can travel through lattice

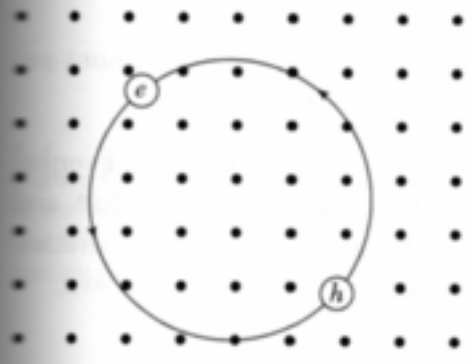


Figure 4a An exciton is a bound electron-hole pair, usually free to move together through the crystal. In some respects it is similar to an atom of positronium, formed from a positron and an electron. The exciton shown is a Mott-Wannier exciton: it is weakly bound, with an average electron-hole distance large in comparison with the lattice constant.

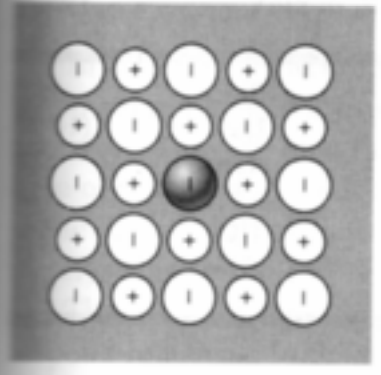


Figure 4b A tightly-bound or Frenkel exciton shown localized on one atom in an alkali halide crystal. An ideal Frenkel exciton will travel as a wave throughout the crystal, but the electron is always close to the hole.

Binding energy of excitons in some examples

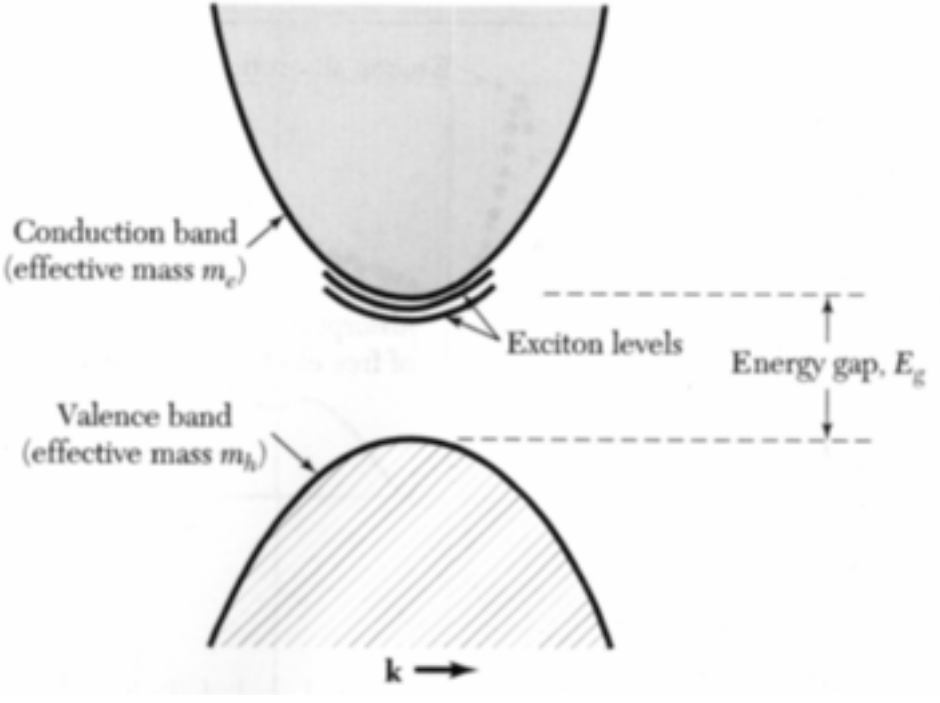
Table 1 Binding energy of excitons, in meV

