Ch4. Excitons

4.1 The concept of excitons

4.2 Wannier excitons (Free excitons)

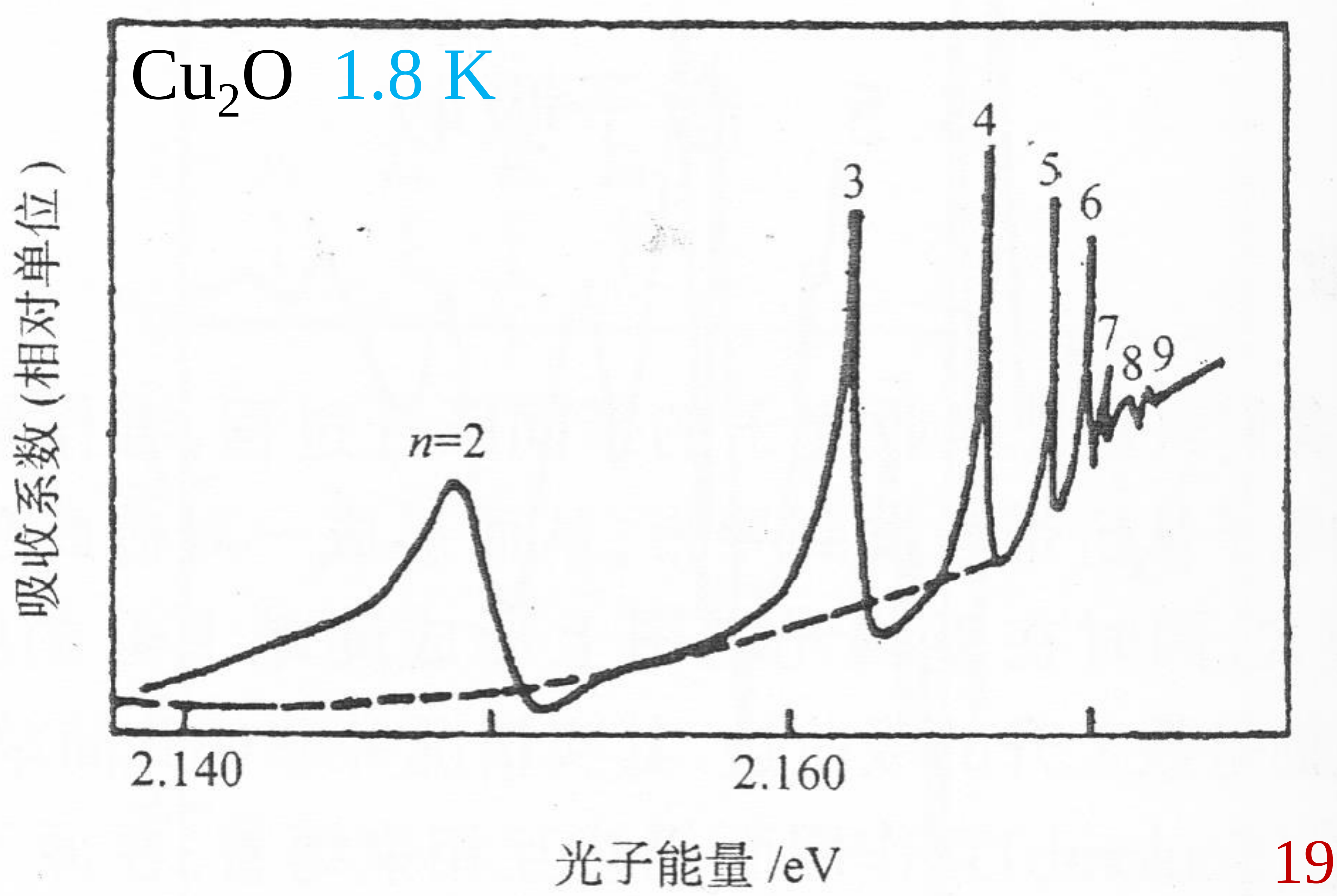
4.3 Free excitons in external fields

4.4 Free excitons at high densities (nonlinearities)

…BEC

4.5 Frenkel excitons

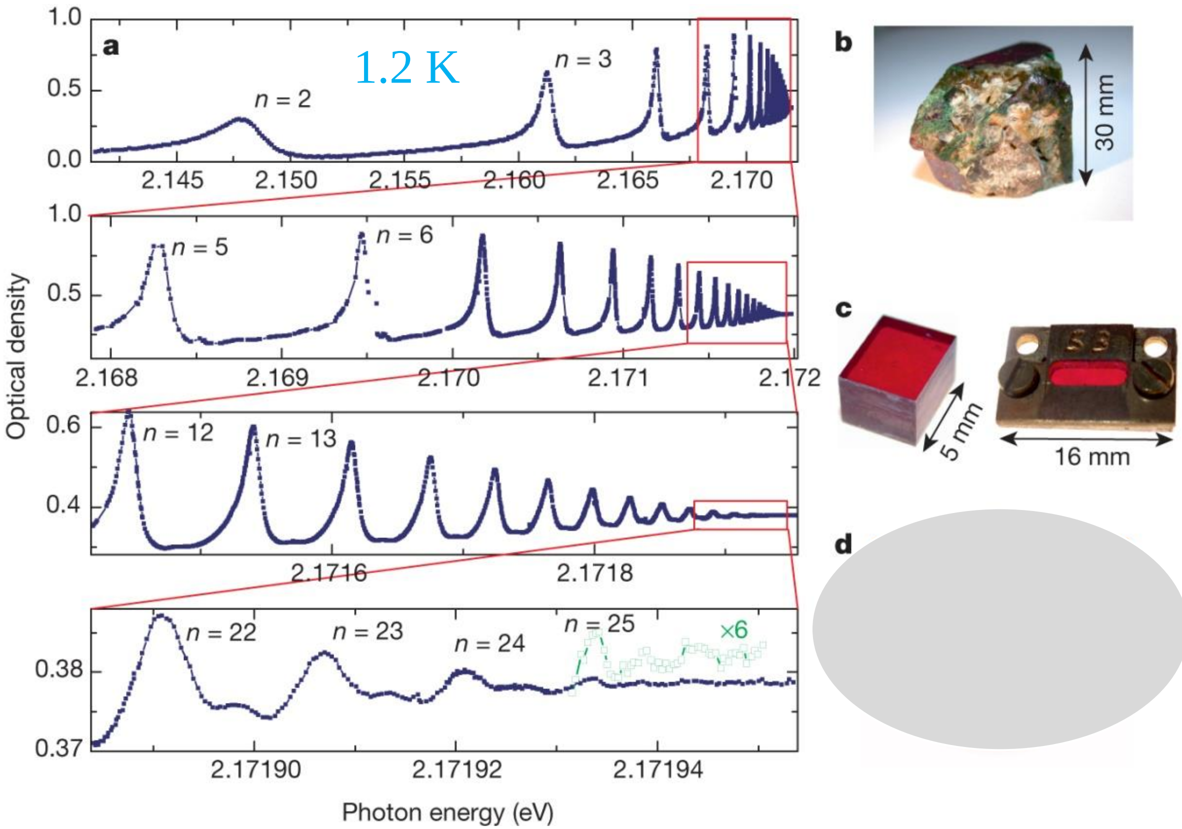
Absorption efficient of semiconductor @LT



1952最早发现

Series of absorption peaks just below the energy gap

High-resolution absorption spectra of Cu_2O



类原子光谱:

满足:

$$\hbar\omega = E_g - R_X / n^2$$

Rx=92 meV

Eg=2.17208

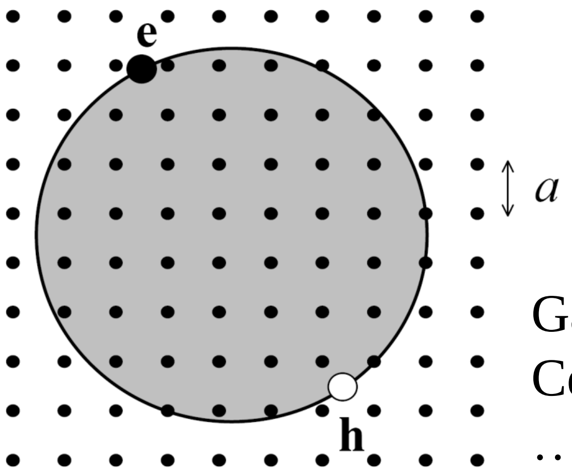
分离尖锐的吸收峰从哪里来?

