Ch 3-2 半导体的载流子跃迁过程

主要参考资料：

1. 半导体物理导论，刘诺，CH3

2. 固体光谱学，科大，方容川

3. Semiconductor Physics， Claus Klingshirn

内容提要

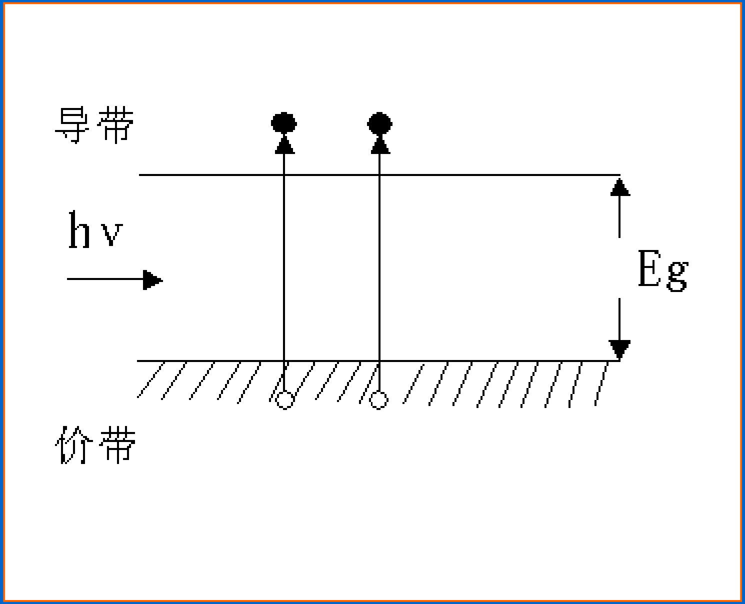
- 半导体中的光吸收
- 半导体中的光复合(荧光)
- （半导体中光跃迁基本测试技术）

一、半导体中的光吸收

半导体材料通常能强烈地吸收光能，具有~$10^5 cm^{-1}$的吸收系数。材料吸收辐射导致电子从低能级跃迁到较高的能级。由于在晶体中有很多能级 ⇒ 连续的吸收带。

A. 本征吸收物理图象

理想半导体在0K时，价带完全被电子占满，导带是空的，价带内的电子是不可能被激发到更高的能级上（由于带隙Eg)。唯一可能的吸收是足够能量的光子使电子激发，越过禁带，而在价带中留下一个空穴，形成电子—空穴对。

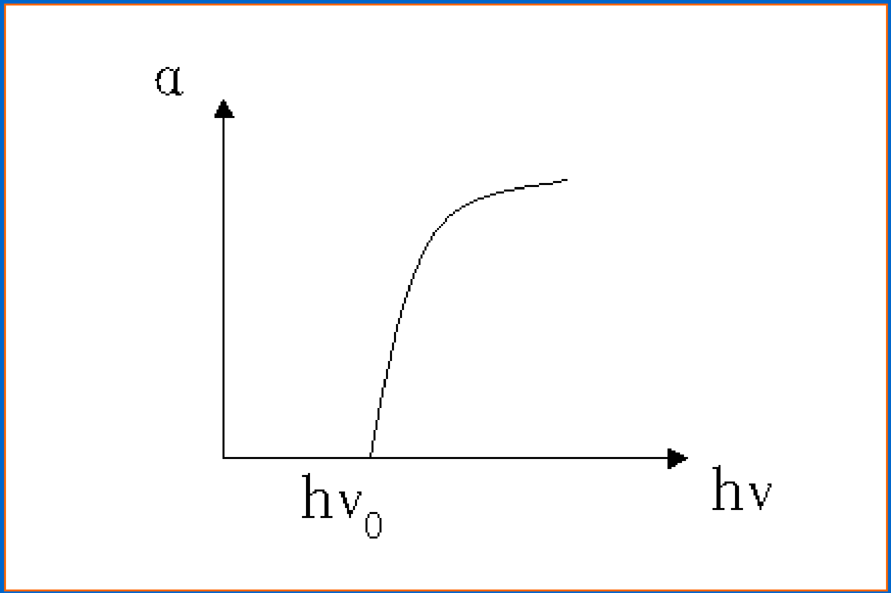


这种由于电子由带与带之间的跃迁所形成的吸收过程—本征吸收（带边吸收）

发生本征吸收，

光子能量必须等于或者大于禁带宽度E_g：　$h\nu \geq h\nu_0 = E_g$

当频率低于ν_0时，不可能发生本征吸收，吸收系数迅速下降。



典型半导体

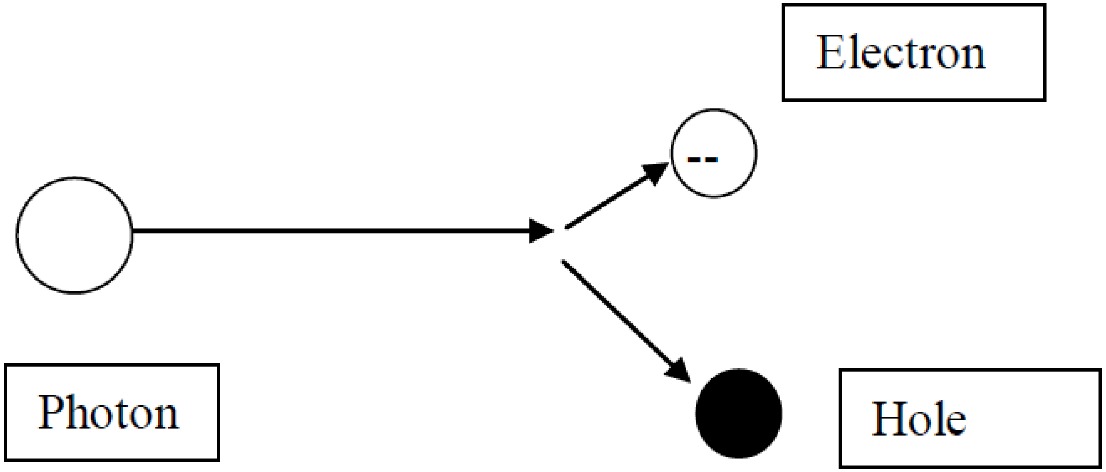
GaAs: $E_g = 1.43eV$, $\lambda_0 = 0.867\mu m$，　$\nu_0 = 3.46 \times 10^{14} Hz$

Si:　　$E_g = 1.12eV$, $\lambda_0 = 1.10\mu m$，　$\nu_0 = 2.73 \times 10^{14} Hz$

吸收限在红外区

光吸收过程中的选择定则

The energy and momentum conservation laws require certain conditions to be satisfied to make this absorption possible.



For the direct photon into e-h pair transformation,

$$E_{ph} = E_g;$$

$$p_{ph} = |p_e - p_h|,$$

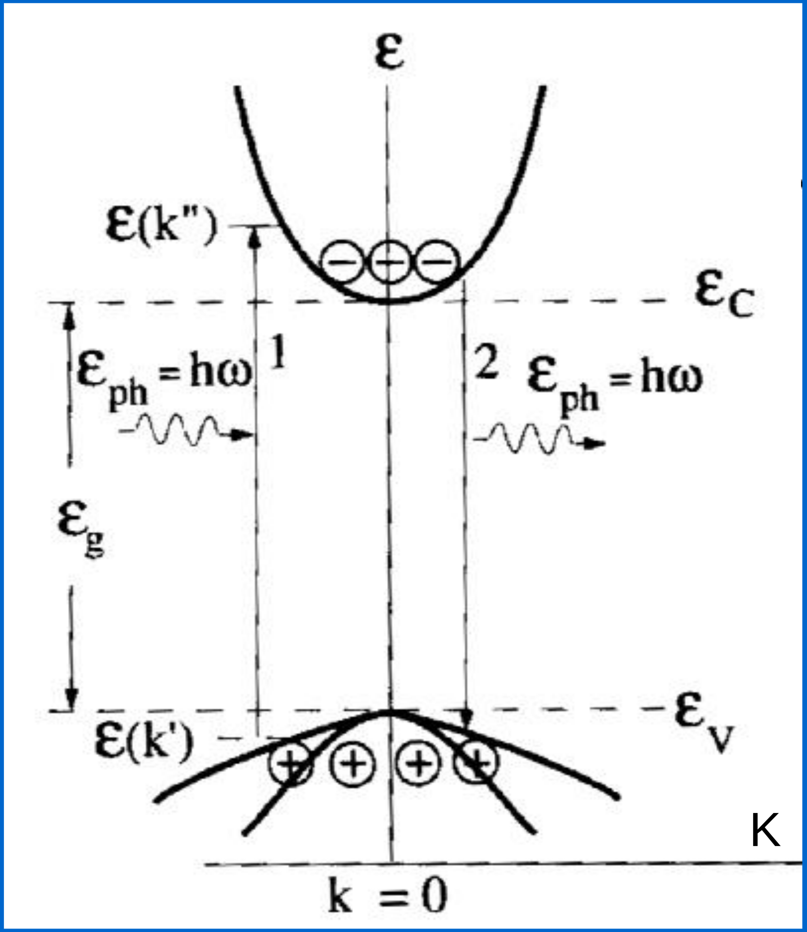
A、直接带隙半导体

The mass of the photon is negligibly small:

$$p_{ph} \approx 0;$$
$$(\text{because } \boldsymbol{p} = \boldsymbol{m} \times \boldsymbol{v})$$

Therefore after the absorption the $\boldsymbol{e}$ and the $\boldsymbol{h}$ must have equal momentums:

$$p_e \approx p_h;$$



无声子参与情况下

电子吸收光子的跃迁过程必须满足能量和动量守恒，电子在跃迁过程中波矢保持不变 (在波矢k空间必须位于同一垂线上）➔直接跃迁

直接跃迁中吸收系数α和光子能量的关系

(Tauc law, Tauc plot)

K=0 处

$$\alpha(h\nu)=\begin{cases}A(h\nu-E_g)^{\frac{1}{2}} & h\nu\geq E_g\\ 0 & h\nu<E_g\end{cases}$$

$$A=\frac{q^2\left(\frac{2m_h^*m_e^*}{m_h^*+m_e^*}\right)^{3/2}}{nch^2m_e^*}$$

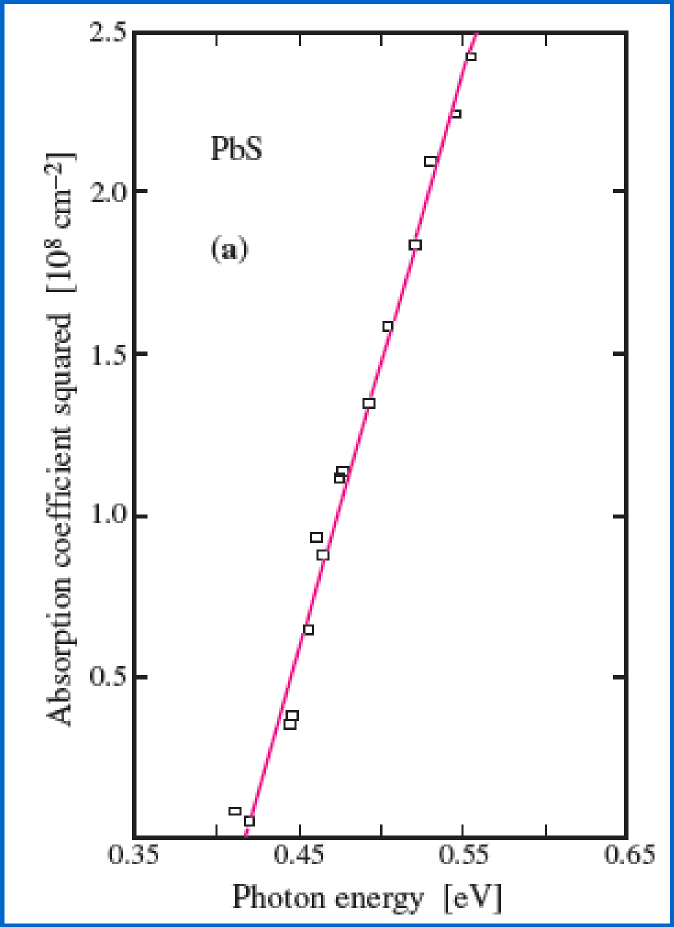
K≠0 处

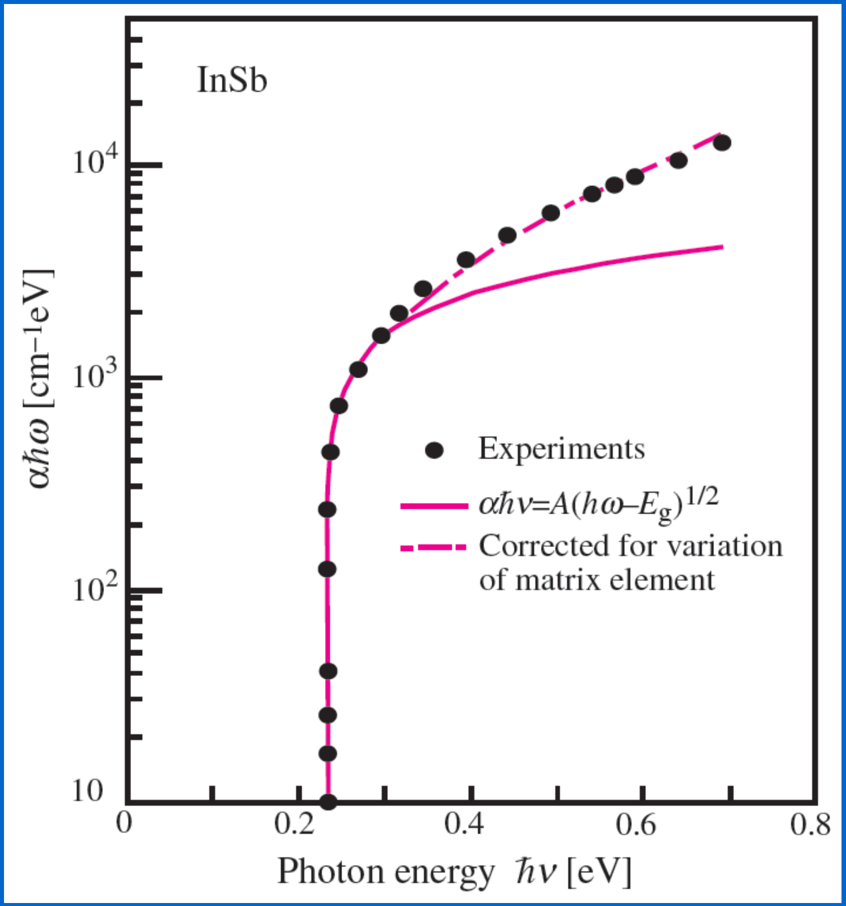
$$\alpha(h\nu)=\begin{cases}A^{'}(h\nu-E_g)^{\frac{1}{2}} & h\nu\geq E_g\\ 0 & h\nu<E_g\end{cases}$$

$$A^{'}=\frac{4}{3}\frac{q^2\left(\frac{2m_h^*m_e^*}{m_h^*+m_e^*}\right)^{5/2}}{nch^2m_e^*m_h^*h\gamma}$$