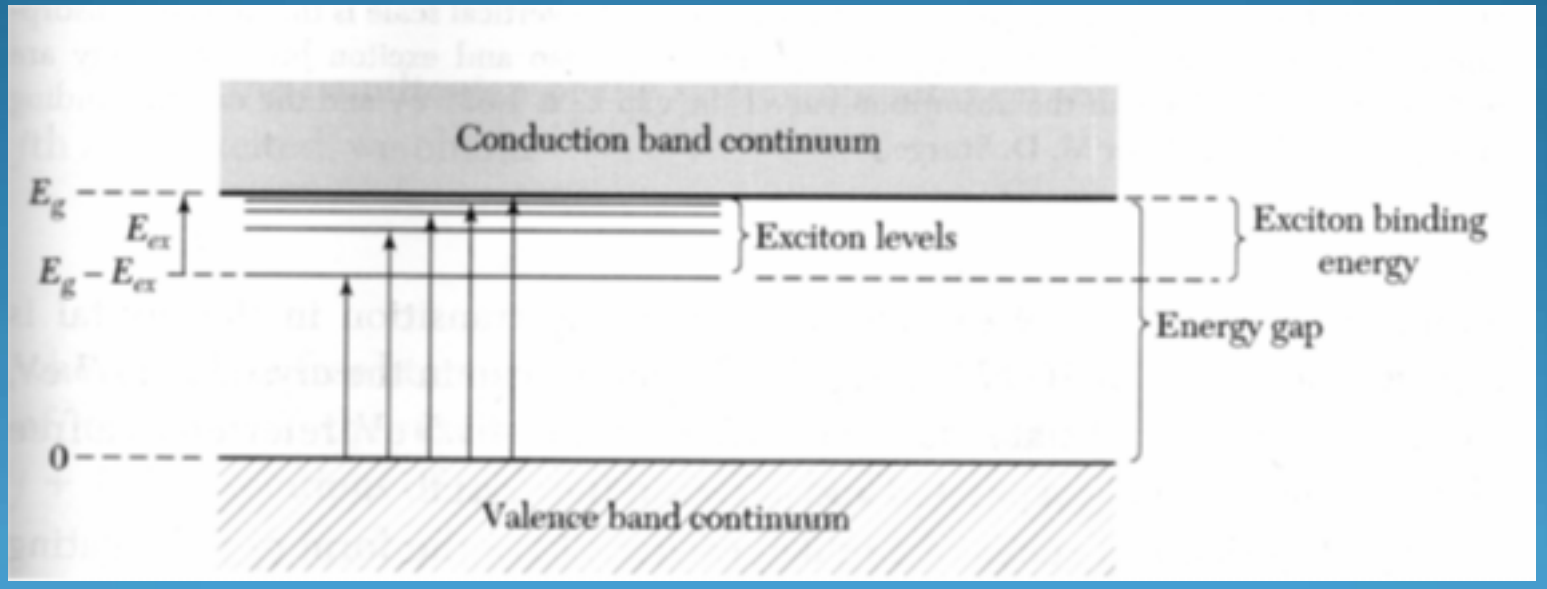
Si	14.7	BaO	56.	RbCl	440.
Ge	4.15	InP	4.0	LiF	(1000)
GaAs	4.2	InSb	(0.4)	AgBr	20.
GaP	3.5	KI	480.	AgCl	30.
CdS	29.	KCl	400.	TlCl	11.
CdSe	15.	KBr	400.	TlBr	6.

Data assembled by Frederick C. Brown and Arnold Schmidt.