T Kazimierczuk *et al.* *Nature* **514**, 343-347 (2014) doi:10.1038/nature13832

Excitons

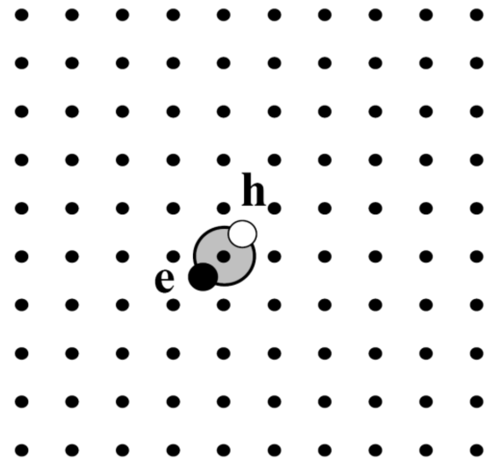
Vs free e-h pair

Excitons



GaAs,
CdS
…

$E_b > k_B T$



Free (Wannier-Mott)

- radius >> *a*
- small binding energy 0.01 eV
- pure crystal semiconductor
- only cryogenic temperature
- particle moves freely through crystal of effective dielectric constant ε_r

Tightly-bound (Frenkel)

- radius ~ *a*
- large binding energy 0.1-1.0 eV
- insulator, rare gas crystals, alkali halides, molecular @ RT
- localized on one lattice site
- Hops from one site to another

Bing energy and radius

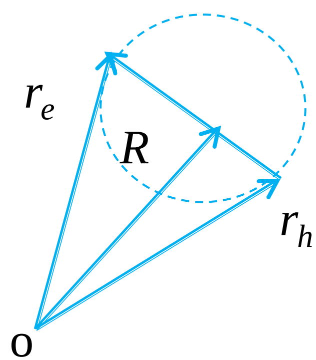
抛物线近似下：

$$H = \frac{P_e^{\ 2}}{2m_e^*} + \frac{P_h^2}{2m_h^*} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r\left|r_e - r_h\right|},$$

$$r = r_e - r_h;$$

$$R = \frac{m_e^* r_e + m_h^* r_h}{m_e^* + m_h^*};$$

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*},$$



变形后：

$$H = \frac{P_R^2}{2(m_e^* + m_h^*)} + \left(\frac{p^2}{2\mu} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right)$$

$$where \quad P_R = (m_e^* + m_h^*)\dot{R}, \quad p = \mu\dot{r}$$

Focus on relative motion

GaAs μ=0.05 m_0 意义

Bing energy and radius

$\Psi = \psi(r)\exp(iK \cdot R)$ 分离变量后：

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r}\right]\psi(r) = E_n\psi(r)$$

$$E_n = -\underline{\underline{\frac{m_0 e^4}{2(4\pi\varepsilon_0)^2\hbar^2}}} \cdot \frac{\mu}{m_0\varepsilon_r{}^2}\frac{1}{n^2} = -\underline{\underline{\frac{\mu}{m_0}\frac{1}{\varepsilon_r{}^2}}}\frac{R_H}{n^2} = -\frac{R_X}{n^2}$$

(R_H: *Hydrogen* Rydberg constant 13.6 eV) (R_X: Exciton Rydberg constant)

$$(R_X = (\frac{\mu}{m_0\varepsilon_r{}^2})R_H)$$

(μ and ε_r=?宽带)

$$r_n = -\frac{m_0}{\mu} \cdot \varepsilon_r \cdot n^2 a_H = n^2 a_X \qquad (a_H = \frac{4\pi\varepsilon_0\hbar^2}{m_0 e^2})$$

(Exciton Bohr radius) (讨论)

随堂练习

（i）Calculate the exciton Rydberg energy and Bohr raidius for GaAs which has ε_r=12.8, m_e*=0.067 m_0, and m_h*=0.2 m_0;

(iii) Estimate the highest temperature at which it will be possible to observe stable exciton in GaAs.

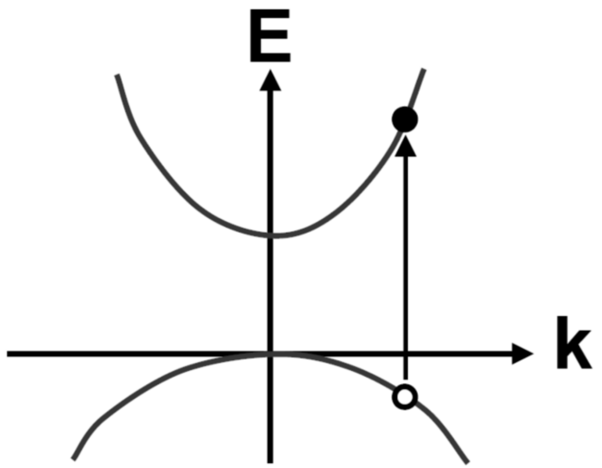
20190318

常见半导体和化合物的激子束缚能

材料	E_b（meV)	材料	E_b（meV)	材料	E_b
Si	14.7	ZnSe	17	MoS_2	50
Ge	3.8-4.1	ZnTe	12	BaO	56
GaAs	4.2	InP	4.0	LiF	1000
GaP	21.5	InSb	0.4	KBr	400
GaSb	1.6	AgBr	20	KCl	400
<u>ZnO</u>	59	<u>Cu_2O</u>	21	RbCl	440
<u>GaN</u>	28*	TiBr	6.0	KI	480
CdS	29.0	AgCl	30		
ZnS	40	TiCl	11		

Dispersion Curve of Exciton

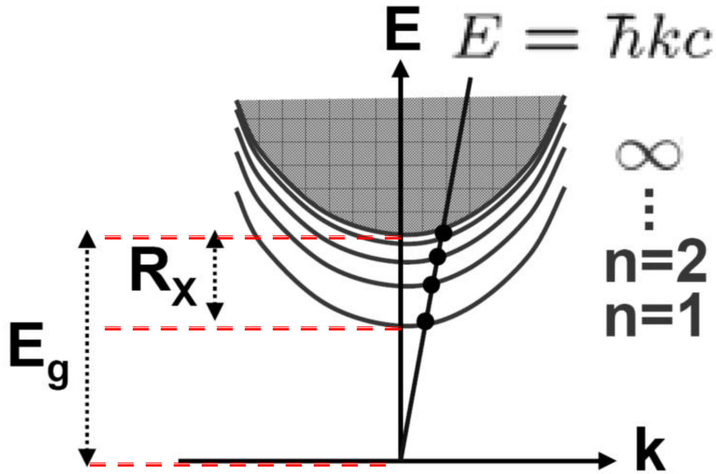
uncorrelated electron-hole pair (one-electron picture)



$$E_e = E_g + \frac{\hbar^2 k_e^{\ 2}}{2m_e} \qquad E_h = \frac{\hbar^2 k_h^{\ 2}}{2m_h}$$

Wave vector conservation

exciton (one-particle picture)

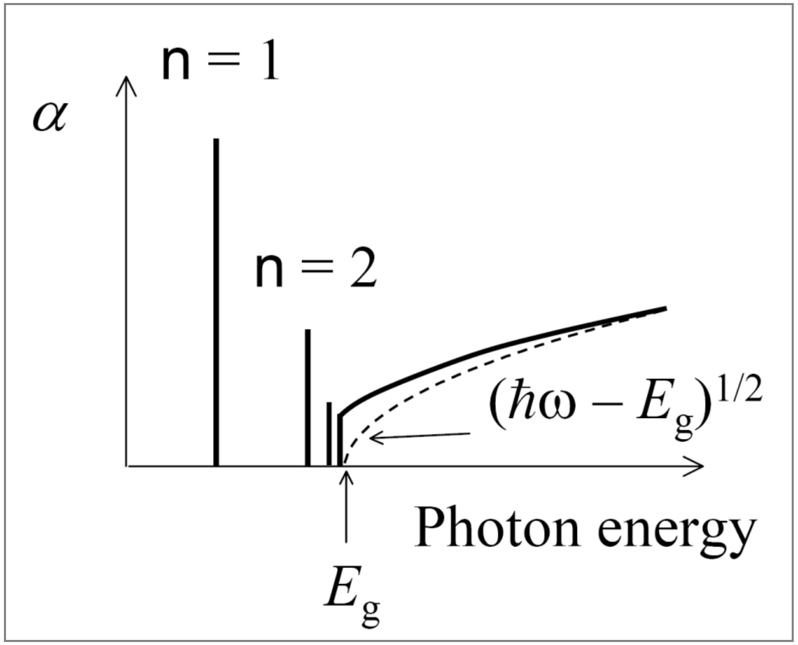


$$E = E_g + \frac{\hbar^2 K^2}{2(m_e + m_h)} - \frac{R_X}{n^2}$$

Wave vector conservation

$$k_X = k_e - k_v = k_{ph}$$

Free exciton absorption



- Hydrogenic series of lines satisfying :

$$\hbar\omega = E_g - R_X / n^2$$

- enhanced absorption for $\hbar\,\omega > E_g$

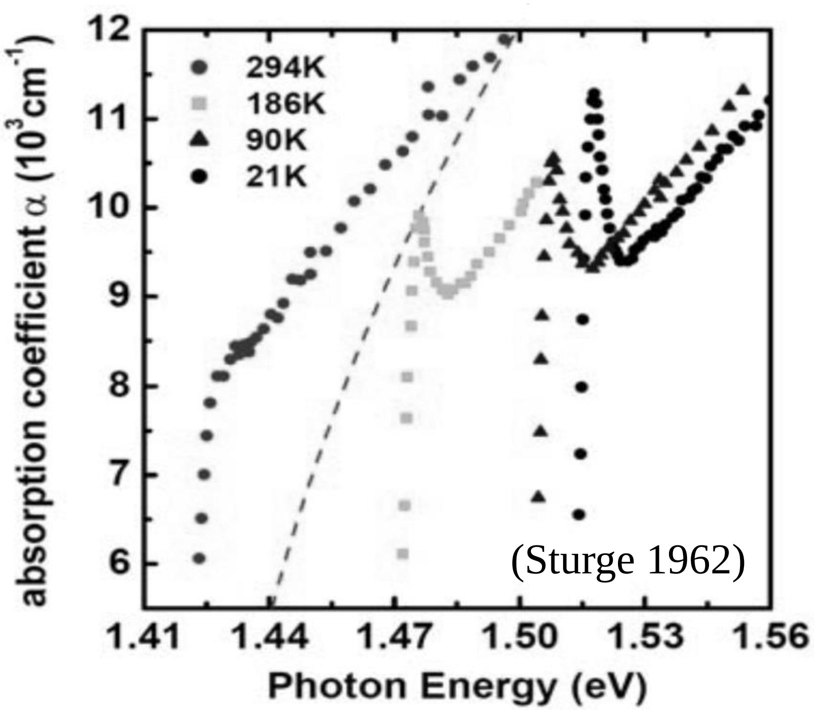
- only observed when $T \leq (R_X / k_B)$

Creating an exciton -> the same group velocity.