Pankove, Optical processes in semiconductors (1975, Dover)

例子1 *Yu, Fundamentals of semiconductors (2010, Springer)*





- Plot of the square of the absorption coefficient of PbS as a function of photon energy showing the linear behavior
- The intercept with the *x*-axis defines the direct energy gap

- Semilogarithmic plot of the absorption coefficient of InSb at 5 K as a function of photon energy. The *filled circles* represent experimental results.
- The intercept with the *x*-axis gives the direct bandgap of InSb

1. Urbach Tail
(低能端)

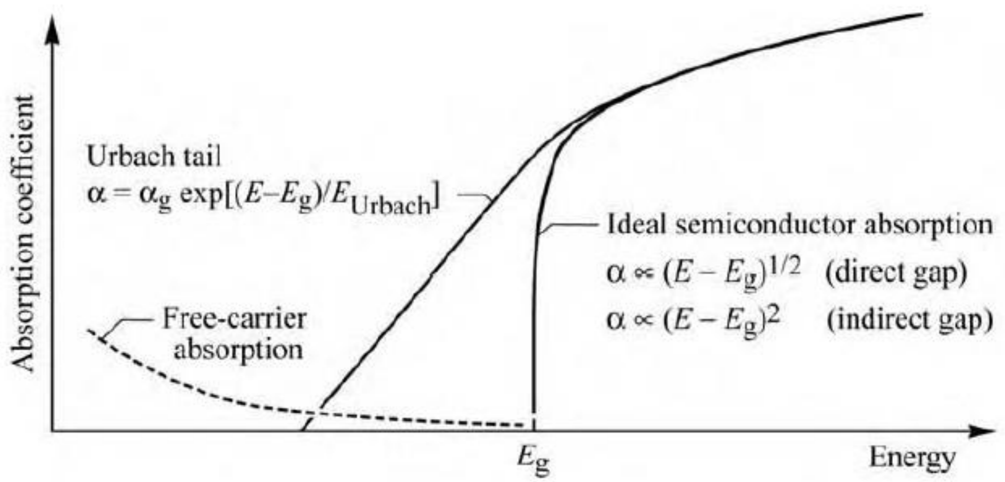


Fig. 9.1. Absorption coefficient of a semiconductor with bandgap E_g versus energy. The "Urbach tail" dominates absorption near but below the bandgap. Absorption further below the bandgap is dominated by free-carrier absorption.

The idealized semiconductor has a *zero* band-to-band absorption coefficient at the bandgap energy ($E = E_g$). The absorption strength in a *real* semiconductor, for below-bandgap light, can be expressed in terms of an exponentially decaying absorption strength. In this absorption tail, called the ***Urbach tail***, the absorption coefficient versus energy is given by

$$\alpha = \alpha_g \exp\left[(E - E_g)/E_{Urbach}\right] \quad (9.3)$$

where α_g is the experimentally determined absorption coefficient at the bandgap energy and E_{Urbach} is the characteristic energy (here called the ***Urbach energy***), which determines how rapidly the absorption coefficient decreases for below-bandgap energies.

J. Phys. Chem. Lett. 2014, 5, 1035−1039

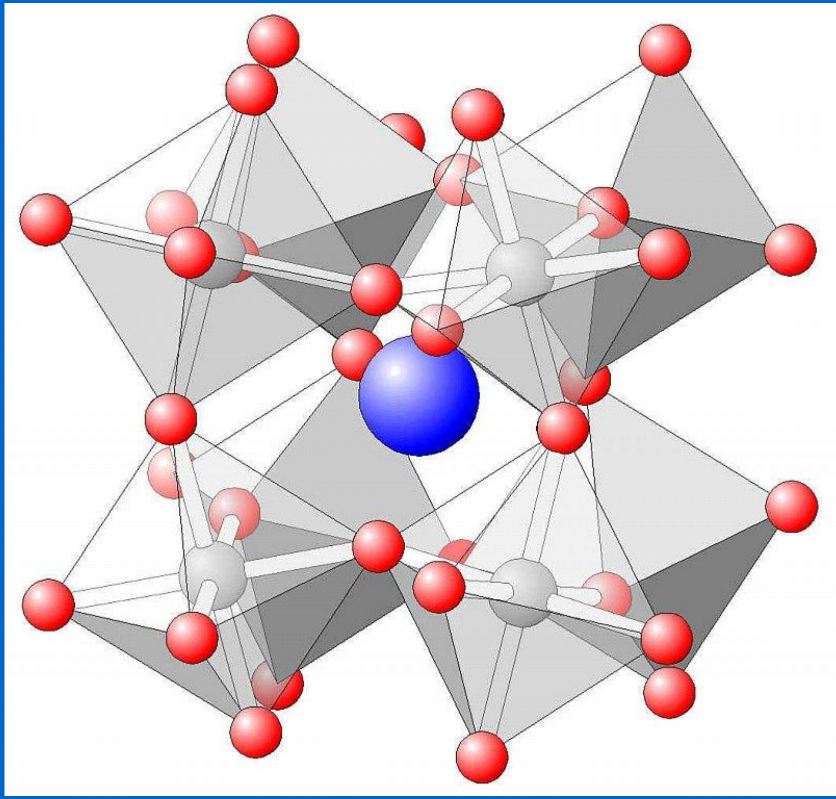
Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance

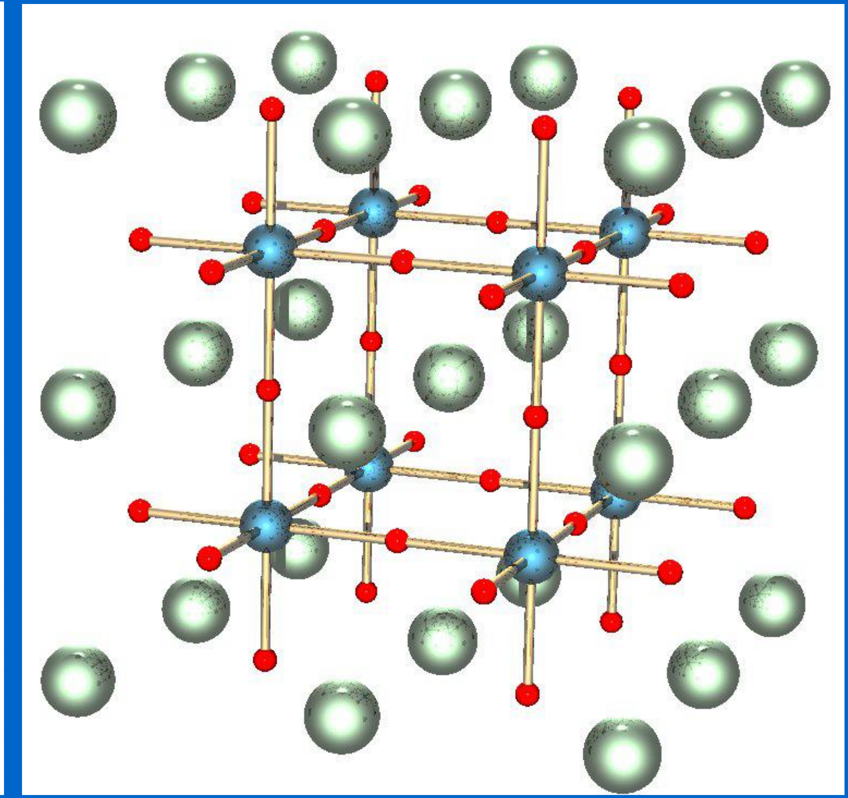
Stefaan De Wolf,*,† Jakub Holovsky,‡ Soo-Jin Moon,§ Philipp Löper,† Bjoern Niesen,† Martin Ledinsky,†,‡ Franz-Josef Haug,† Jun-Ho Yum,§ and Christophe Ballif†,§

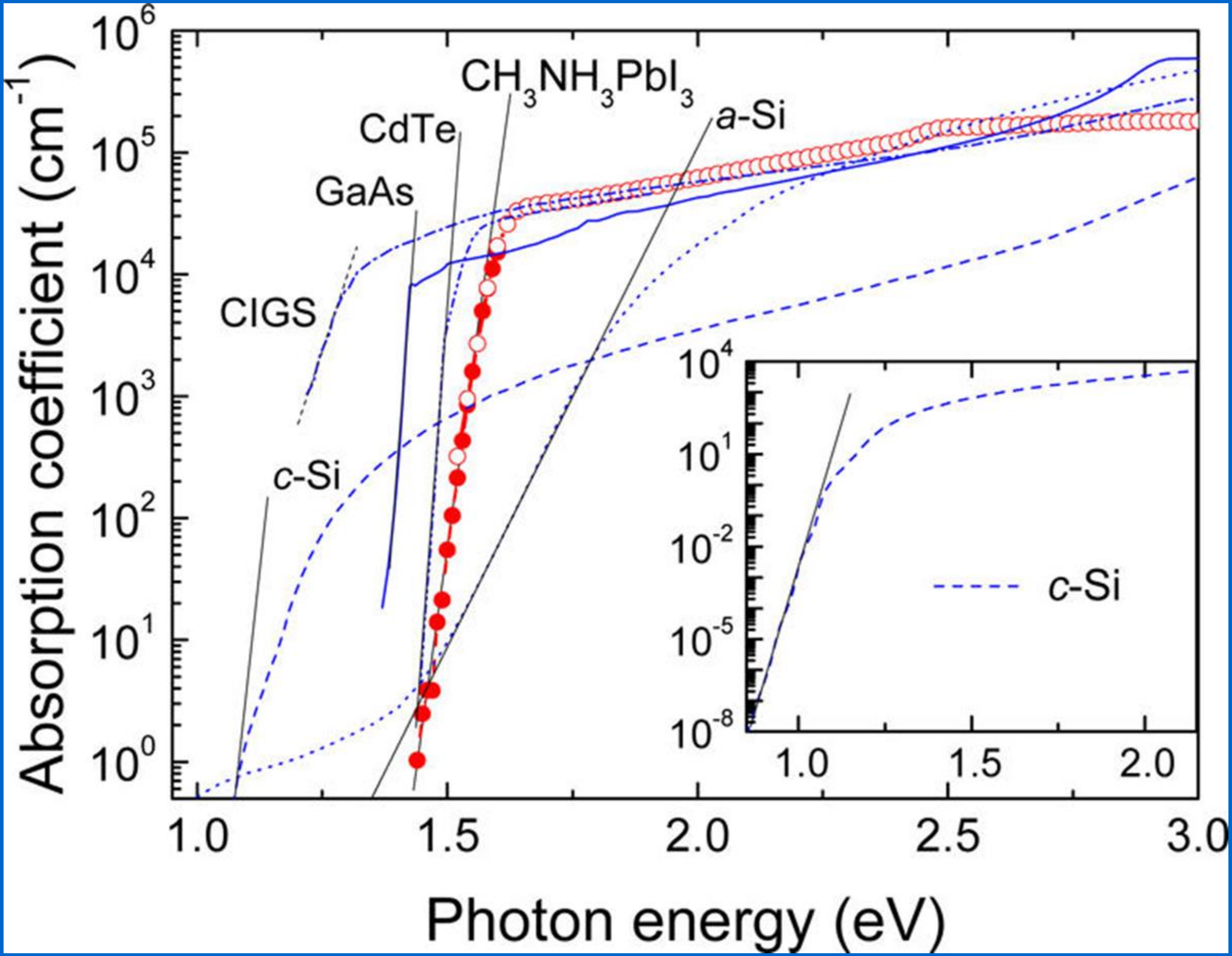
†Photovoltaics and Thin-Film Electronics Laboratory, Institute of Microengineering (IMT), Ecole Polytechnique Fédérale de Lausanne (EPFL), Maladière 71, Neuchâtel 2000, Switzerland

‡Institute of Physics, Academy of Sciences of the Czech Republic, v. v. i., Cukrovarnická 10, 162 00 Prague, Czech Republic

§PV Center, Centre Suisse d'Electronique et de Microtechnique (CSEM), Jacquet Droz 1, Neuchâtel 2000, Switzerland







E_{urbach} = 15 meV

B、间接带隙半导体（间接跃迁）

1. 电子不仅吸收光子，同时还和晶格交换一定的振动能量，即放出或吸收一个声子从而达到动量守恒.