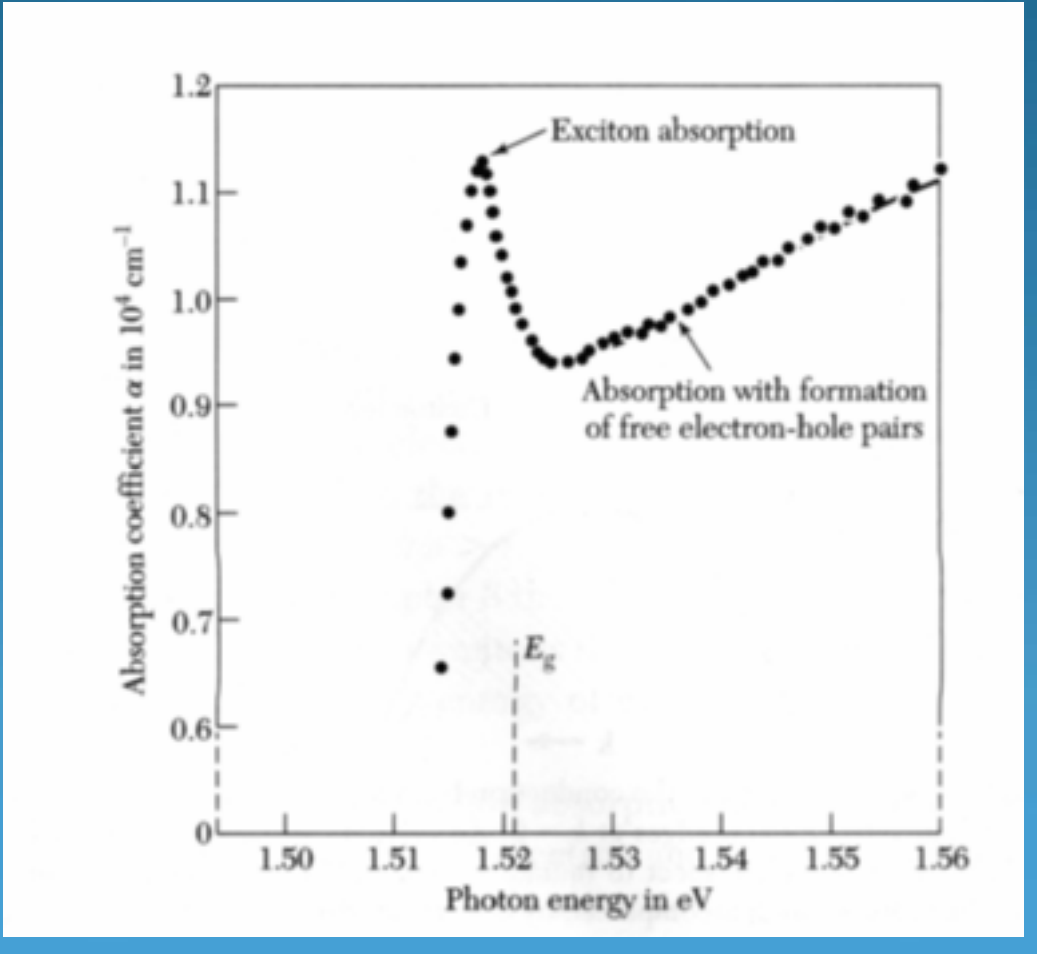
Exciton Energy levels

- The energy required to create an exciton is lower by the exciton binding energy than that of a electron and a hole.
- This energy difference will reflect in the absorption spectra.