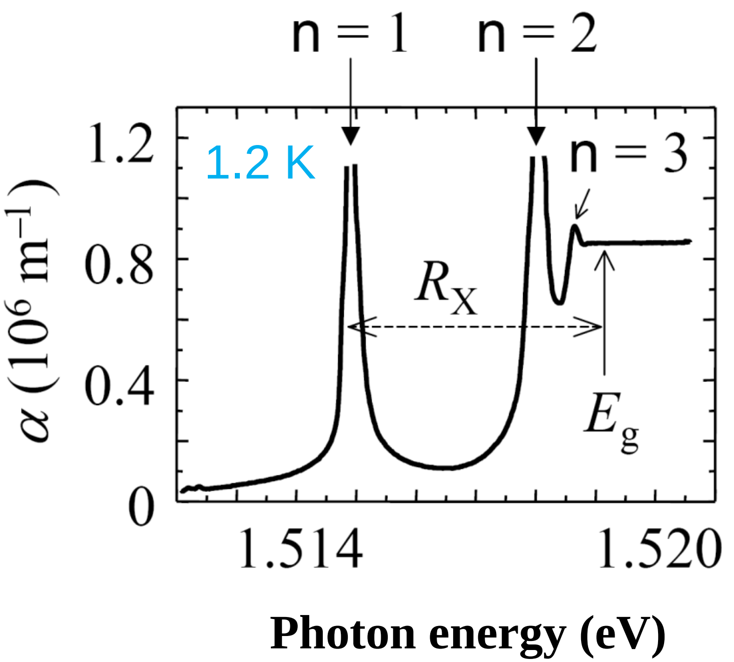
$$\upsilon_g = \frac{1}{\hbar}\frac{\partial E_V}{\partial k} = \frac{1}{\hbar}\frac{\partial E_C}{\partial k} = 0$$

(high symmetry points, k=0 et al; indirect exciton ?)

Experiment: Excitons in bulk GaAs



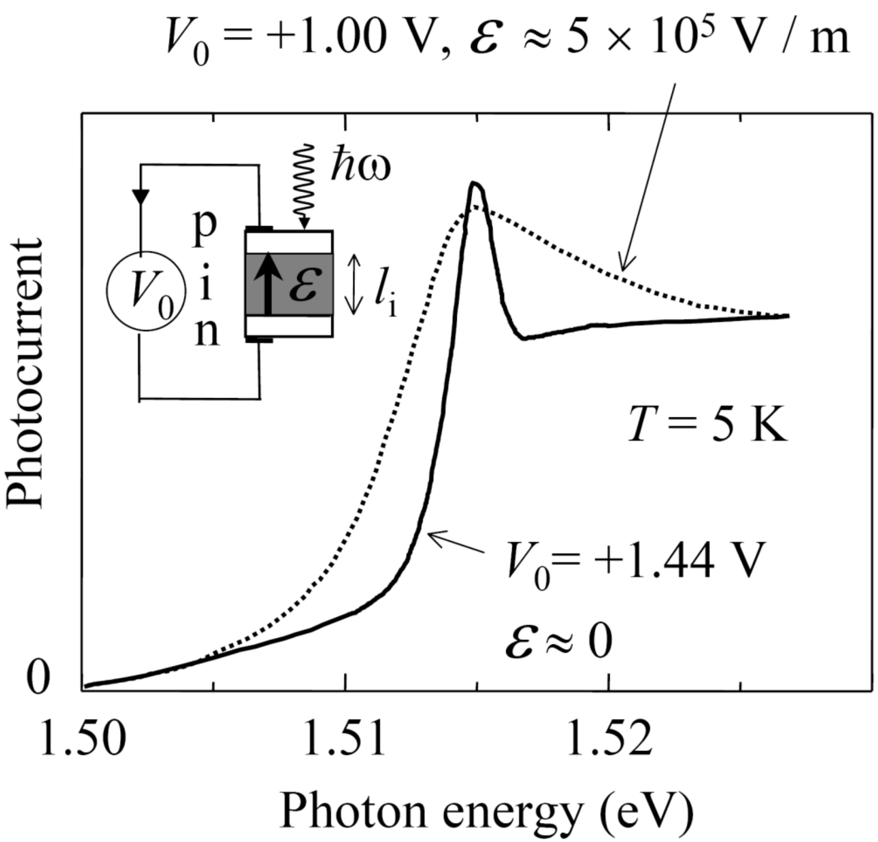
- standard purity sample

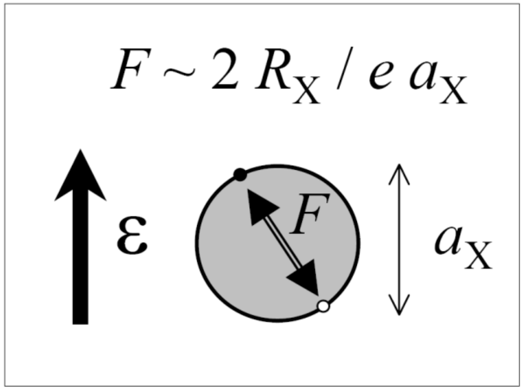


- ultra pure sample (Fehrenbach 1985)
- $R_X = 4.2\ meV$ (fitted)

Impurities release free e & h that can screen the Coulomb interaction in the exciton.

Field ionization in GaAs





GaAs parameters :

$R_X \sim 4.2\ meV$

$a_X \sim 13\ nm$

$l_i = 1\ \mu m$ (typical)

$F \sim 6 \times 10^5\ V/m$

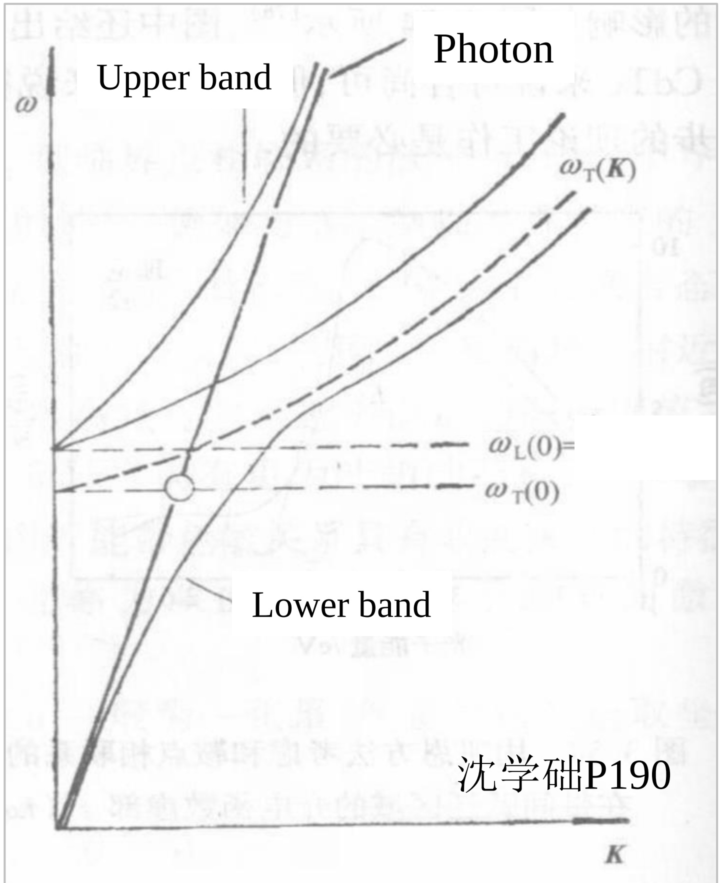
$\varepsilon \sim 1.5 \times 10^6\ V/m$

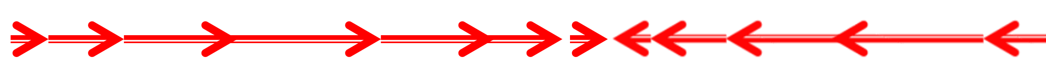
for $V_0 = 0$!

ionized if $\varepsilon > F$

In electric field, Franz-Keldysh effect > the exciton effect; In B field? …In EM field→