2. 光吸收系数（1-10^3 cm^{-1}）比直接跃迁（10^4 - 10^6 cm^{-1} ）小得多。

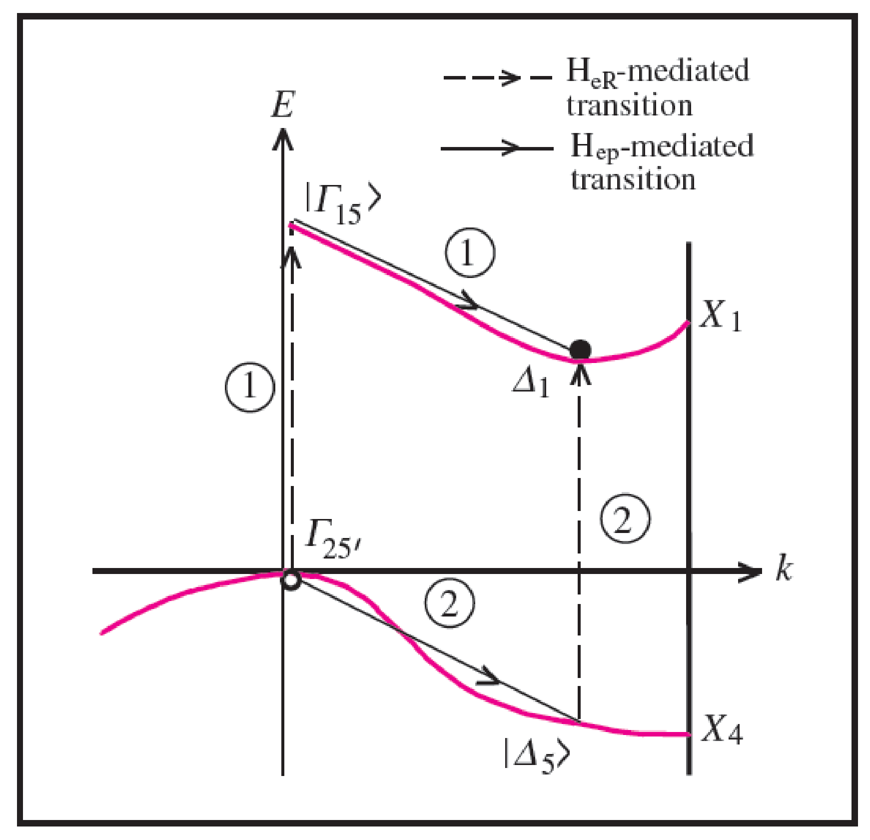


Fig. 6.16. Schematic band structure of Si as an indirect-bandgap semiconductor showing the phonon-assisted transitions (labeled **1** and **2**) which contribute to the indirect absorption edge. $|\Gamma_{15}\rangle$ and $|\Delta_5\rangle$ represent intermediate states

间接跃迁中吸收系数α和光子能量的关系

吸收声子过程：

$$\alpha_a = \frac{A(h\gamma - E_g + E_p)^2}{e^{E_p/kT} - 1}$$

发射声子过程：

$$\alpha_e = \frac{A(h\gamma - E_g - E_p)^2}{1 - e^{-E_p/kT}}$$

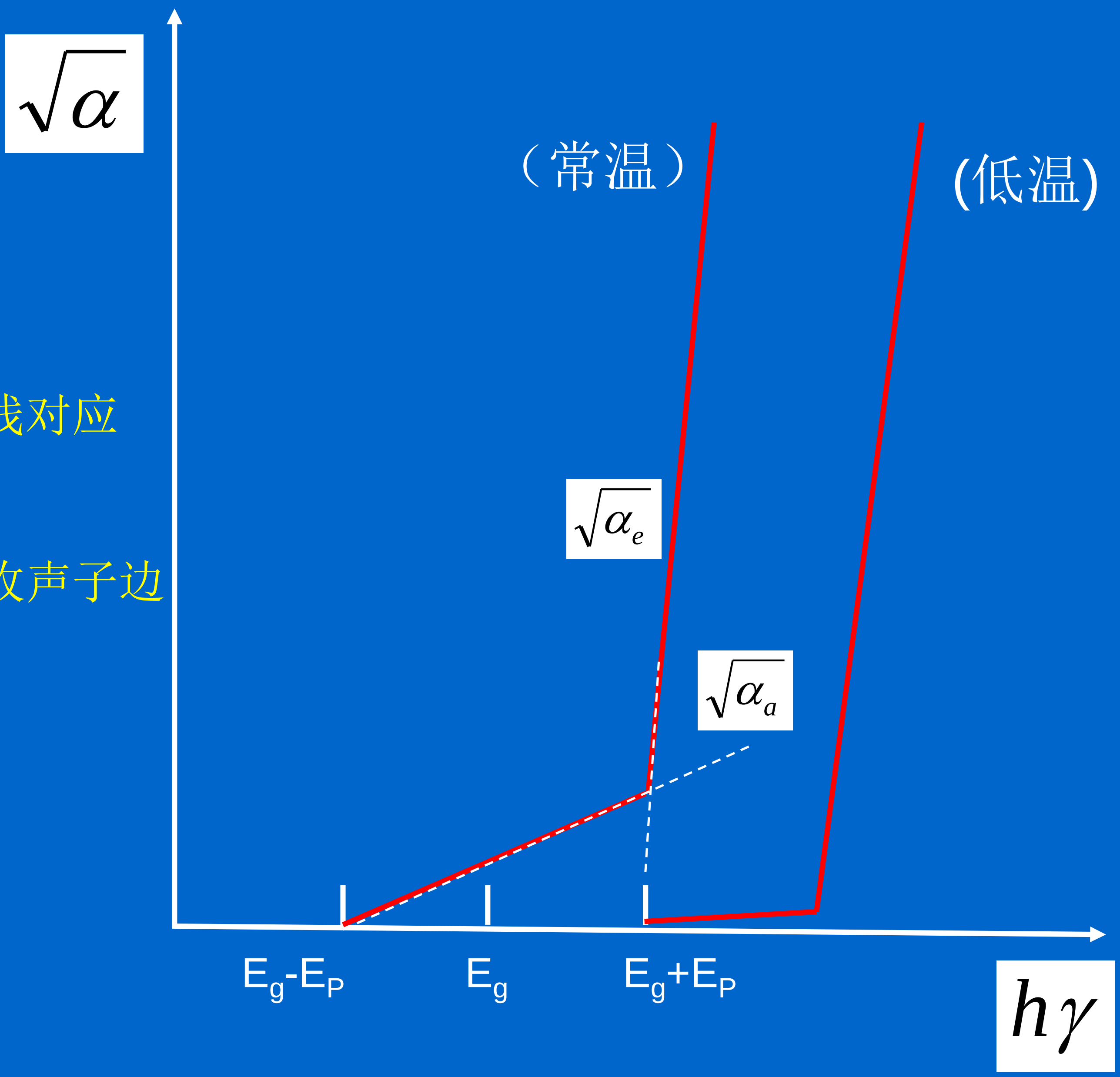
总的过程：

$$\alpha = \alpha_e + \alpha_a$$

- 不仅与能量有关系，而且温度有关系。
- 相同能量，温度越高， 吸收系数越大

1. 每条吸收曲线对应两个吸收边

2. 低温下，吸收声子边不出现



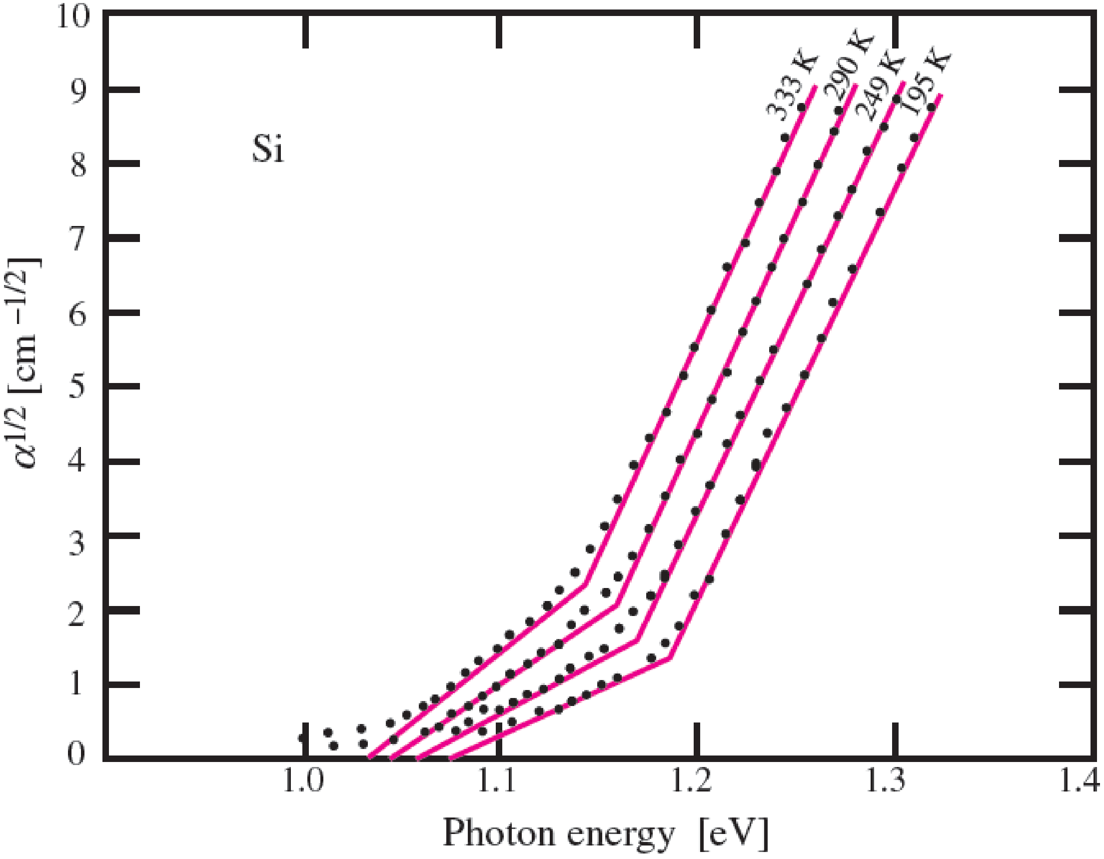


Fig. 6.17. Plots of the square root of the absorption coefficients of Si versus photon energy at several temperatures. The two segments of a straight line drawn through the experimental points represent the two contributions due to phonon absorption and emission [6.33]

C. 其他吸收过程

(i) 激子吸收

- 电子和空穴受库伦互相作用而束缚结合在一起而成为一个新的系统 — 激子。
- Frenkel激子和Wannier激子
- 激子吸收发生在带隙E_g低能处, 束缚能E_b

$$E_r(n) = E_r(\infty) - \frac{R^*}{n^2}$$

$$R^* = \frac{\mu e^4}{2\hbar^2 (4\pi\varepsilon_0)^2 \varepsilon_0^2} = \left(\frac{\mu}{m\varepsilon_0^2}\right) \times 13.6\ \text{eV}$$

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

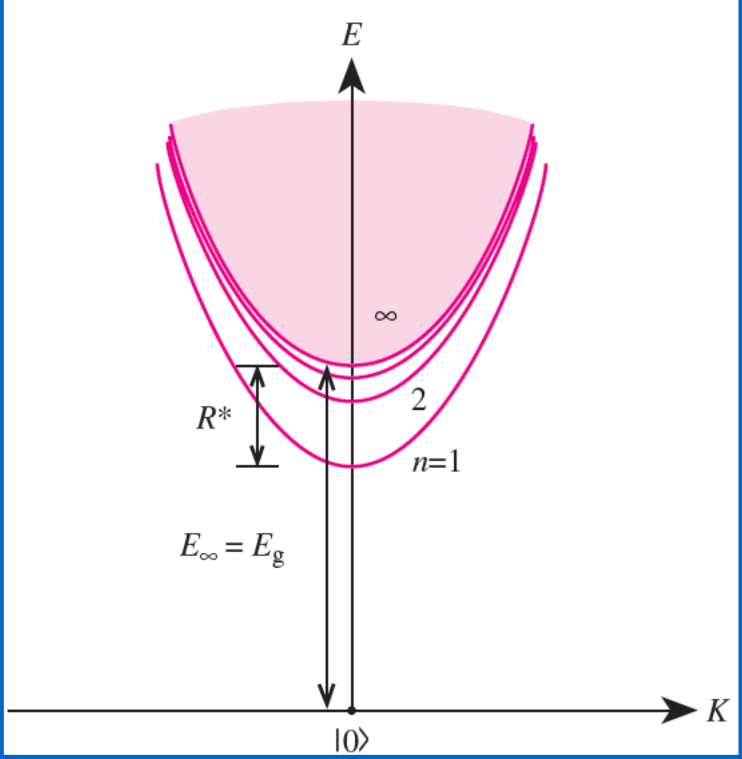


Fig. 6.21. The energy states of a Wannier exciton showing both its bound states n =1 to 3 and the continuum states. E_g is the bandgap and R_* the exciton binding energy.