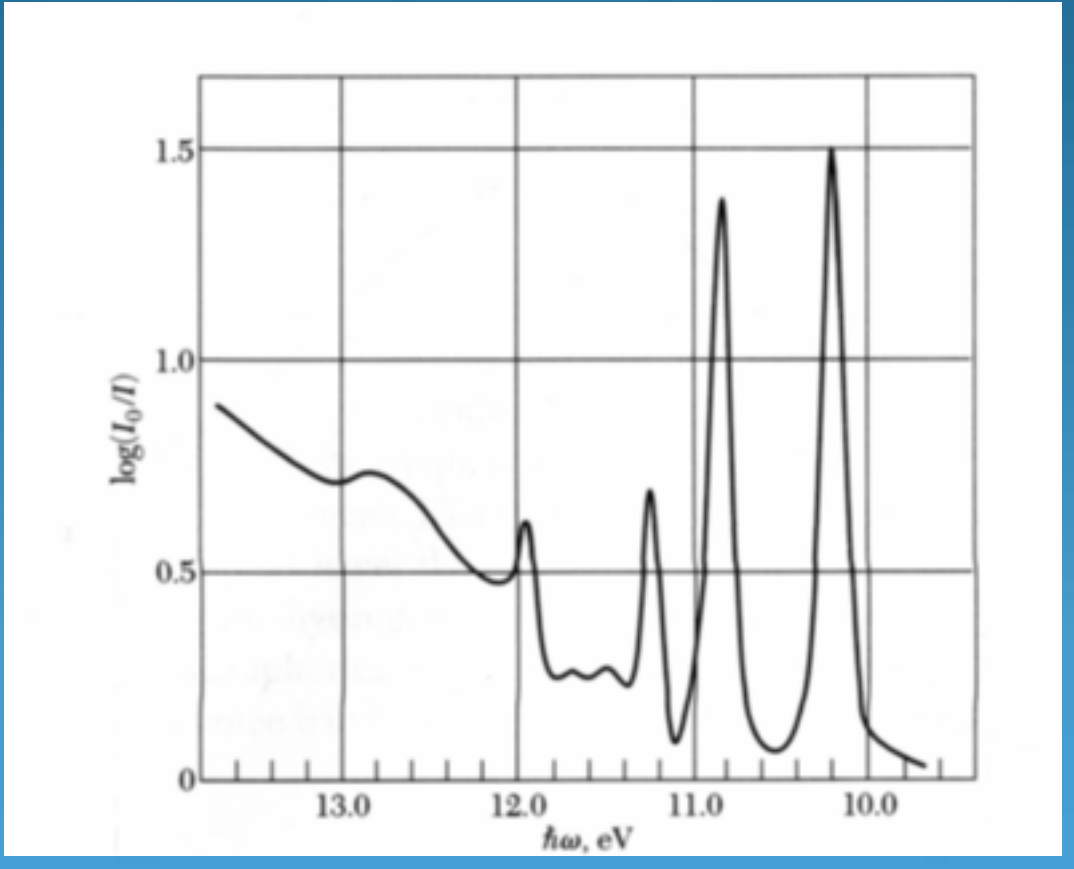



Conduction band continuum
E_g
E_{ex}
$E_g - E_{ex}$
Exciton levels
Exciton binding energy
Energy gap
0
Valence band continuum