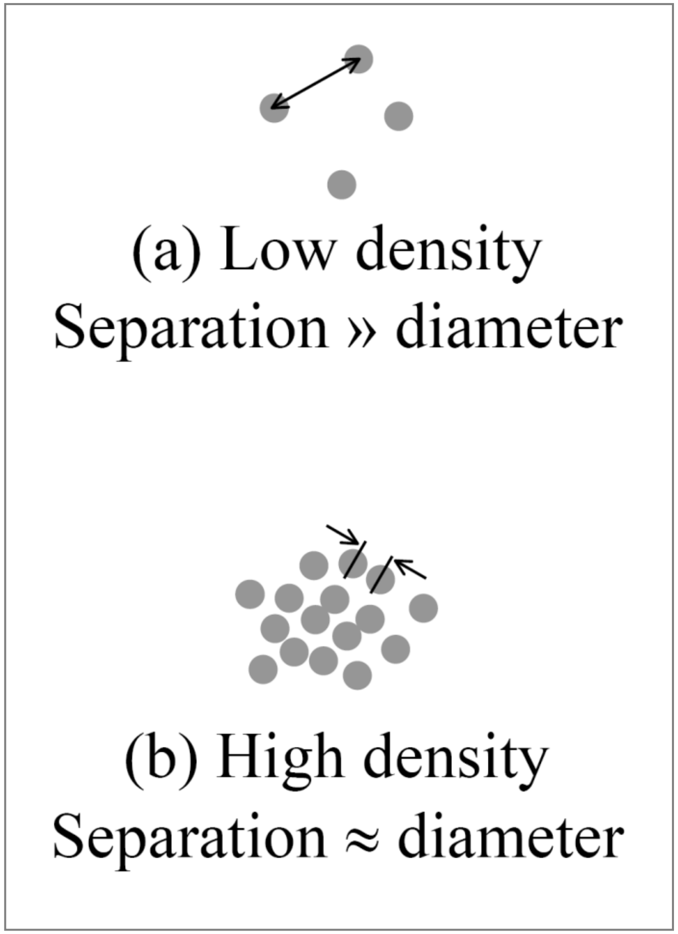
Exciton-Polariton

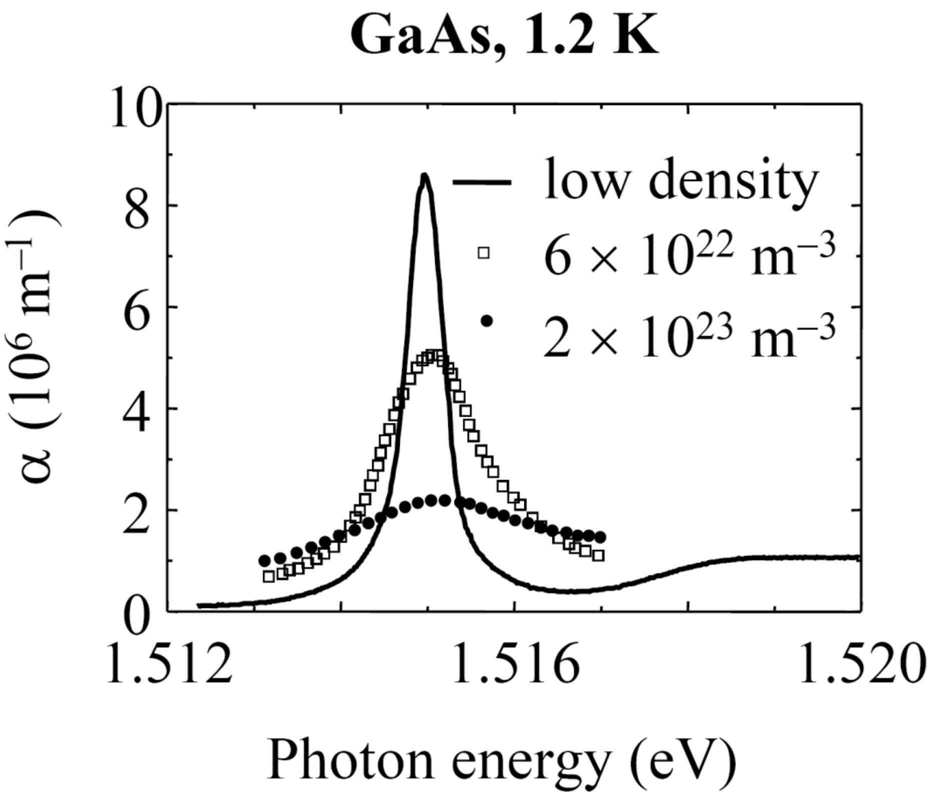




- Absorption occurs at point where photon dispersion intersects exciton dispersion curve.
- exciton-photon interaction leads to coupled EM and polarization wave (polariton) travelling in the medium altered dispersion curve (2 branches)
- But: if exciton damping (phonon scattering...) > exciton photon interaction , we can treat photons and excitons separately.

Nonlinear excitonic absorption





$$N_{Mott} \approx \frac{1}{\frac{4}{3}\pi r_n^3}$$ ~ 1.1 × 10^{23} m^{-3} in GaAs

Near N_{Mott}, a number of effects

Effect 1: **electron- hole plasma**

The collisions between cause the exciton gas to dissociate into an electron-hole plasma Absorption coefficient dependent exitation power. (a kind of nonlinear optical effect).

Effect 2: **biexcitons**

exciton molecules called biexcitons. (CdS, ZnSe, ZnO, CuCl…)

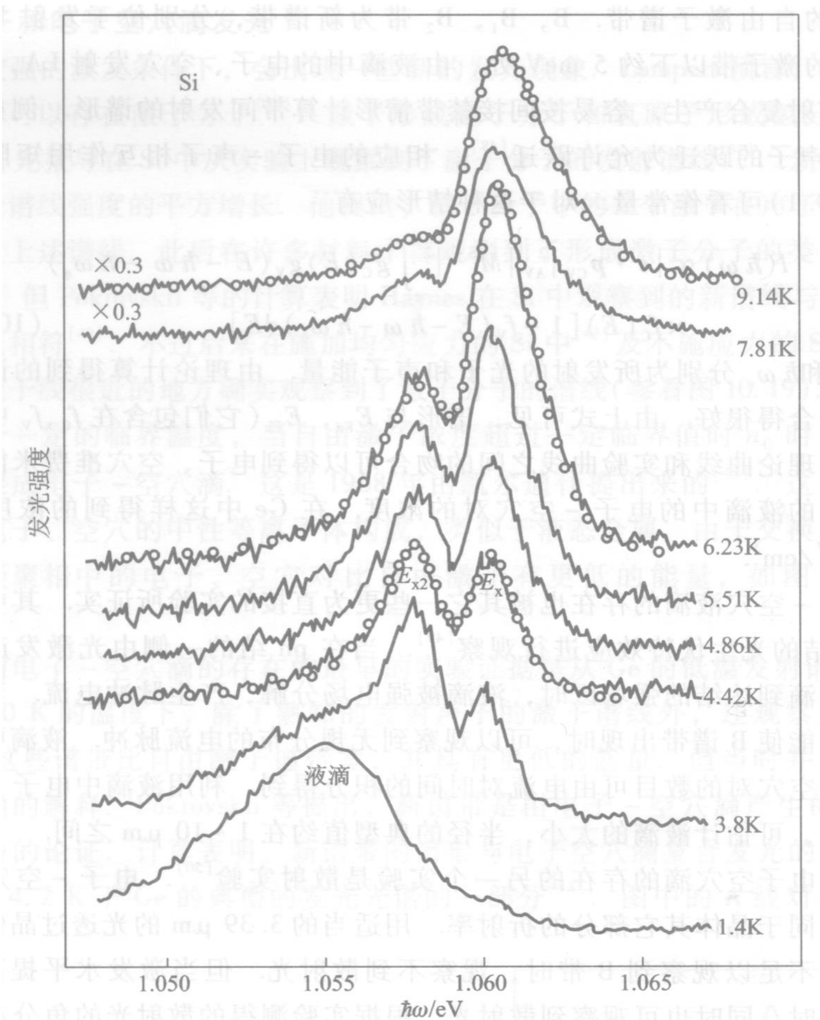
Effect 3: **electron- hole droplets:** In Si and Ge

Effect 4: **electron- hole liquid:** Exciton in QWs

Effect 5: **Bose-Einstein condensation**

Excitons consist of two spin ½ particles, and so their total spin is either 0 or 1. they are bosons. T_C : $N = 2.612\left(\frac{mk_B T_C}{2\pi\hbar^2}\right)^{\frac{3}{2}}$,

Si 低温光谱 Effect 2,3



温度降低

电子空穴对在阱中聚集

超过临界温度

形成液滴

此时 发光区域陡然收缩

Luminescence (与吸收对应)

图 10.19 低温下 Si 的光致发光谱．光自应力阱发出．E_x，E_{x2} 分别为激子和激子分子的发射带．由上述光谱得到的激子分子的结合能为 1.53 meV．温度进一步降低，出现液滴．图中的圆圈为理论计算得到