激子吸收例子 --- 理论

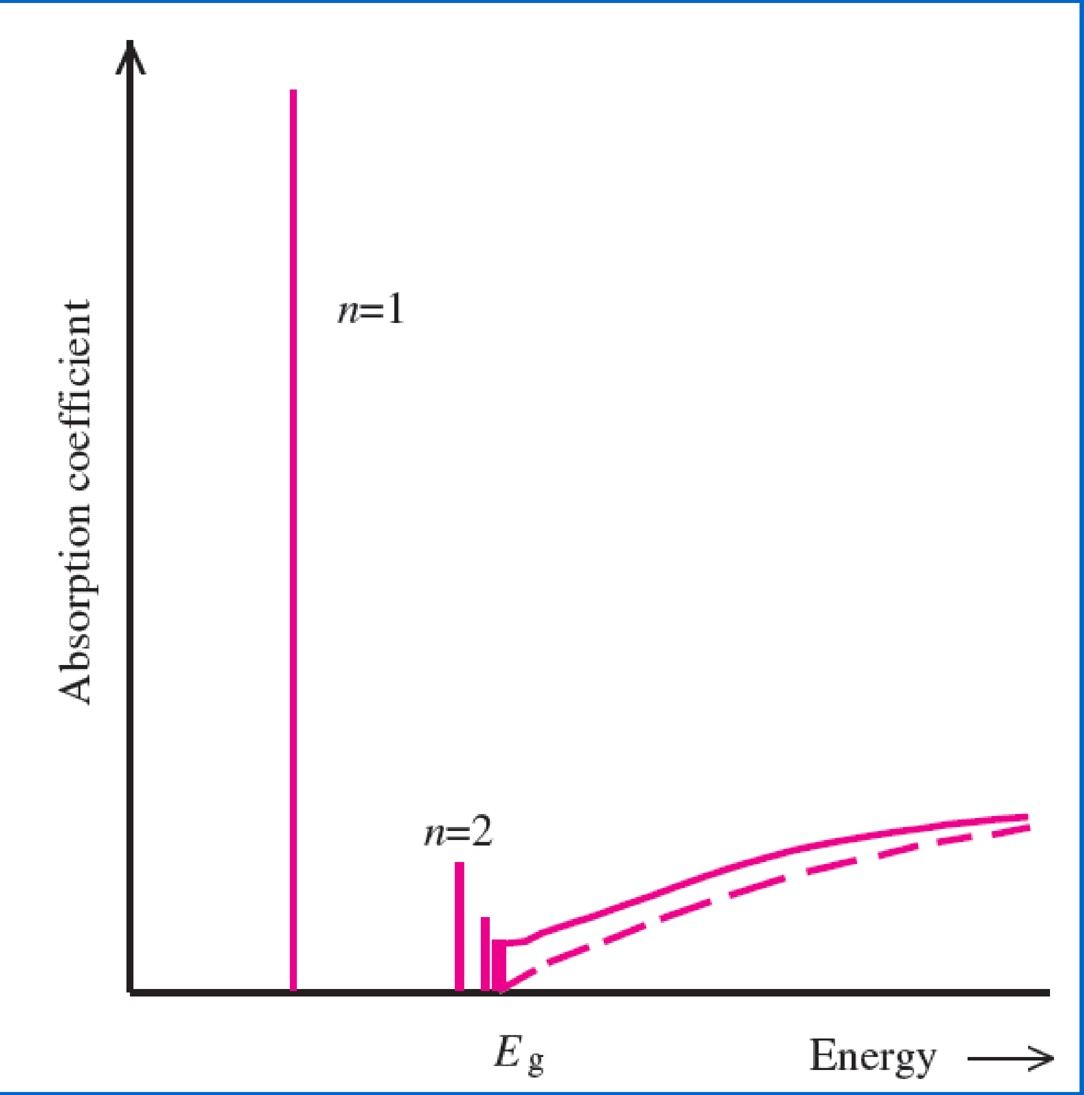


Fig. 6.24. Comparison between the absorption spectra in the vicinity of the bandgap of a direct-gap semiconductor with (*solid lines*) and without (*broken curve*) exciton effects

激子吸收例子 --- 实验

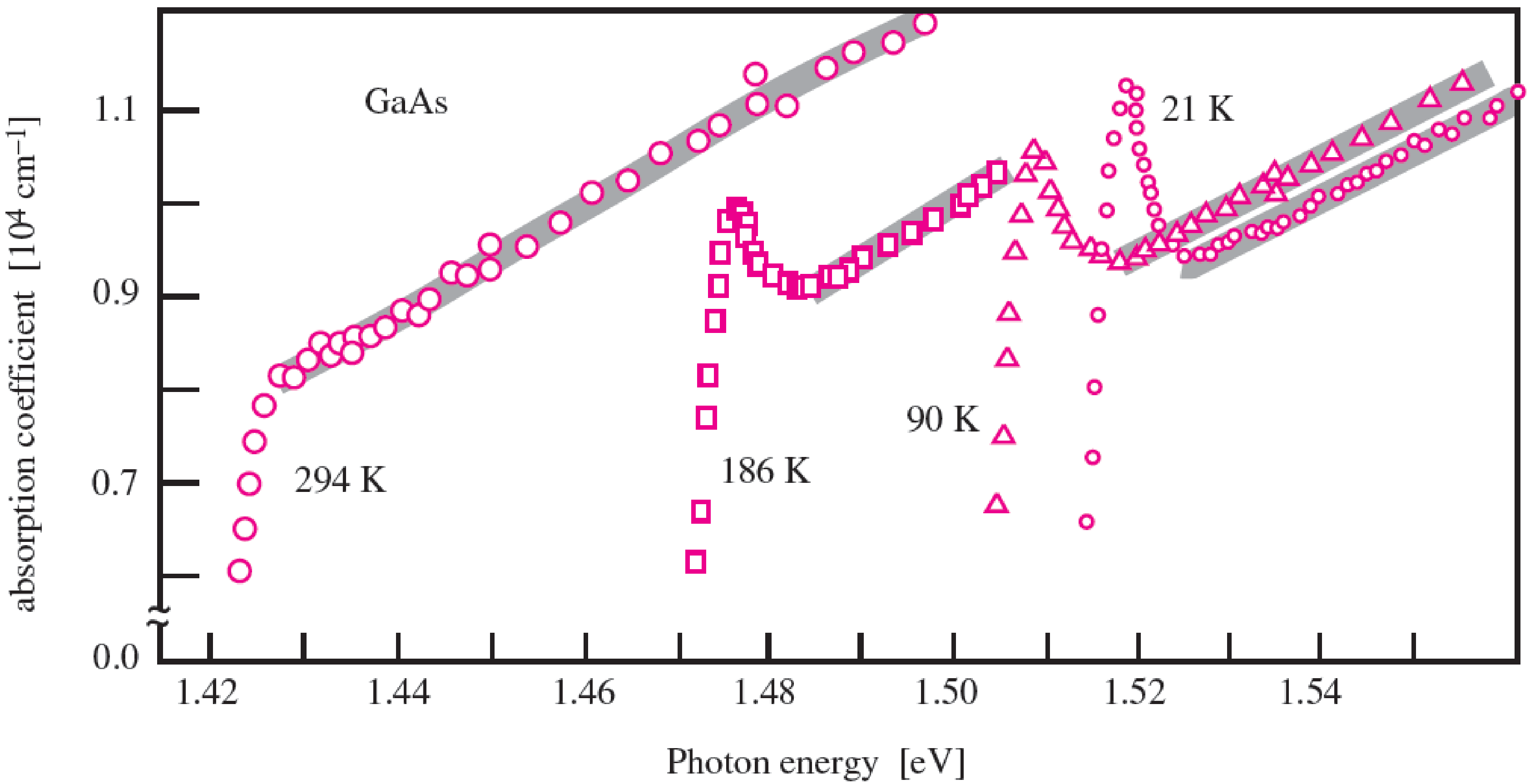


Fig. 6.25. Excitonic absorption spectra of GaAs near its bandgap for several sample temperatures. The *gray lines* drawn through the 21, 90 and 294 K data points represent fits with (6.90) [6.54]

（ii） 自由载流子吸收

入射光子能量hv<E_g，不能引起带隙间的跃迁，但可以引起同一带内的跃迁

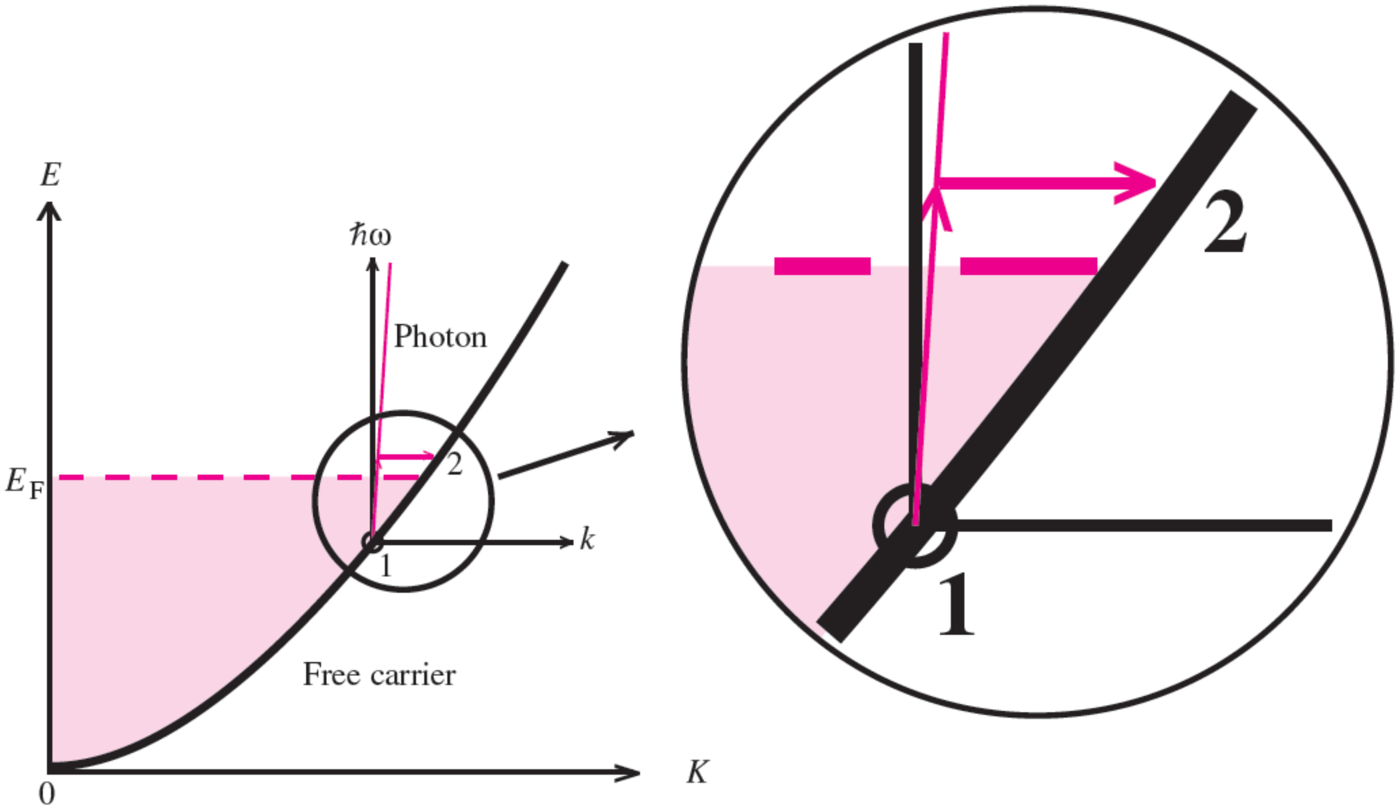
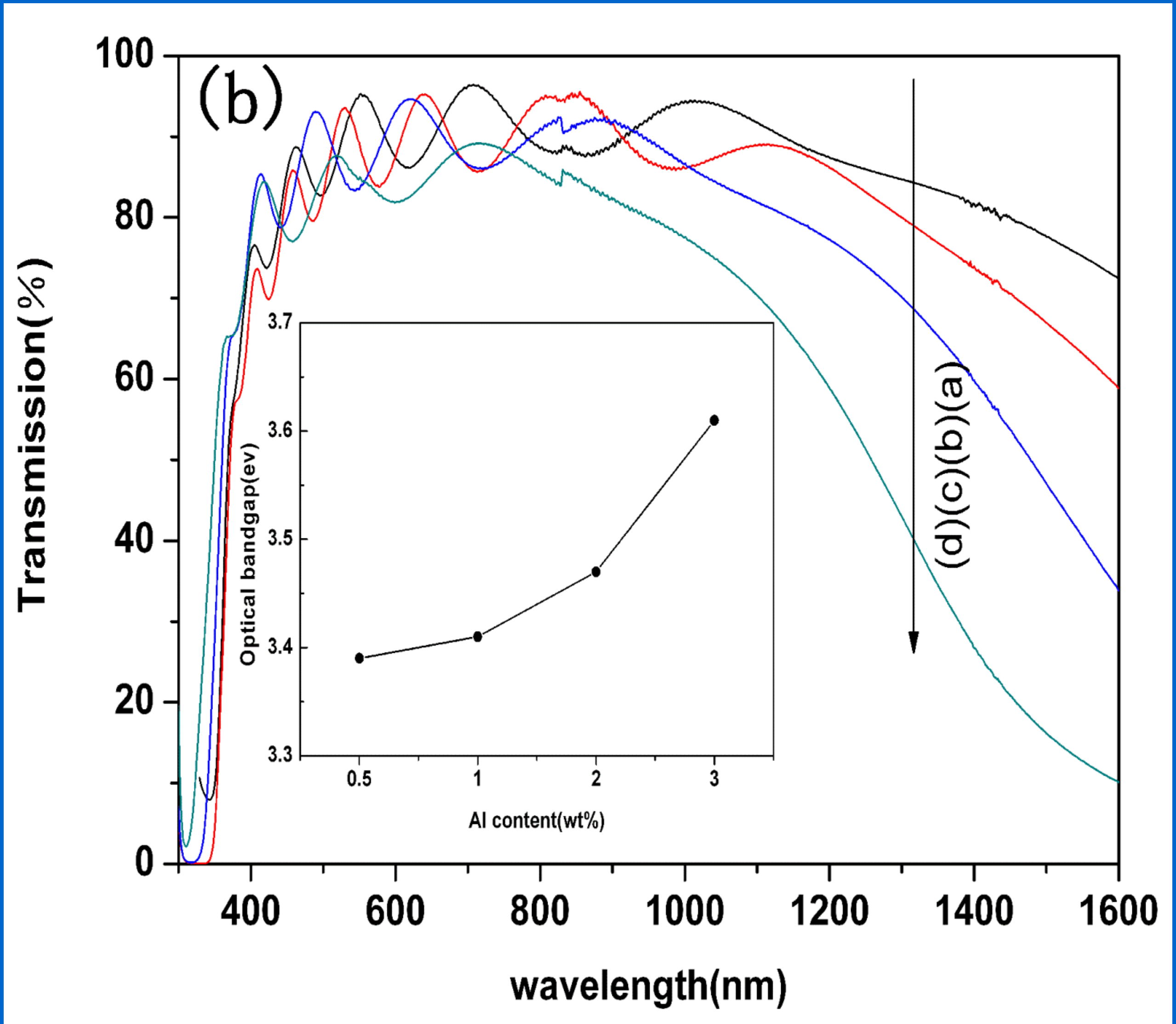