Exciton absorption spectrum

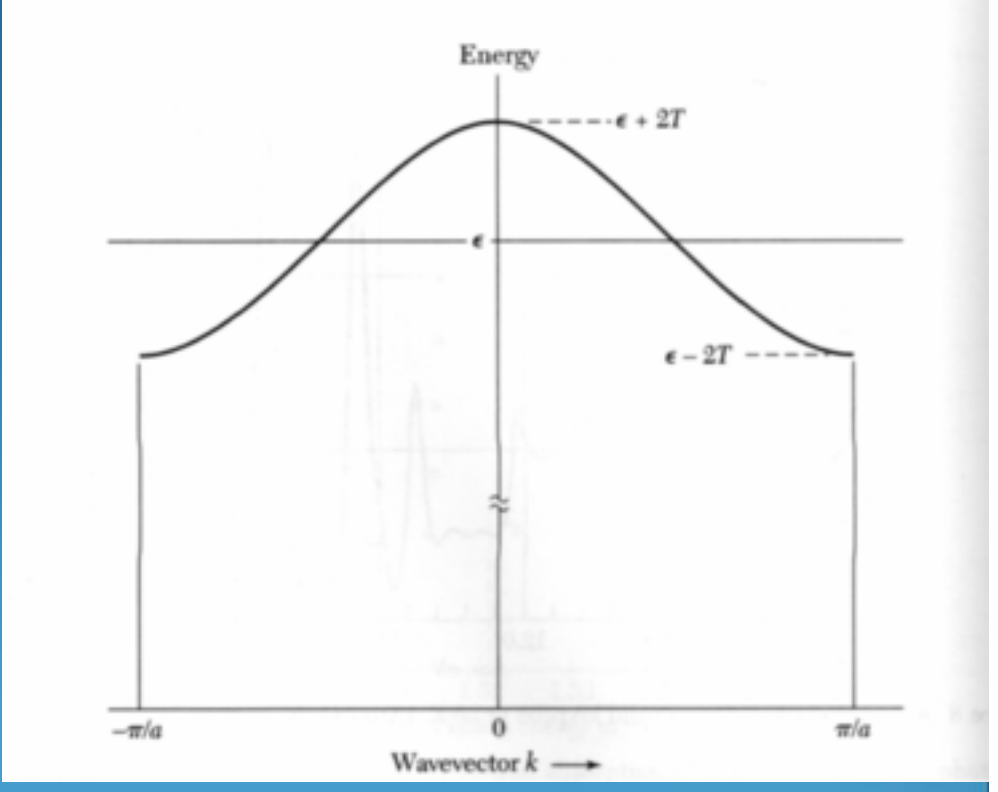


Absorption spectrum of solid Kr at 20K



Energy vs. Wavevector for a Frenkel exciton

Derivation of the energy states of Frenkel exciton



$$E_{\kappa} = \varepsilon + 2T\cos\kappa\alpha$$

$$k = 2\pi s / Na;$$

$$s = -\frac{1}{2}N, -\frac{1}{2}N + 1, \ldots, \frac{1}{2}N - 1$$

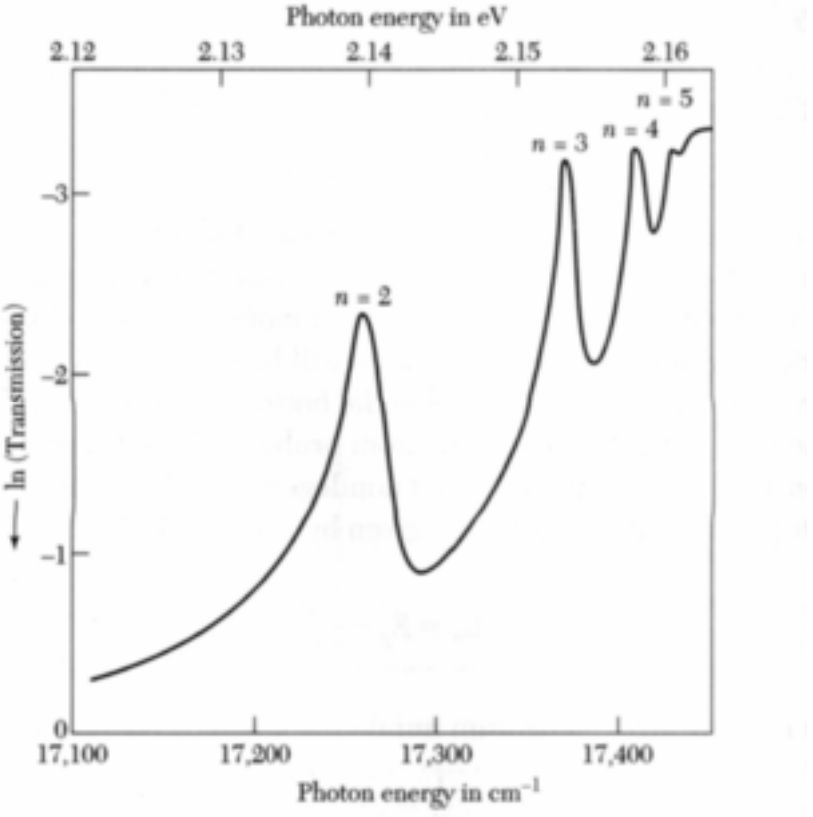
Transmission spectrum (log) in CuO at 77K showing exciton spectral lines—