激子分子和e-h液滴发光 Effect 2, 3

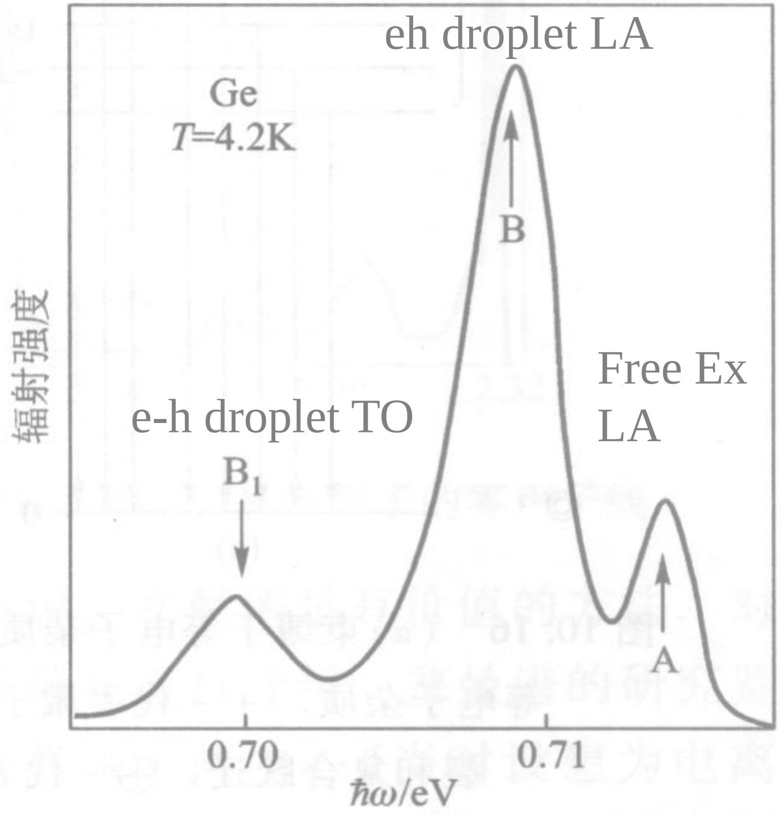


图 10. 18　4. 2 K 下纯 Ge 的发光光谱

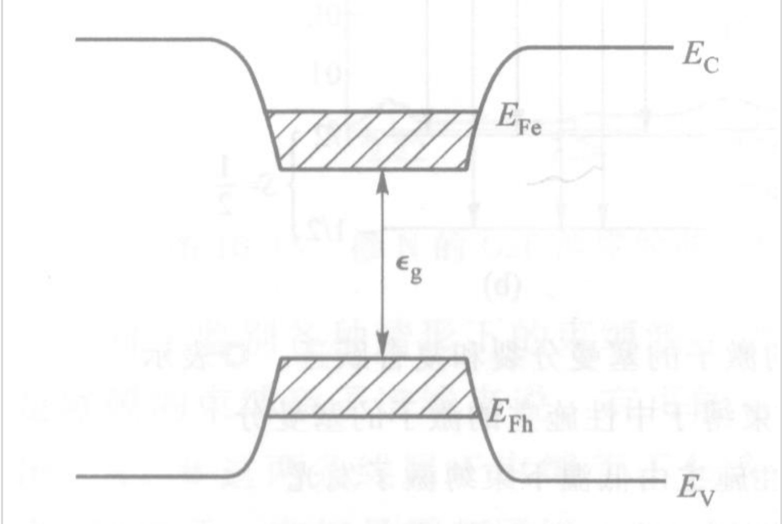


图 10. 17　电子－空穴滴的能带示意图．由于交换和相关作用，ϵ_g 降低．图中 E_{Fe} 和 E_{Fh} 分别为电子和空穴准费米能级

e-h droplet image

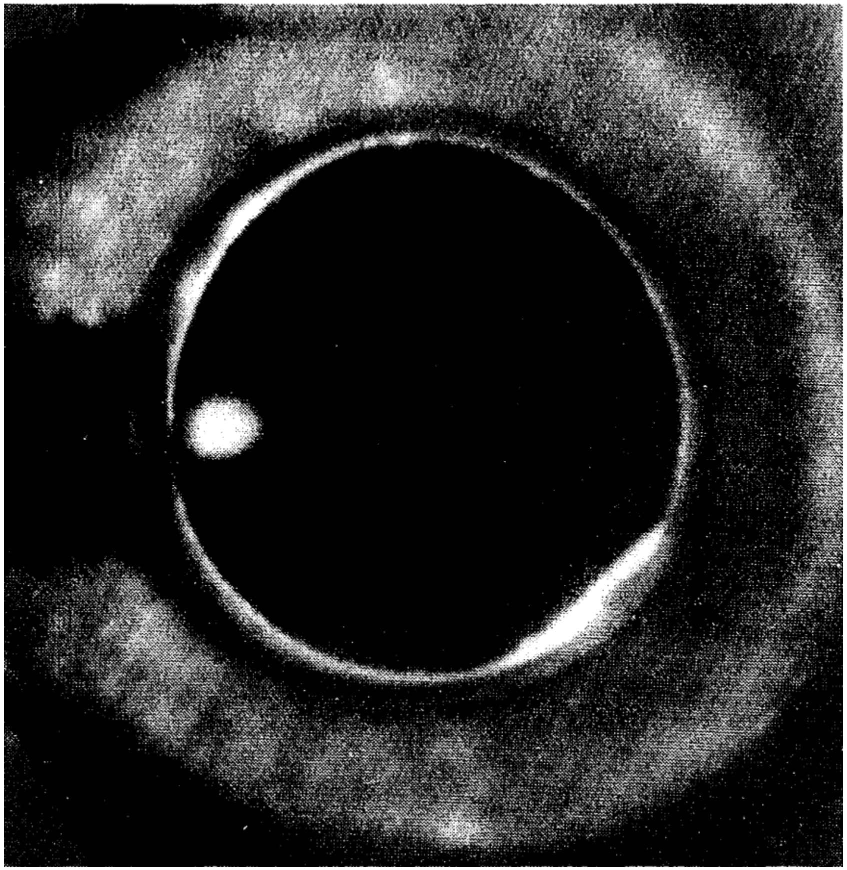
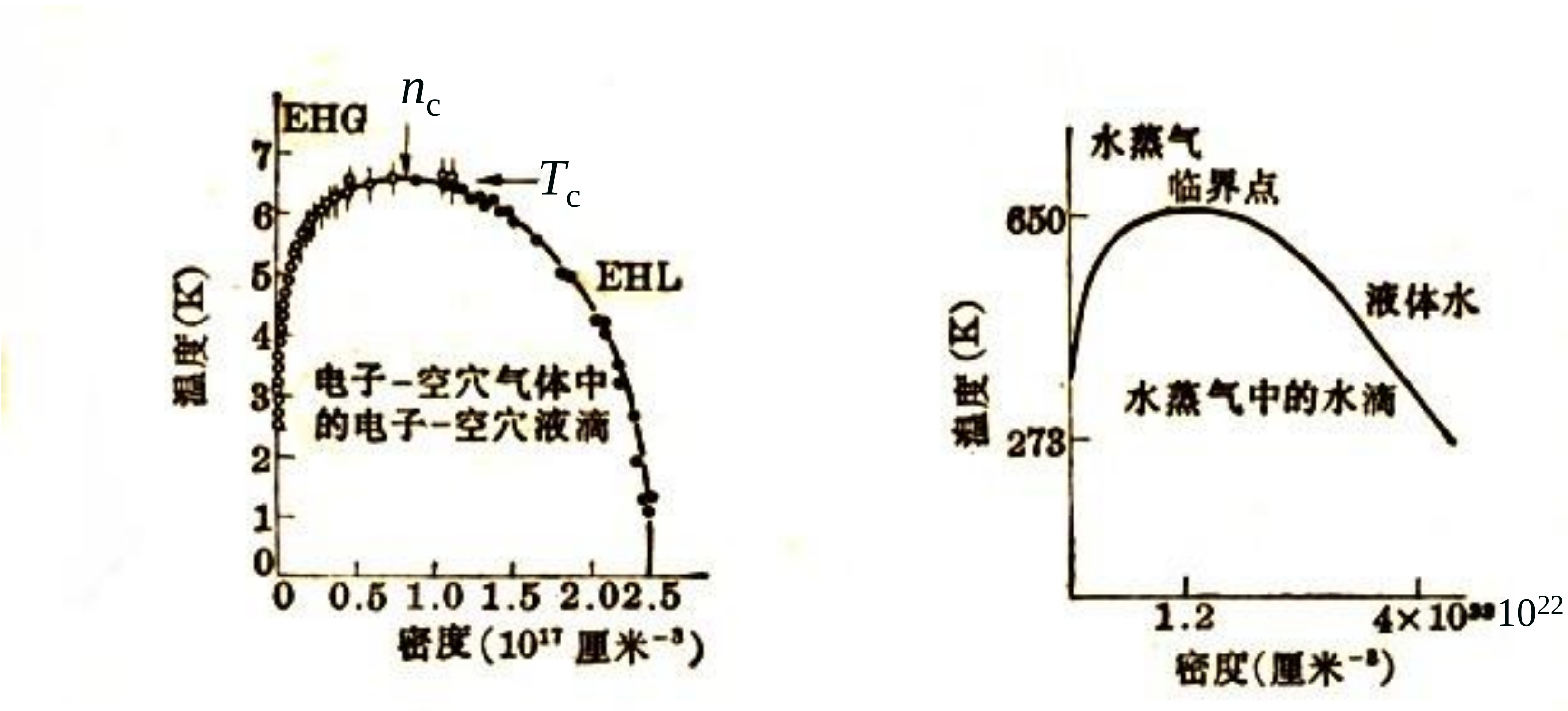


FIG. 1. Photograph of a long-lived electron-hole drop in a 4-mm disk of pure germanium. The sample is mounted in a dielectric sample holder (Ref. 2, Fig. 3) and stressed by a 1.8-mm-diam screw discernible on the left. The drop is the intense spot adjacent to the screw. The bright ring is drop-luminescence light scattered from the sample boundary. The bright line along the lower right crystal rim is scattered luminescence from an orientation mark along the ⟨100⟩ axis. The outer gray ring is the dielectric holder made visible by external illumination.

Wolfe, et al PRL 34, 1292 (1975)