Fig. 6.34. Schematic diagram of a free-carrier absorption process near the Fermi level E_F. The thin red straight line labeled "photon" represents the light dispersion. During absorption a carrier from state 1 below E_F is excited to an empty state 2 above E_F. Scattering with a phonon or impurity, represented by the horizontal arrow, is needed to conserve energy and wavevector in this process

AZO薄膜的光透过谱



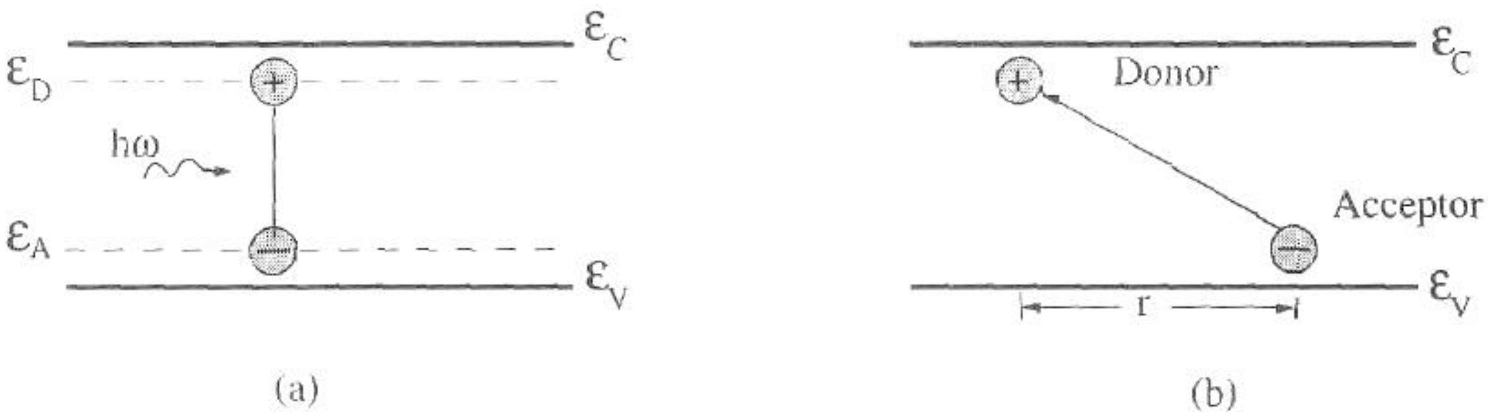
$$\alpha_c = \frac{4\pi N_c e^2}{4\pi\varepsilon_0 n_r c m^* \gamma_c}$$

$$\alpha_c \propto \lambda^p$$

a~d铝元素含量依次增大

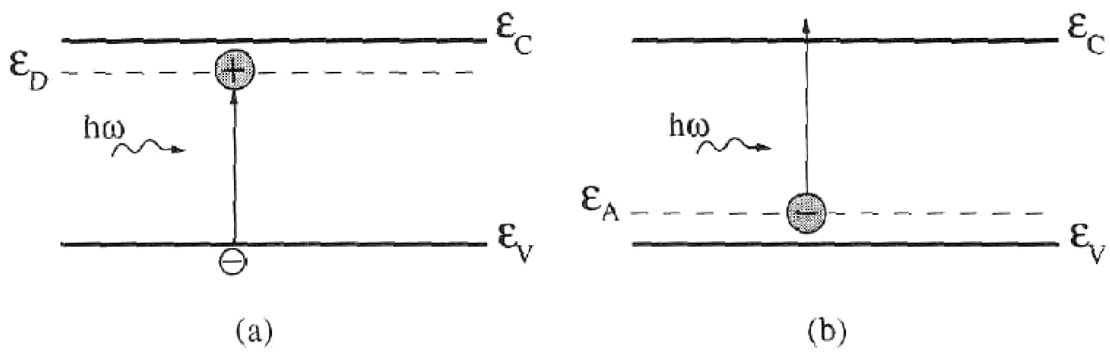
(iii) 杂质吸收：与杂质能级

Donor - Acceptor and Impurity-band Absorption

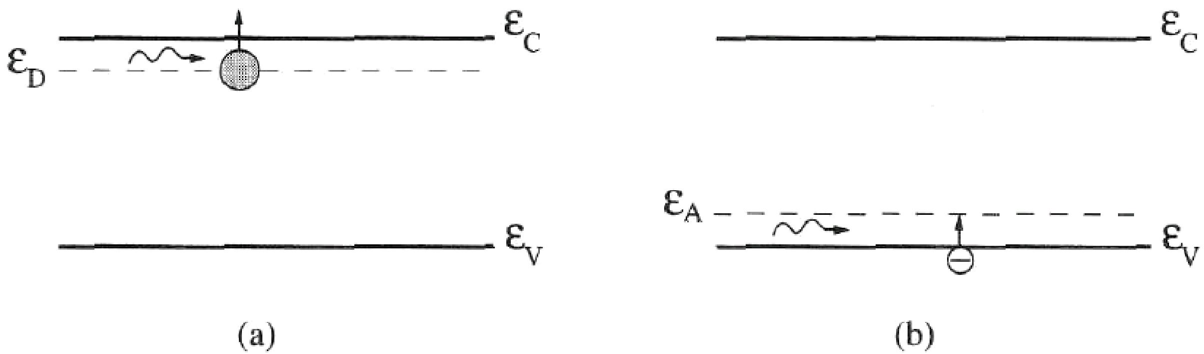


$$\hbar\omega = \mathcal{E}_g - \mathcal{E}_D - \mathcal{E}_A + \frac{q^2}{\epsilon_0 \epsilon_r r}$$