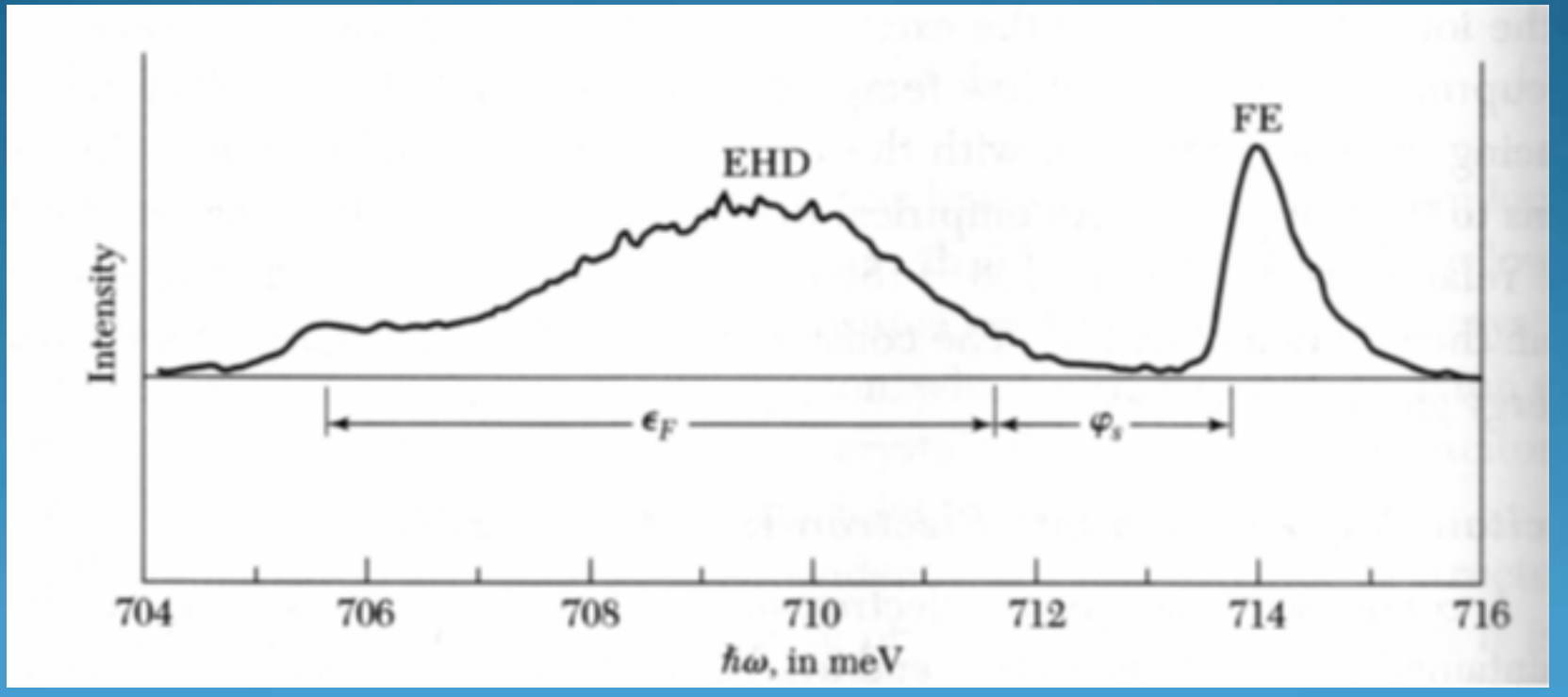
- Example of a weekly bound (Mott-Wanier) Exciton
- Use the derivation below and the figures on the right to obtain the energy gap