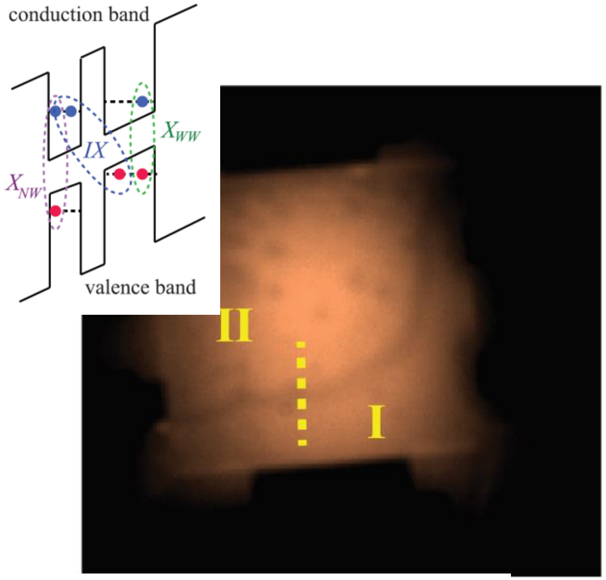
E-H droplet phase diagram

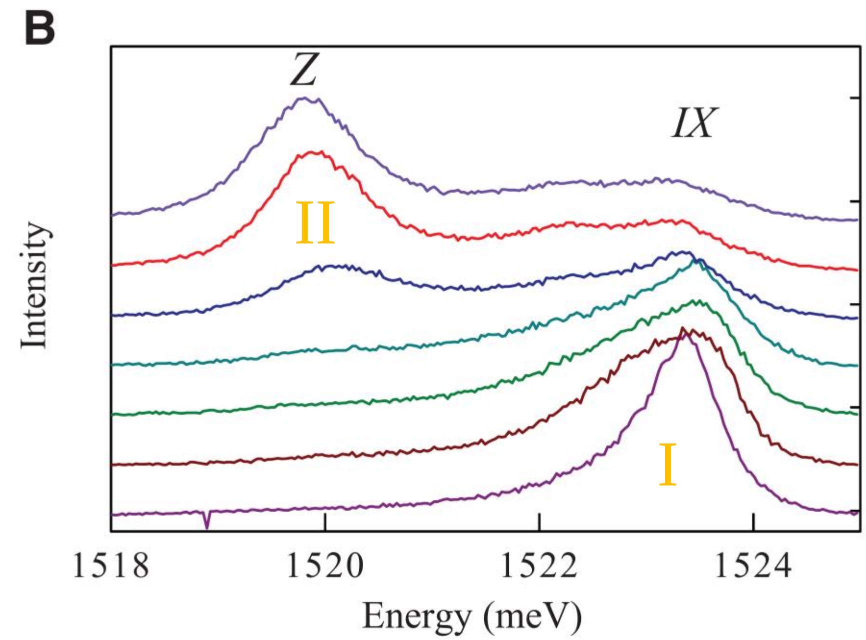


CdS 晶体中 EHG 与 EHL 并存区的相图　　(b) 水与水汽并存时的相图

电子-空穴液的相图与水的相图比较

Exciton Liquid in Coupled Quantum Wells





Phase Boundary

Boundary Instability

Nucleation Experiment

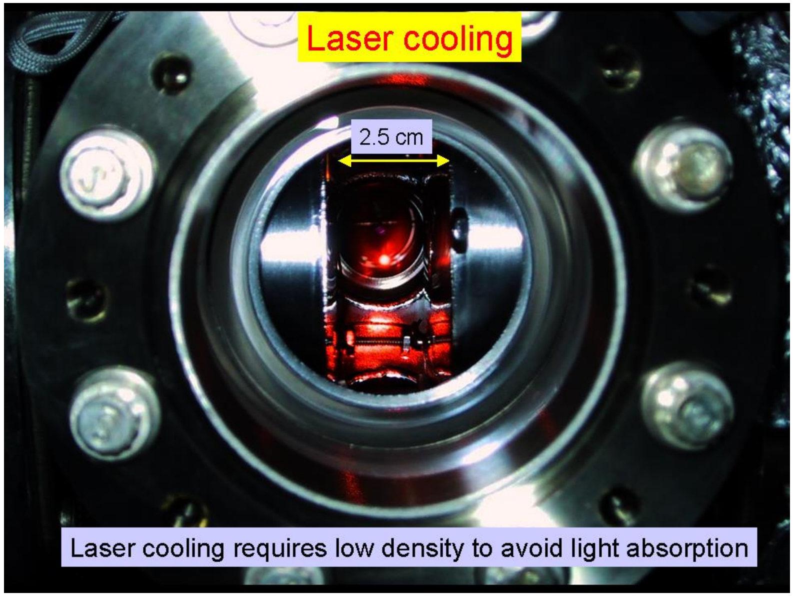
Michael Stern et al. Science 343, 55 (2014)

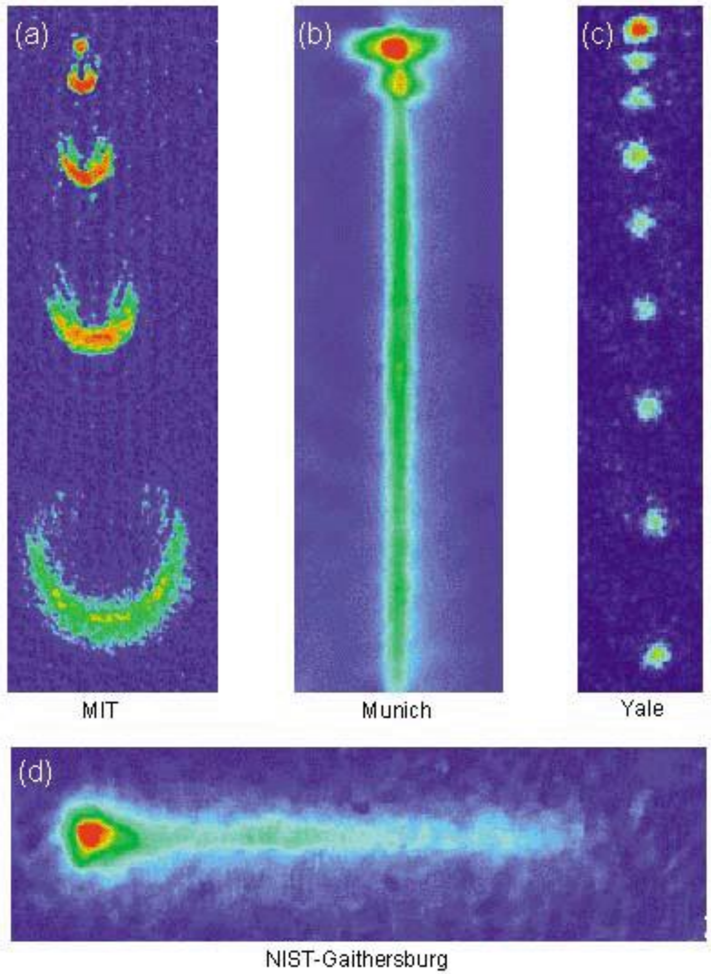
?

BEC in semiconductors

How cold? how dense?