Band – donor (a) and acceptor - band (b) absorption

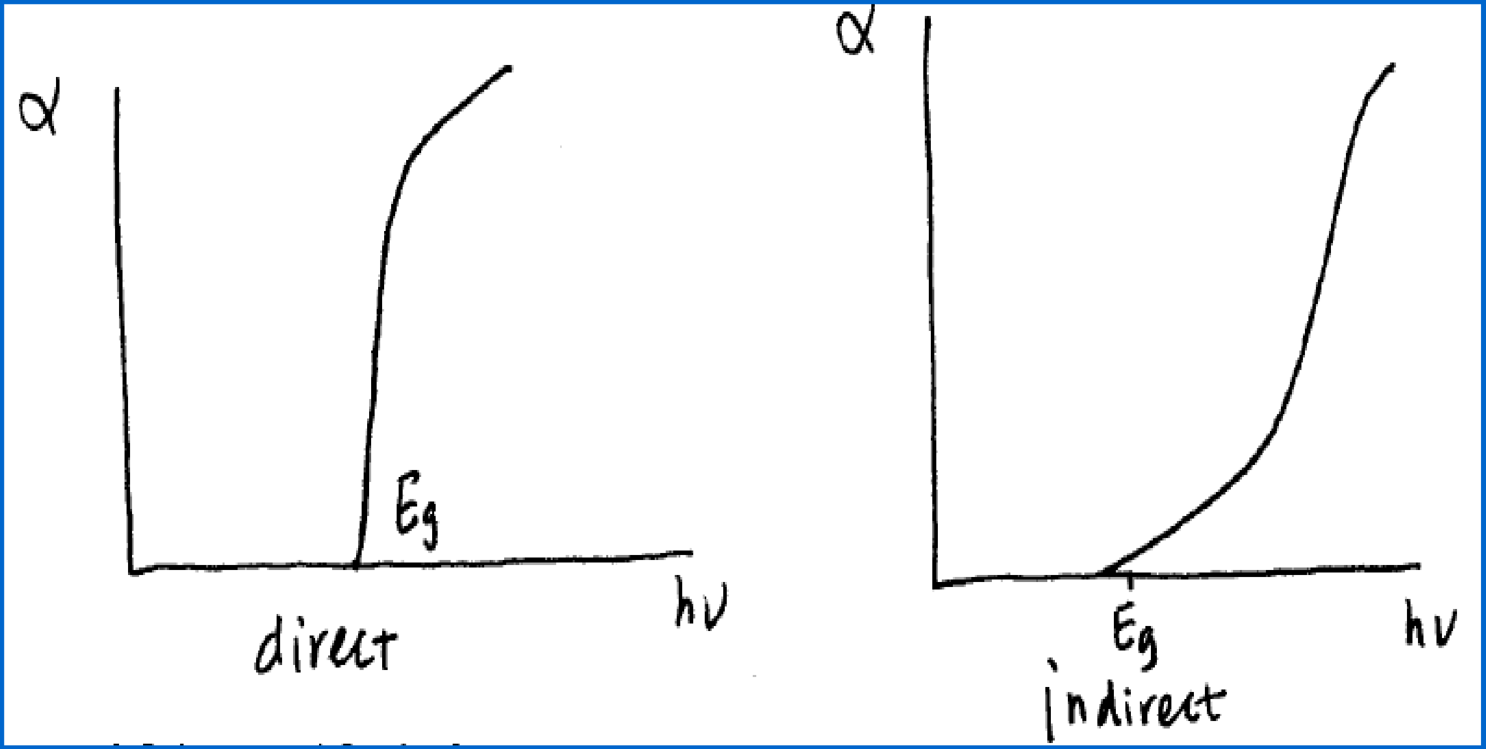


Low-energy (a) donor-band and (b) acceptor-band absorption

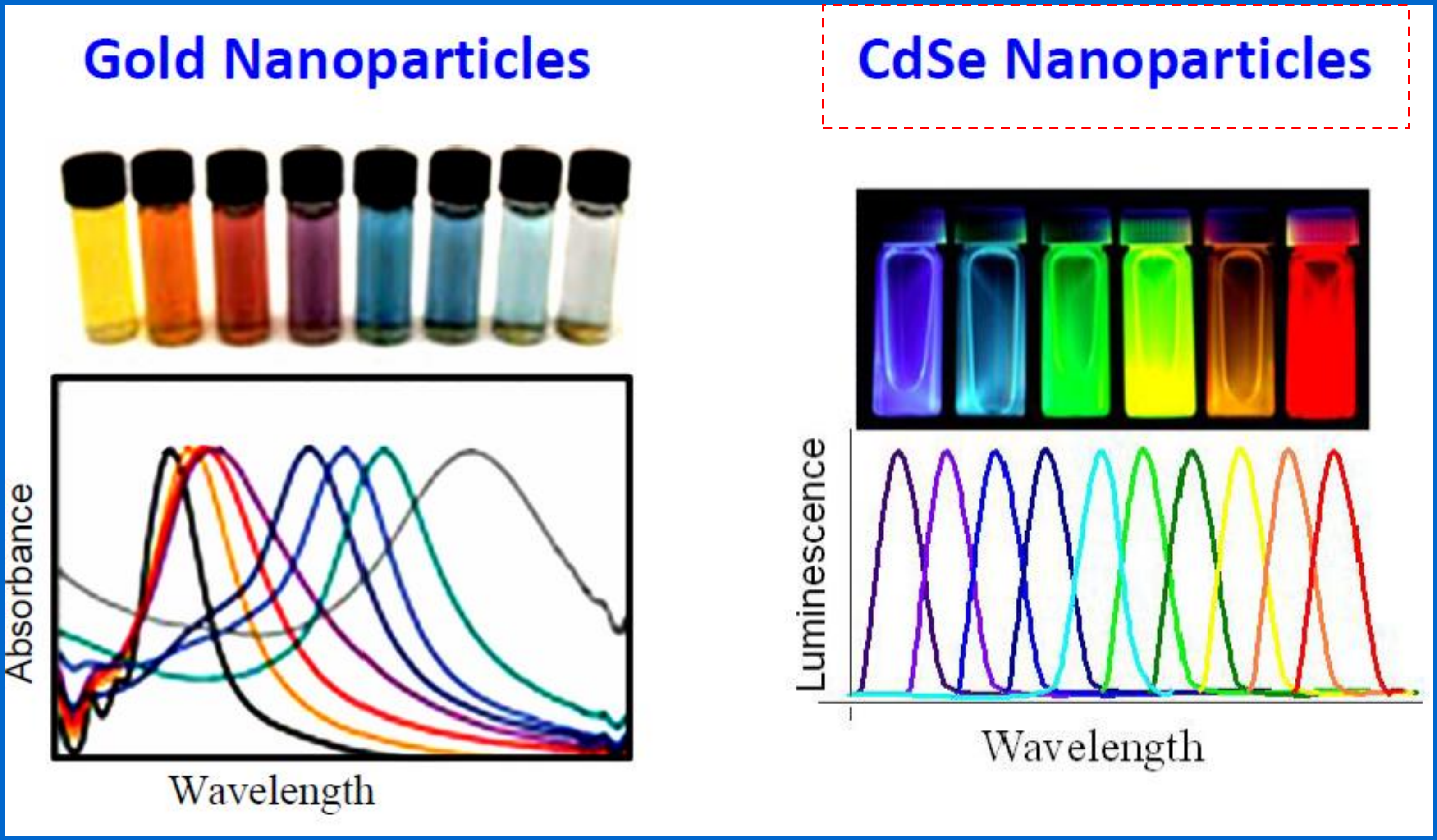


三、光吸收曲线的用途

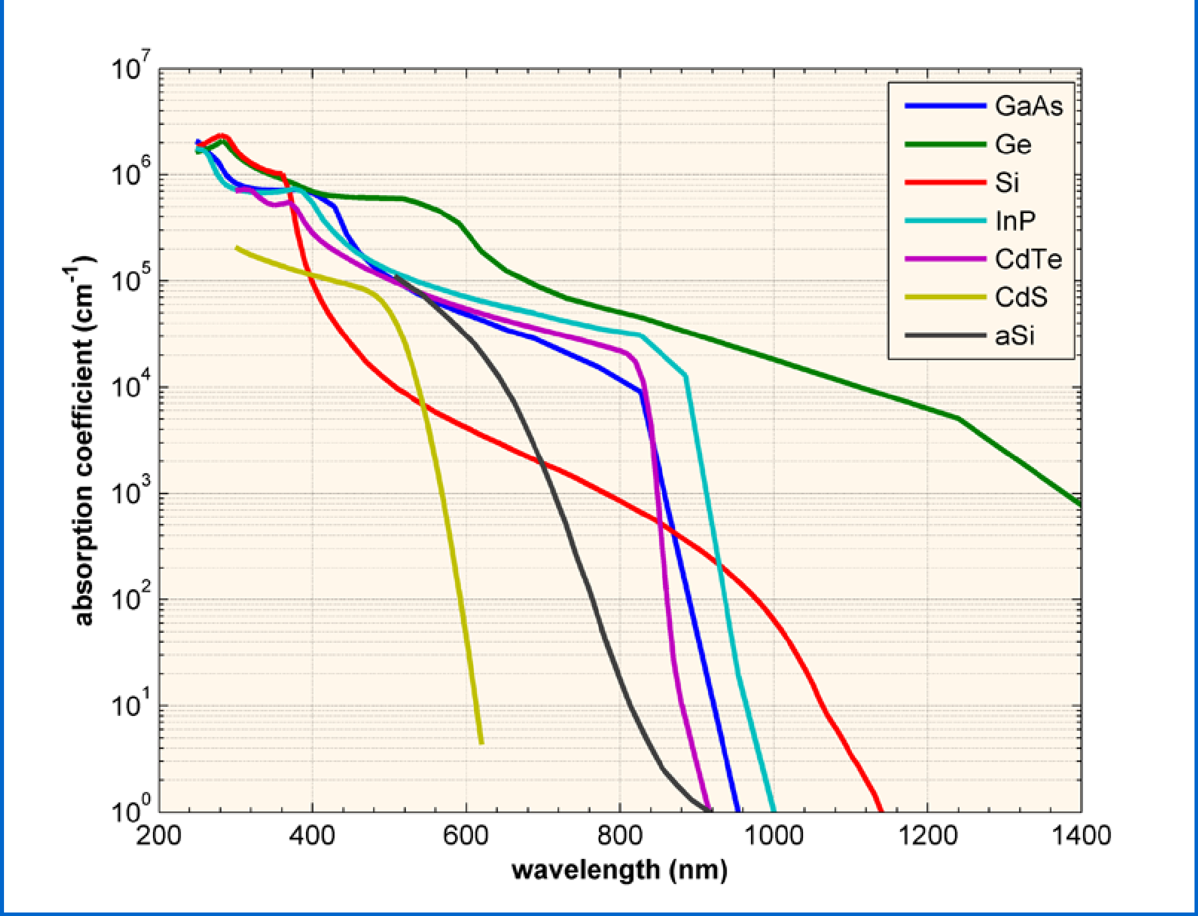
- 判断半导体能带类型，求光学带隙



- 根据光学吸收边，确定尺寸、成分



• 太阳能电池设计



- Knowing the absorption coefficients and bandage of materials aids engineers in determining which material to use in their solar cell designs.

其它用处

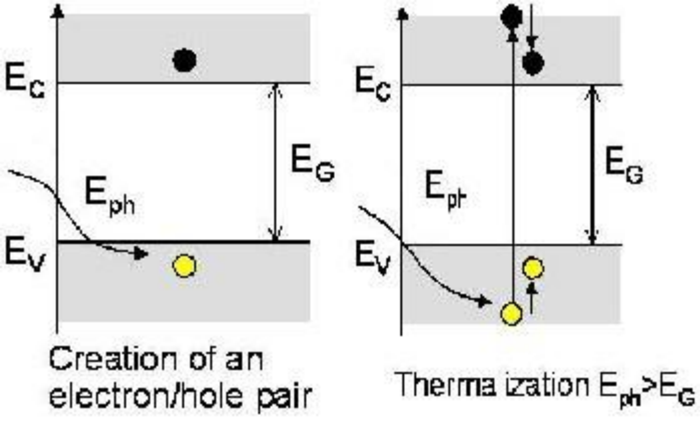
- You will find more.

反射率/透射率/吸收系数如何测量？

- 在各种实验室，紫外-可见-近红外分光光度计已非常普遍
- UV-3600， Cary 5E，Lamda750/950/1050

二、激发态载流子的运动形式

- 电子被激发后，处于非平衡态，经过各种形式的耦合达到平衡态, 该过程叫**弛豫**。
- **晶格弛豫**：依赖于电子态的晶格畸变现象. 激发态的电子通过晶格弛豫，有两种主要运动形式：**热化和无辐射跃迁**



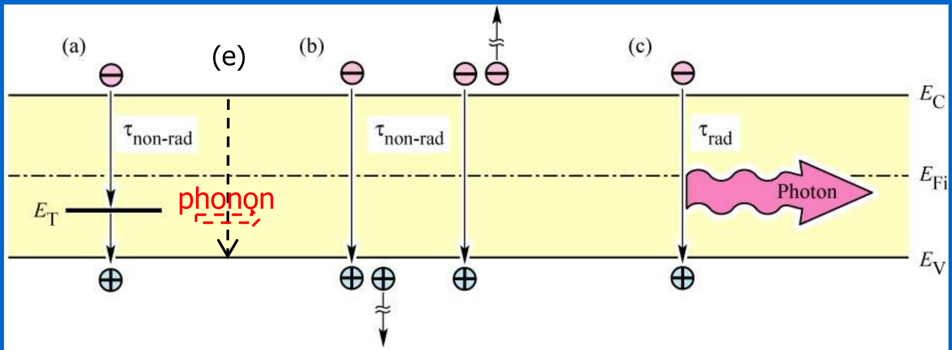


Fig. 2.6. Band diagram illustrating non-radiative recombination: (a) via a deep level, (b) via an Auger process and (c) radiative recombination.

E. F. Schubert

辐射跃迁（发光）

- **辐射跃迁**: 各类发光过程的物理机制

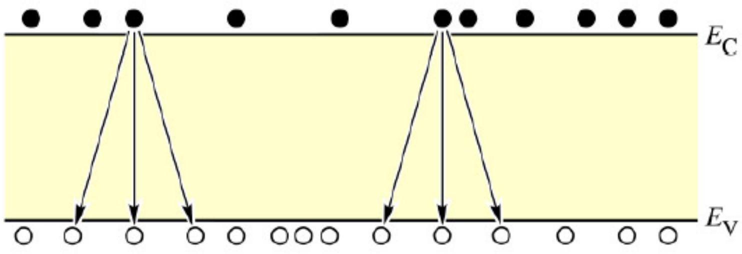


Fig. 2.1. Illustration of electron-hole recombination. The number of recombination events per unit time per unit volume is proportional to the product of electron and hole concentrations, *i. e.* $R \propto n\,p$.

- Recombination rate is proportional to the product of the concentrations of electrons and holes

- $R = B\,n\,p$

  where

  B = bimolecular recombination coefficient

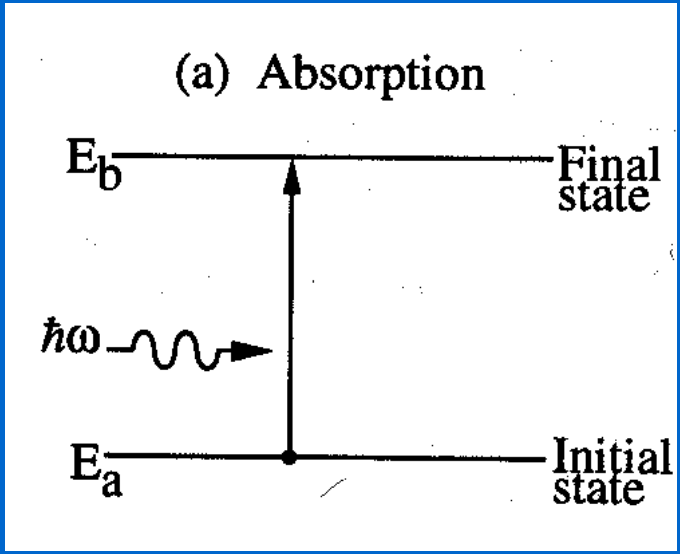
  n = electron concentration

  p = hole concentration

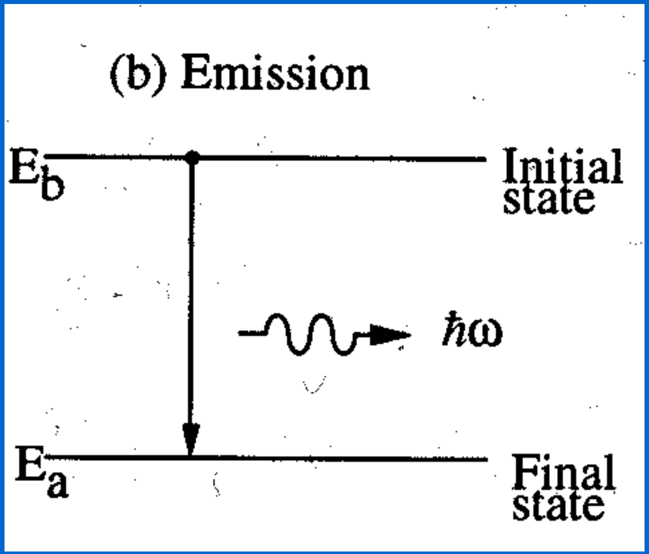
发光过程三部曲

Thus a luminescence process involves three separate steps:

- *Excitation:* Electron–hole pairs have to be excited by an external source of energy.
- *Thermalization:* The excited e-h pairs relax towards quasi-thermal-equilibrium distributions.
- *Recombination:* The thermalized e-h pairs recombine radiatively to produce the emission.