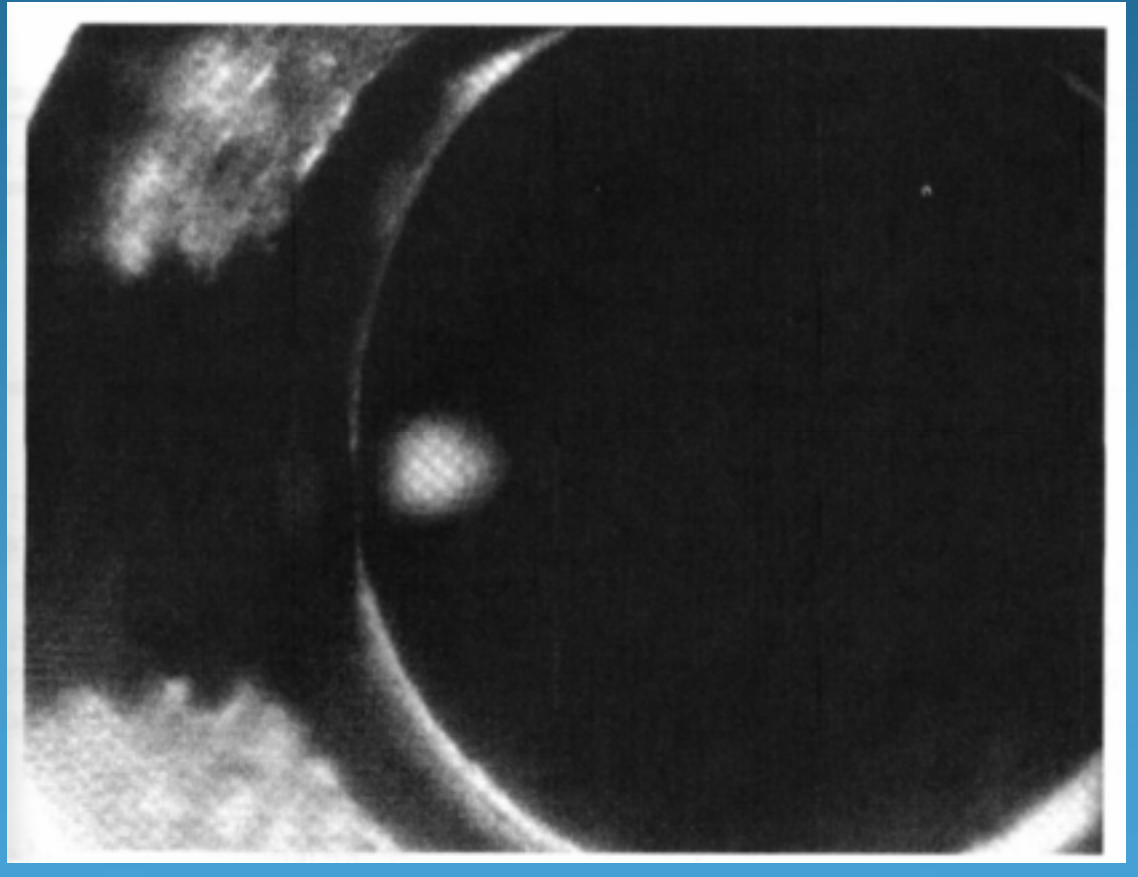
$$U(r) = -e^2 / \varepsilon r$$

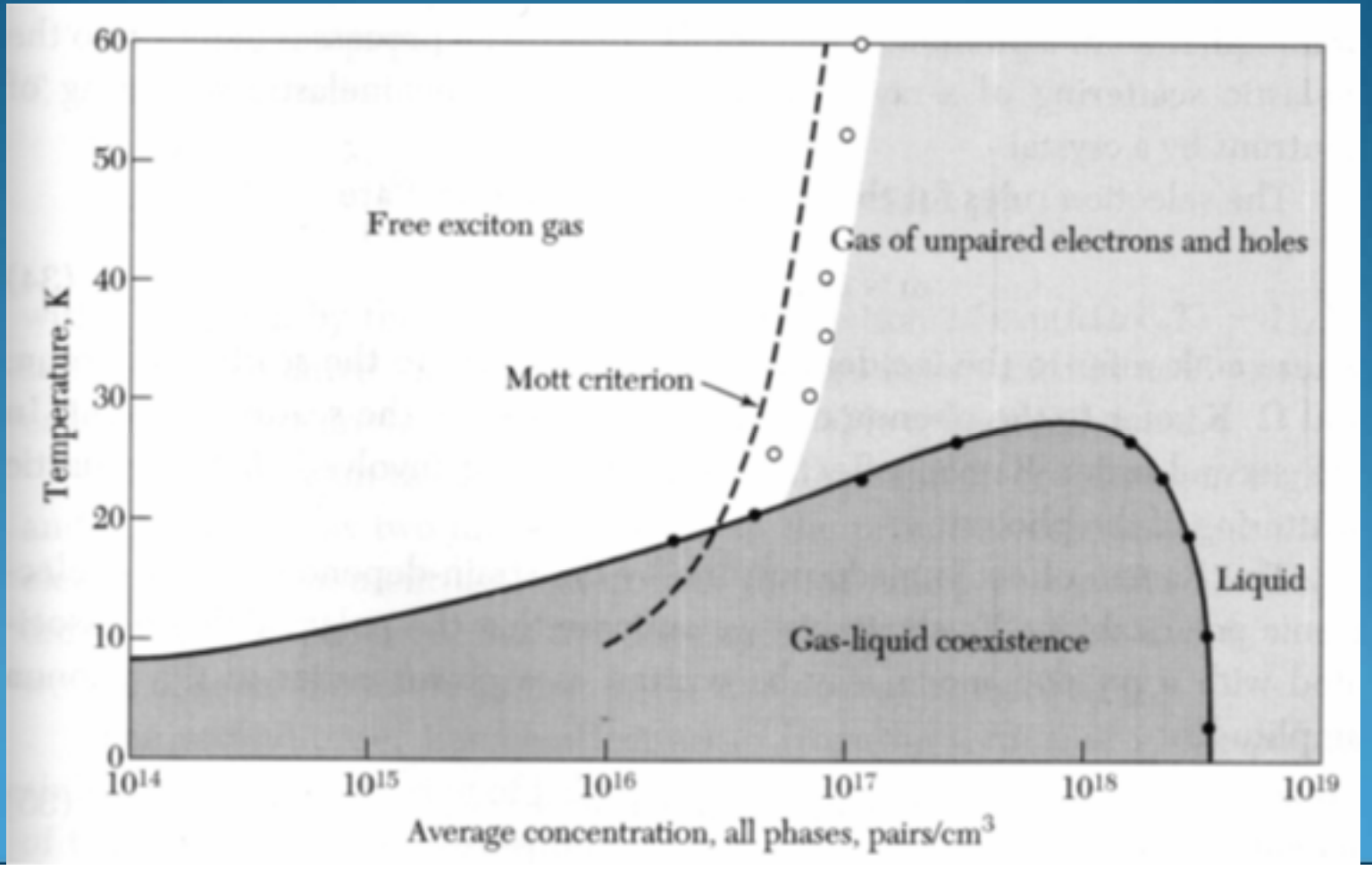
$$E_n = E_g - \frac{\mu e^4}{2\hbar^2 \varepsilon^2 n^2}$$

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}$$




FE
EHD
Intensity
ϵ_F
φ_s
704
706
708
710
712
714
716
$\hbar\omega$, in meV




Free exciton gas
Gas of unpaired electrons and holes
Mott criterion
Liquid
Gas-liquid coexistence
Temperature, K
60
50
40
30
20
10
0
10^{14}
10^{15}
10^{16}
10^{17}
10^{18}
10^{19}
Average concentration, all phases, pairs/cm^3

Electron Spectroscopy with X-Rays

- XPS and UPS