Bose-Einstein condensation

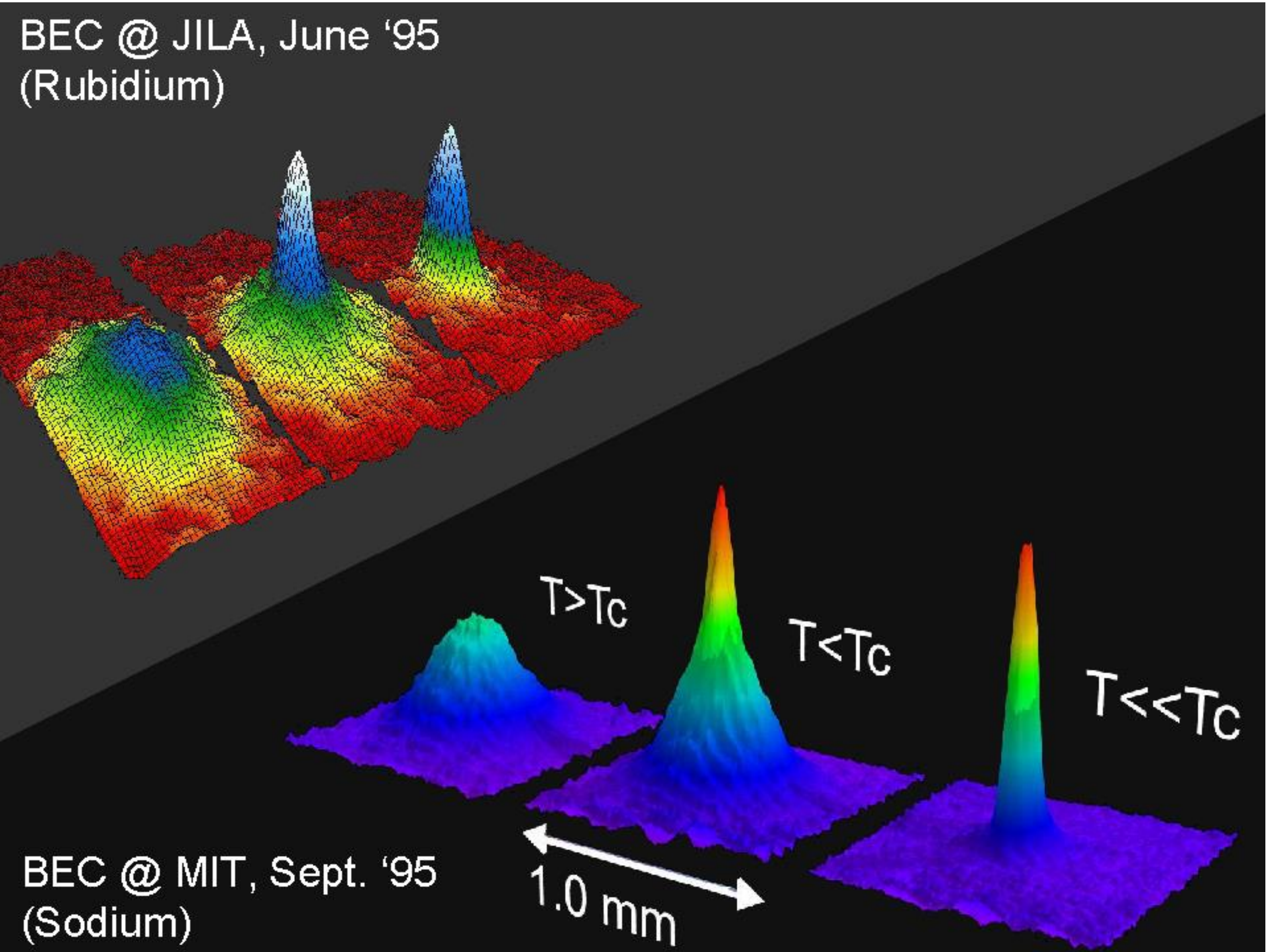




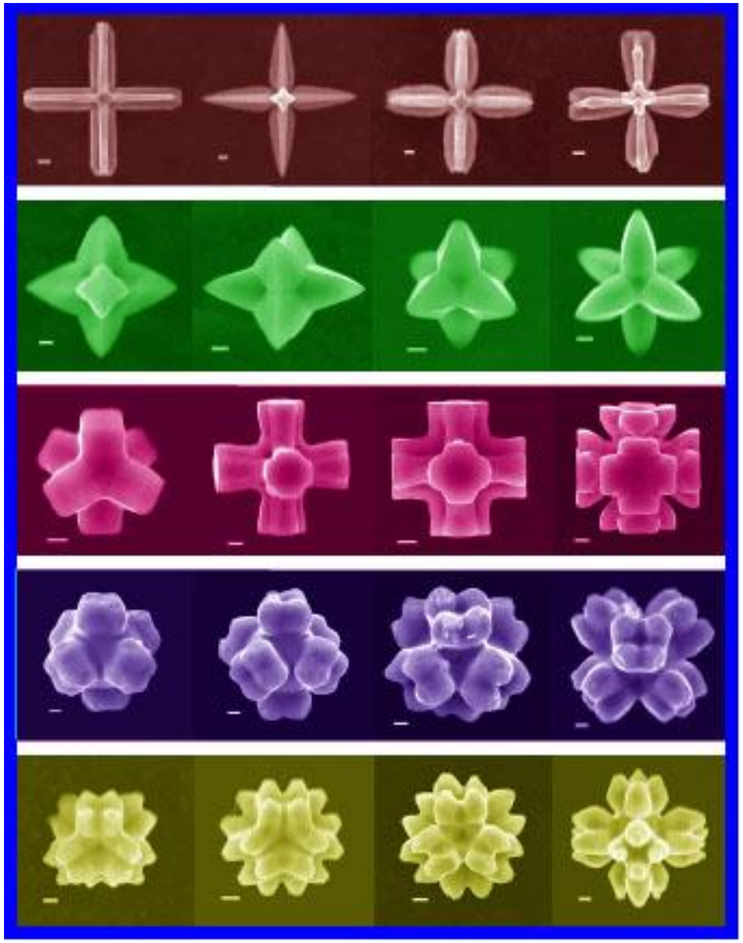
BEC is to matter
as laser is to light

Nature, 385(1997), 685


SCIENCE
AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE
22 DECEMBER 1995
$7.00
VOL. 270 • PAGES 1893–2064
Molecule of the Year
the Bose-Einstein Condensate


BEC @ JILA, June '95
(Rubidium)
T>Tc
T<Tc
T<<Tc
BEC @ MIT, Sept. '95
(Sodium)
1.0 mm

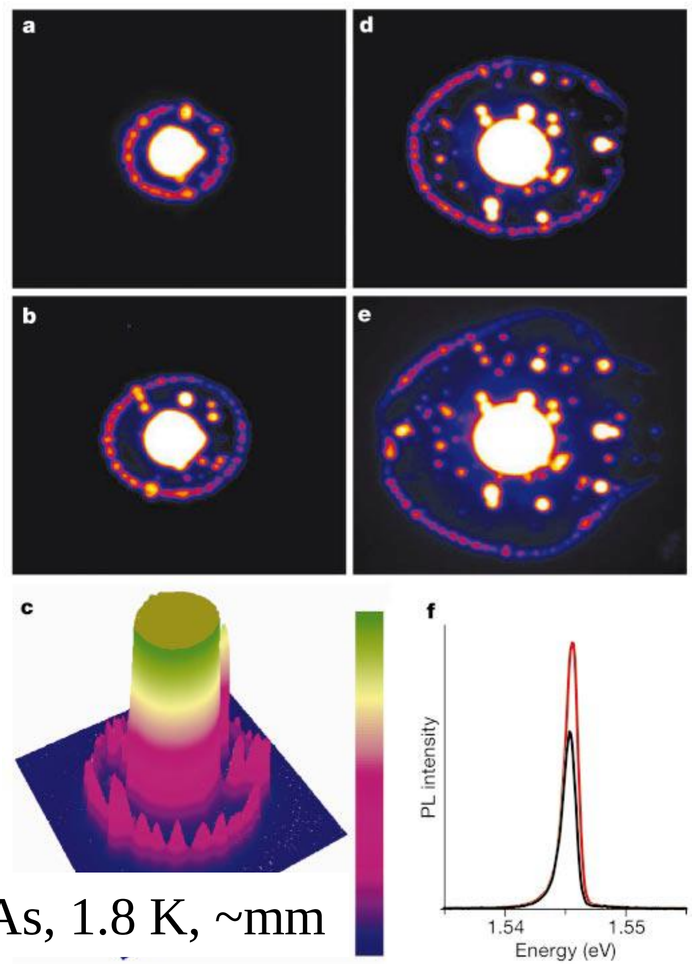
Cu_2O



Cu2O 微晶，带隙1.6-2.2 eV

From Wiki

quasi 2D exciton gas in semiconductors



GaAs, 1.8 K, ~mm

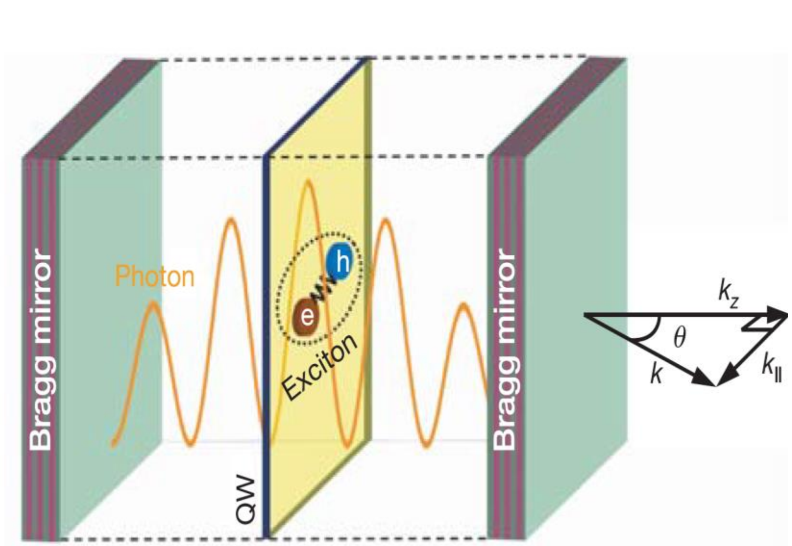
- 在半导体中，激子的有效质量很小，在相同密度条件下，激子凝聚可以在比原子的玻色－爱因斯坦凝聚转变温度高得多的温度发生，可达到1K的量级。
- 其二，高密度的激子凝聚状态和BCS超导状态相类似，所以激子的玻色－爱因斯坦凝聚研究也提供了研究玻色－爱因斯坦凝聚体向BCS超导转变的一种手段。
- 其三，激子玻色－爱因斯坦凝聚体的载体是半导体量子阱，而半导体具有人工物性裁剪的特点。

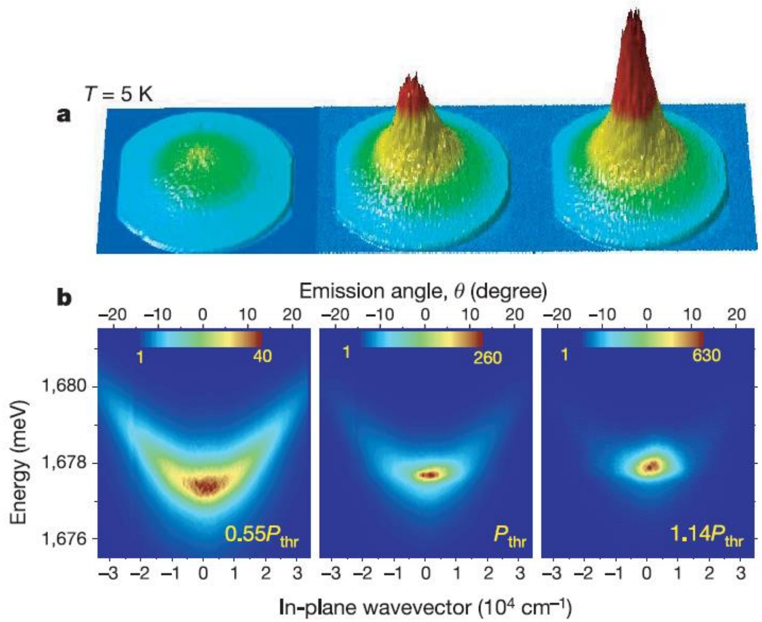
GaAs/AlGaAs coupled QWs

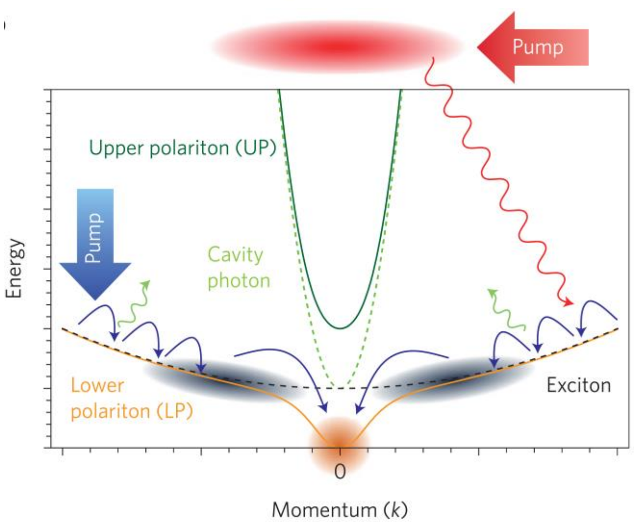
逐渐变强的强激光束照射点（中间的大亮点）周围出现的发光外环和环上出现的周期激子发光点

NATURE 418 751(2002)

Bose–Einstein condensation of exciton polaritons







Far-field emission measured at 5 K for three excitation intensities.