热化



按激发类别，发光分类

- 光致发光 （Photoluminescence，PL）
- 电致发光 （Electroluminescence，EL）
- 阴极射线发光（Chathodoluminescence，CL）
- 热释光、摩擦发光、化学发光等

光致发光与吸收的关系

（*van Roosbroeck-Shockley relation*）

- 辐射复合率与光吸收系数之间的关系：

$$R(\nu) = \frac{\alpha(\nu) 8\pi \nu^2 n^2}{c^2 e^{h\nu/k_B T - 1}} \approx \frac{8\pi \nu^2 n^2}{c^2} \alpha(\nu) e^{-h\nu/k_B T}$$

- 光吸收谱和光发射谱有何不同？

半导体发光基本物理过程

1. 直接带间复合

2. 间接带隙符合

3. Free-to-Bound Transitions

4. Donor-to-Acceptor Transitions（DAP）

5. Exciton transition

1. 直接带间复合

Emission spectrum

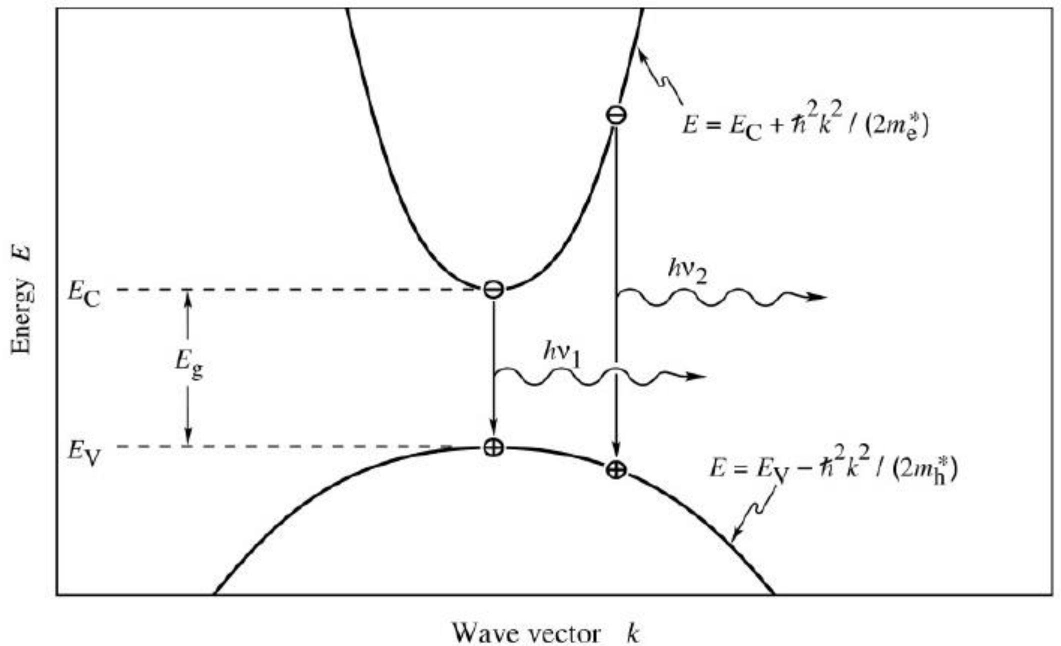


Fig. 5.1. Parabolic electron and hole dispersion relations showing "vertical" electron-hole recombination and photon emission.

- Electron and hole momentum must be conserved
- Photon has negligible momentum

Emission spectrum

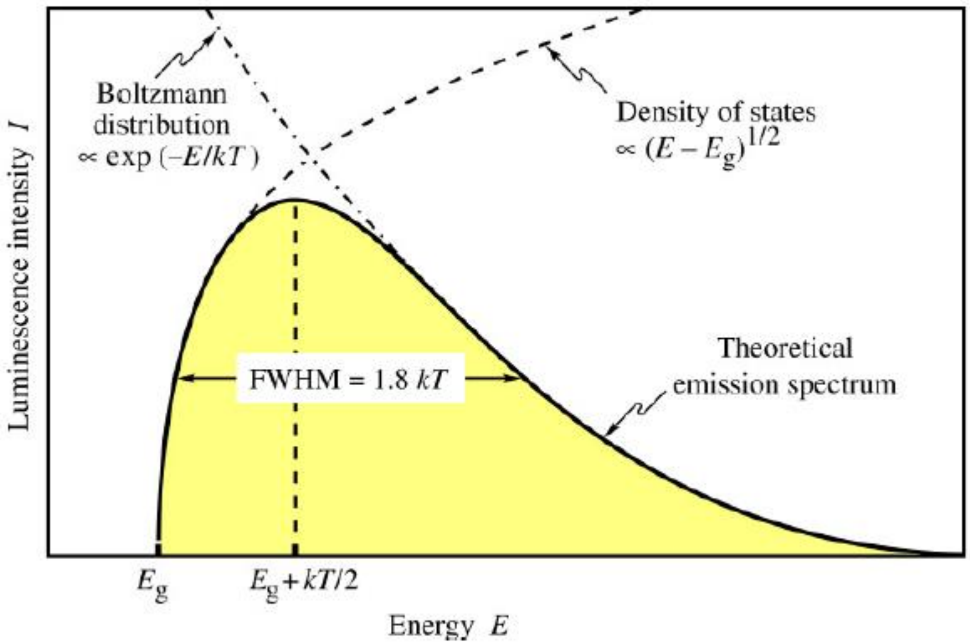


Fig. 5.2. Theoretical emission spectrum of an LED. The full width at half maximum (FWHM) of the emission line is 1.8 kT.

$$I_{\mathrm{PL}}(\hbar\omega) \propto \begin{cases} (\hbar\omega - E_{\mathrm{g}})^{1/2} \exp[-(\hbar\omega - E_{\mathrm{g}})/(k_{\mathrm{B}}T)] & \text{for } \hbar\omega > E_{\mathrm{g}}, \\ 0 & \text{otherwise,} \end{cases}$$

$$E = E_{\mathrm{g}} + \frac{1}{2} kT$$ Energy of maximum emission intensity

$$\Delta E = 1.8 \; kT$$ Spectral width

例　子

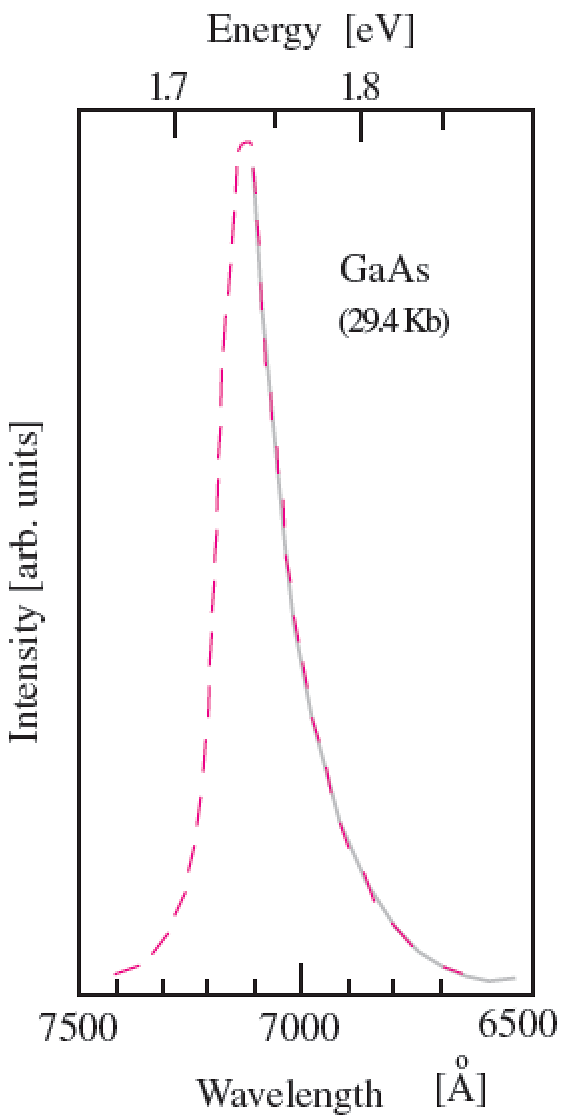


Fig. 7.3. Photoluminescence spectrum due to band-to-band transition in GaAs measured (*broken line*) at room temperature and a pressure of 29.4 kbar. The theoretical curve (*solid line*) is a plot of the expression (7.12), approximately proportional to $\exp[-(\hbar\omega - E_g)/(k_B T)]$, with $T = 373$ K. (From [7.16])

2. 间接带间复合

- In indirect bandgap semiconductors, such as Si and Ge, e-h pairs can recombine radiatively only via **phonon-assisted transitions.**

- Since the probability of these transitions is smaller than for competing nonradiative processes, **these materials are not efficient emitters**.

- Si *nanocrystals. It is argued that by physically confining electrons and holes* one can enhance their radiative recombination rate.

- *Porous Si has been shown to produce efficient visible photoluminescence and electroluminescence*. The reasons are, however, still controversial .

- The indirect bandgap semiconductor GaP is an exception

3. Free-to-Bound Transitions

- At sufficiently low temperatures, carriers are frozen on impurities（未电离）.
- Band-to-band transitions tend to dominate at higher temperatures where all the shallow impurities are ionized.
- Such transitions, involving a free carrier and a charge bound to an impurity, are known as **free-to-bound transitions**

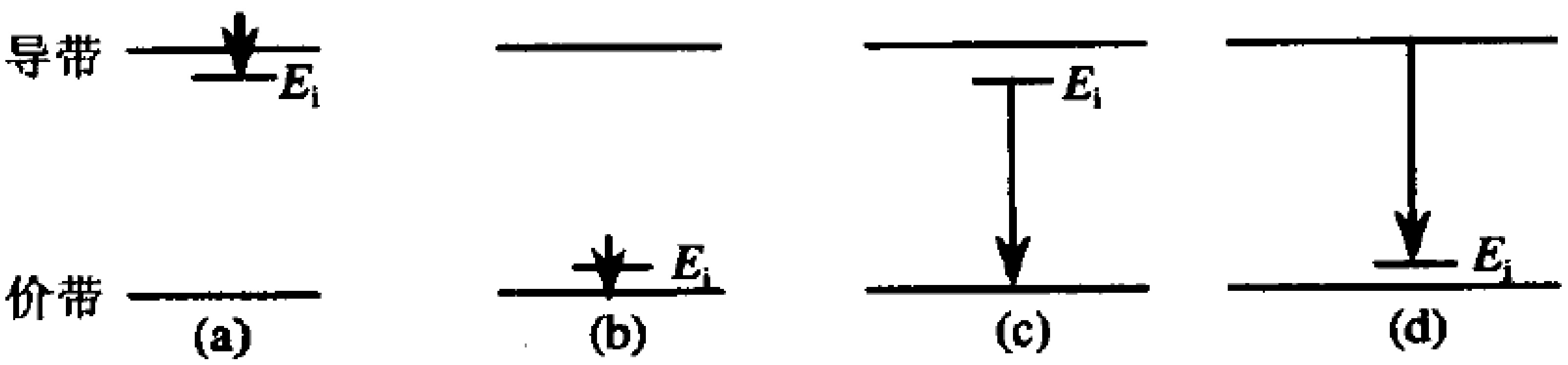
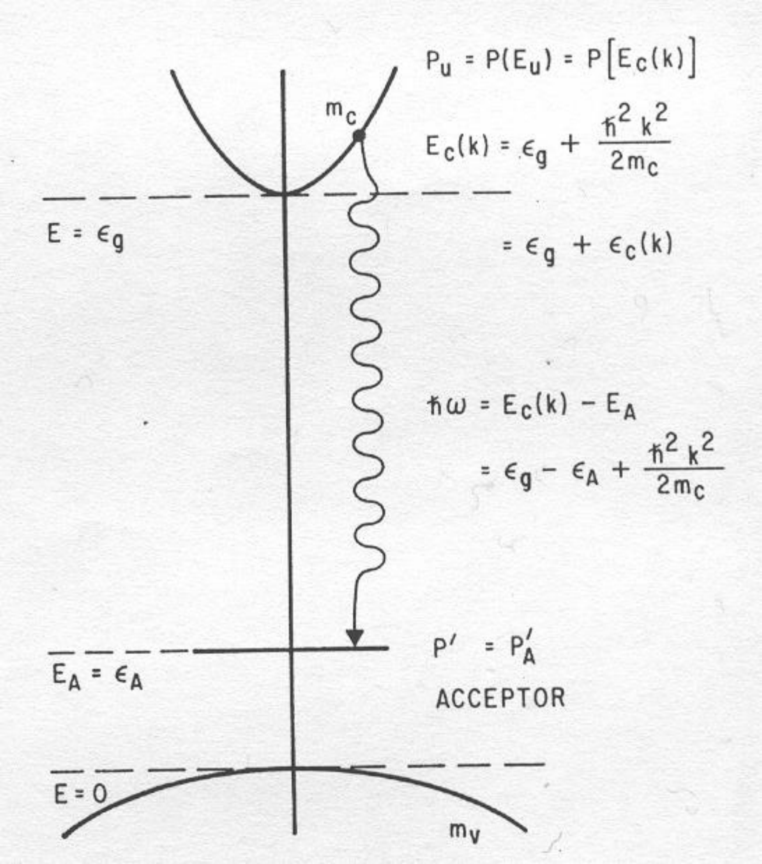