NATURE|Vol 443|409, 28 September 2006

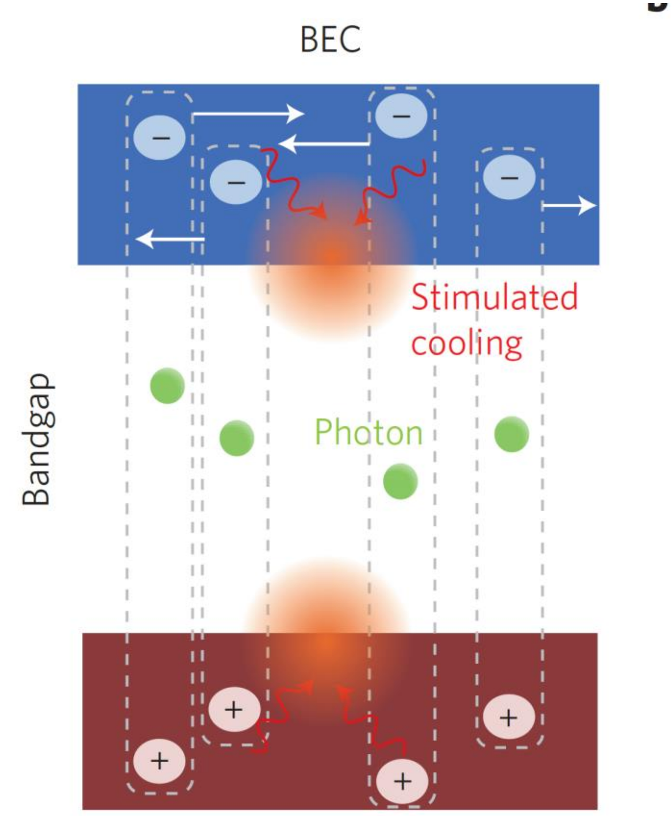
NATURE PHYSICS 31 OCTOBER 2014 | DOI: 10.1038/NPHYS3143

Exciton polariton BEC

Table 1 | Differences between an exciton-polariton BEC,

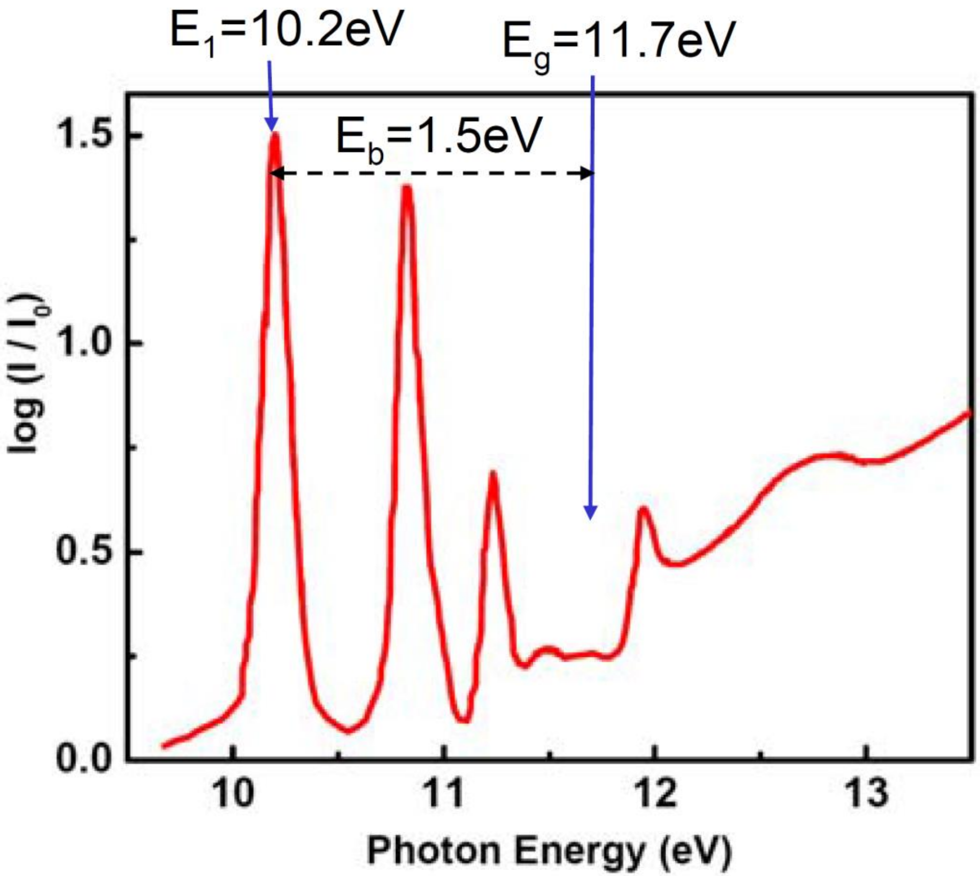
Property
Thermal equilibrium below threshold[5,6]
Bose distribution above threshold
Threshold corresponds to onset of degeneracy[5-7]
Linewidth narrowing[5,6]
Increase of temporal coherence $g^{(1)}(\tau)$[5,113]
Spontaneous polarization[14]
Long-range spatial coherence $g^{(1)}(r)$[5,6,47]
Polaritons are the particles that accumulate coherence (strong c
Heisenberg-limited position and momentum uncertainty produc

The properties that have been experimentally demonstrated for polariton condensate



Frenkel excitons in rare gas crystals

absorption spectrum of crystalline Kr at 20K:

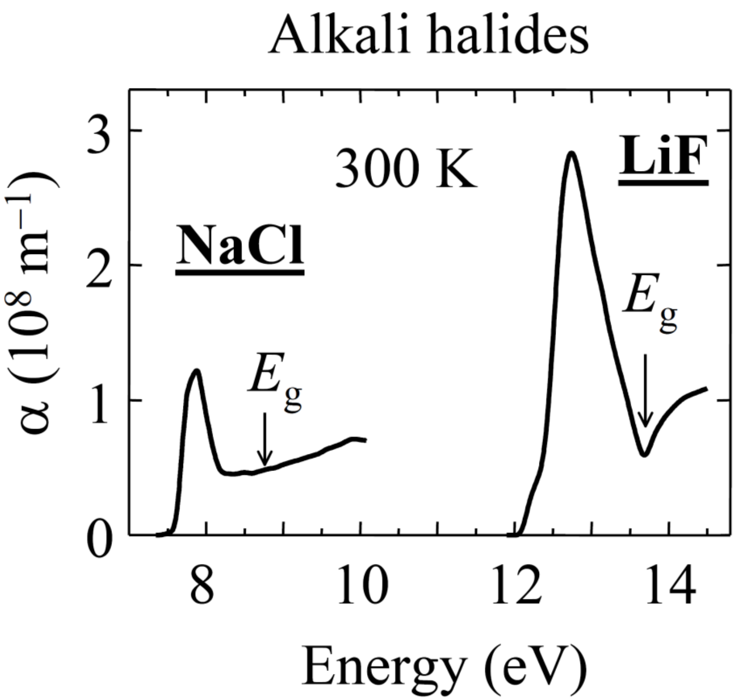


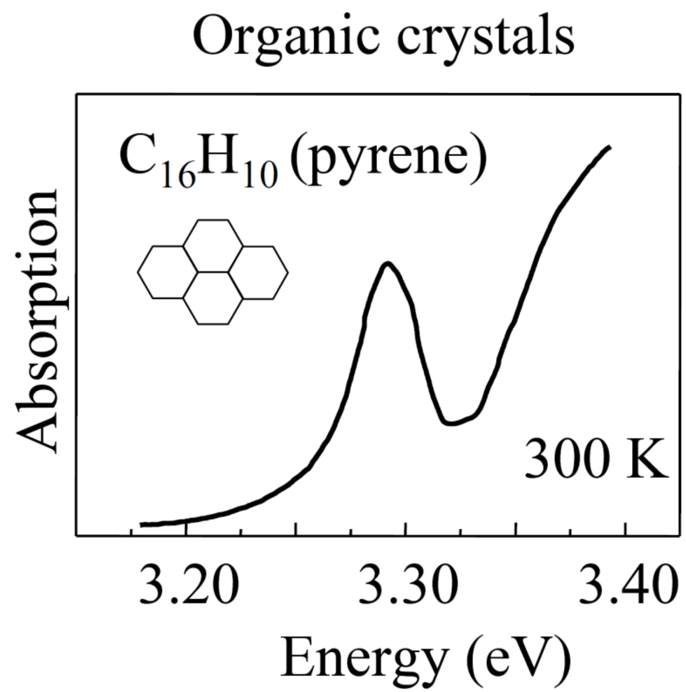
Note: the lowest strong absorption in isolated Kr is at 9.99eV
↓
close to lowest excitonic transition E1 in crystal

(solid Ne, Ar, Kr, Xe)

The widest gap 21.6 eV: Ne crystal

Frenkel exciton example:





S
T

	E_g(eV)	R_X (eV)
NaCl	8.8	0.9
LiF	13.7	1.9

Also: Rare gas crystals (solid Ne, Ar, Kr, Xe)

Transition energies for Frenkel excitons

- transition energies often correspond to those found in the isolated atom or molecule that the crystal is composed of
- Tight binding or quantum-chemical methods
- often need to include effects of strong coupling between excitons and the crystal lattice (polaronic contributions)

课后作业

4.2 （选做) Show that the wavefunction $\psi(r,\theta,\phi) = C\exp(-r/a_0)$ is a solution of the Schrödinger equation ,

$$\hat{H}\psi = E\psi \,,$$

where $\hat{H}$ is the Hamilton of an exciton indicated in exercise 4.2 , page 110 in text , 2nd edition)

4.17 Calculate the Bose-Einstein condensation temperature for excitons in cuprous oxide when the exction density is 10^{24} m^{-3}. The electron and hole effective masses are $0.1m_0$ and $0.7\ m_0$.

Bose-Einstein condensation of photons

In a optical cavity