图 5.22 (a)导带到施主;(b)受主到价带;
(c)施主到价带;(d)导带到受主的复合

例子：（e，A^0）发光



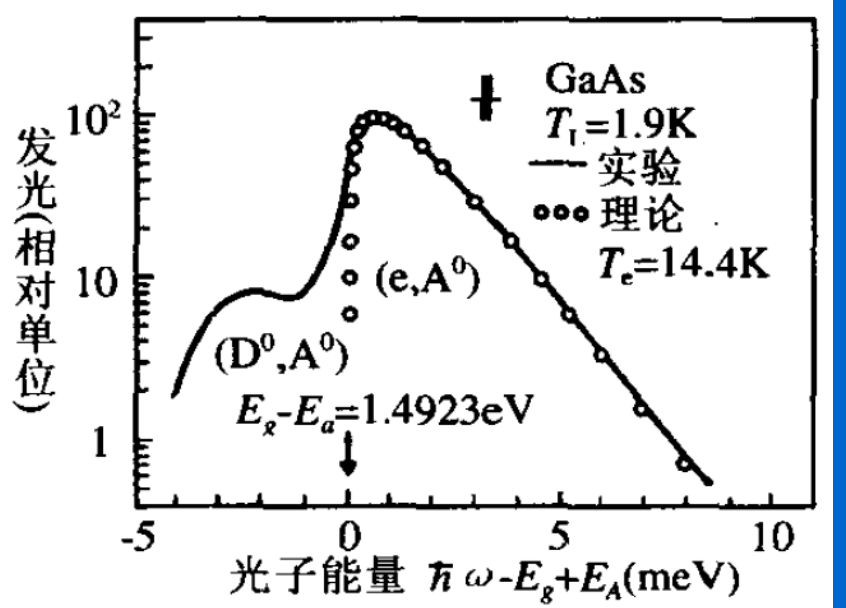
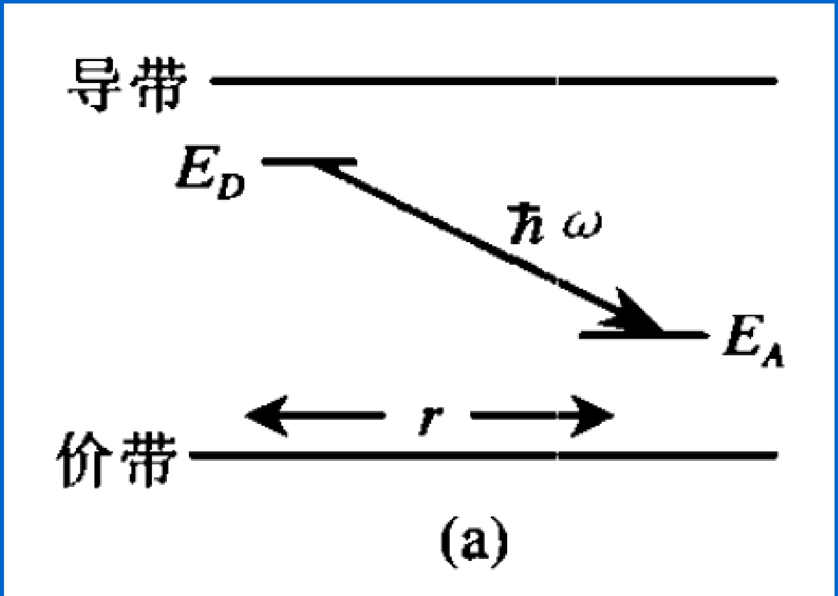


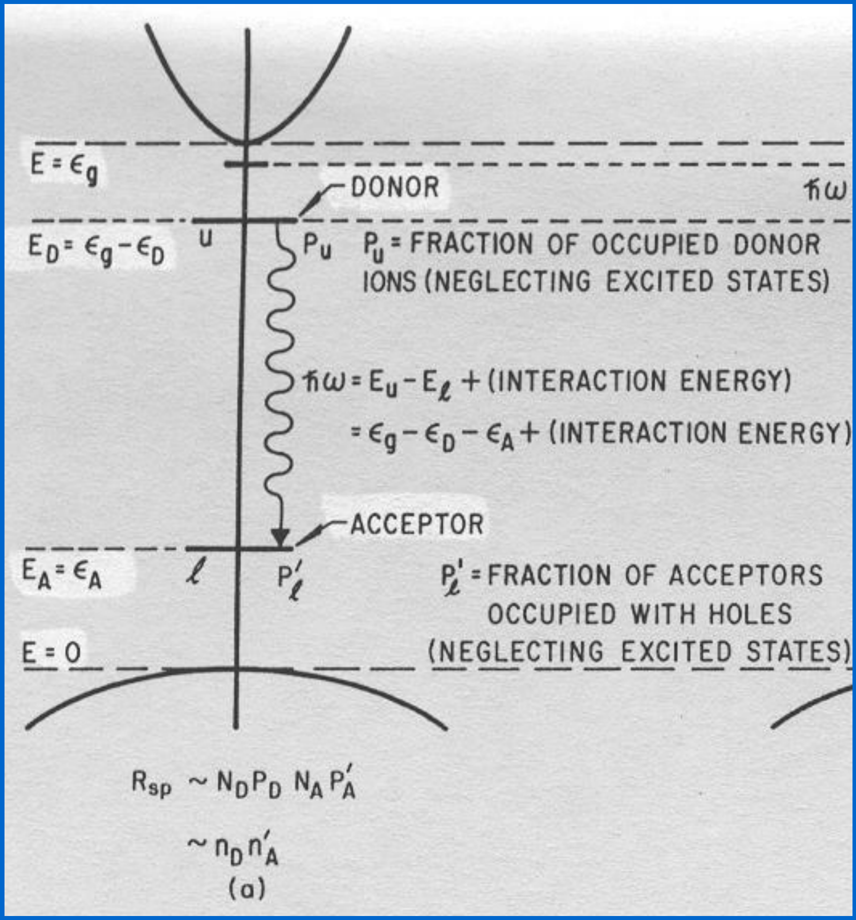
图 5. 23　低温下 GaAs 的光致发光与发光线形拟合[5.15]

$$I_L(\omega) \propto [\hbar\omega - (E_g - E_A)]^{1/2} \exp\left[-\frac{\hbar\omega - (E_g - E_A)}{k_B T}\right]$$

4. Donor-to-Acceptor Transitions



$$D^0 + A^0 \rightarrow \hbar\omega + D^+ + A^-$$



$$\hbar\omega = E_g - E_A - E_D + e^2/(4\pi\varepsilon_0\varepsilon_0 R)$$

5. Exciton Transitions @ Low Temp.

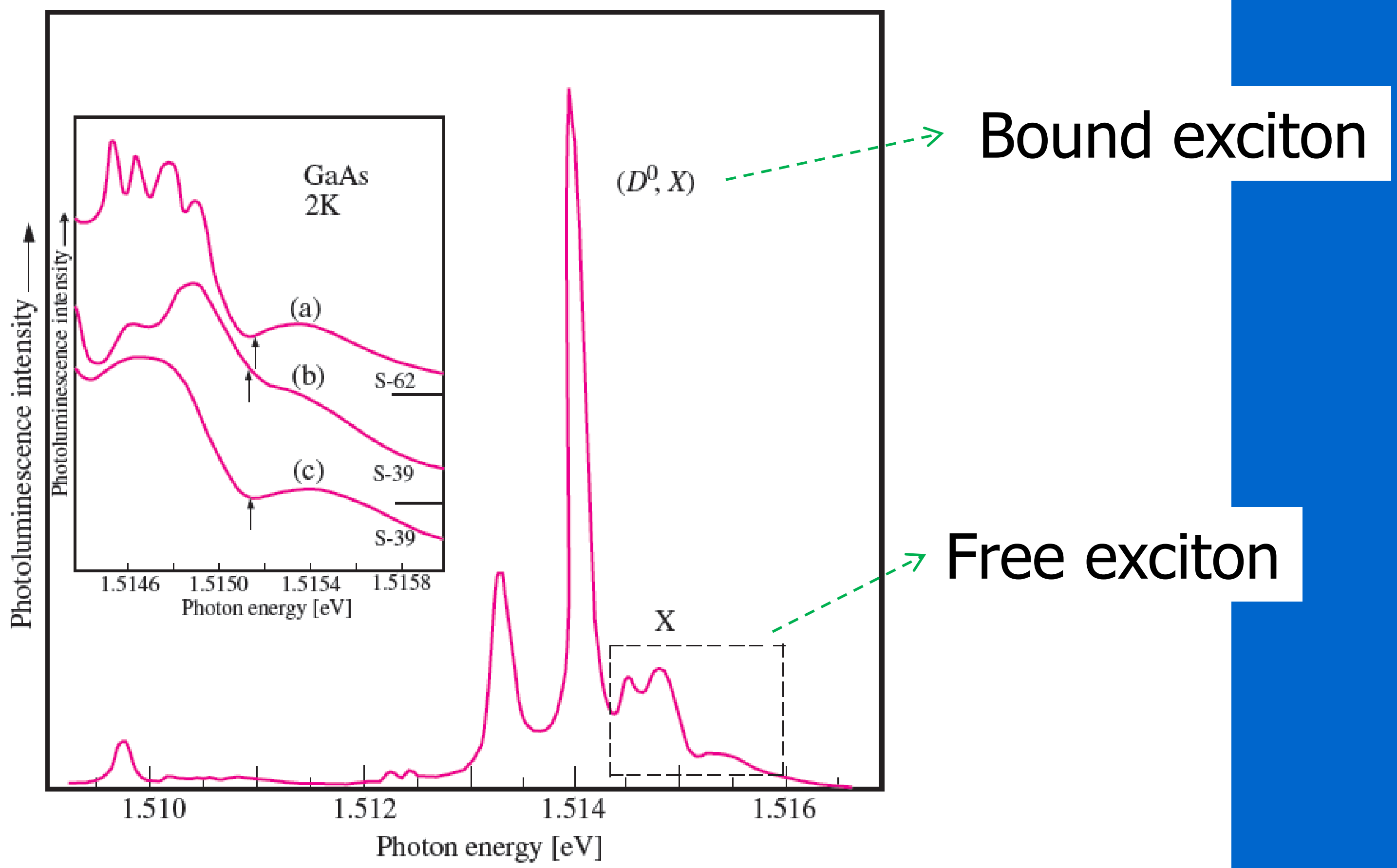


Fig. 7.10. Photoluminescence of GaAs at 2 K measured by *Sell* et al. [7.25]. The *inset* is an enlargement of the spectra within the rectangle labeled X. It contains the part of the emission spectrum associated with free excitons. The spectrum in the inset labeled (*a*) and those labeled (*b*) and (*c*) correspond to two different samples. The spectrum (*c*) was excited by light intensity ten times higher than that used for spectrum (*b*). The peak labeled (D^0,X) is attributed to recombination of excitons bound to neutral donors

5.1 Free exciton Transitions

- 表示形式：FX；或X
- 自由激子谱线常为非对称形状
- 自由激子发光能量：

$$\hbar\omega = E_g - \frac{R^*}{n}$$

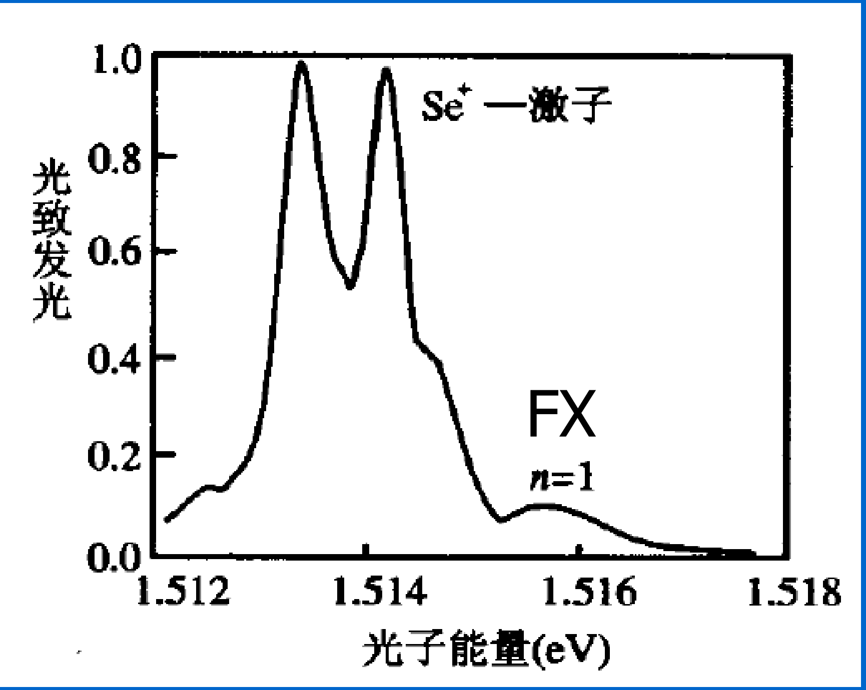


图 4.9 掺微量硒(Se)的高纯 GaAs 低温下的发光光谱，除了 $n=1$ 的自由激子发光外，还出现 Se 中心束缚激子的发光[4.11]

5.2 Bound exciton Transitions

- 存在形式：D^0X；D^-X；A^-X；A^0X
- 被束缚在杂质周围，能量比自由激子低
- 束缚激子谱线比自由激子低
- 常伴有声子伴线
- 随温度升高，会发生两步离化

1：自由激子

2：束缚激子

3~5：束缚激子的声子伴线

I~II：深能级缺陷发光

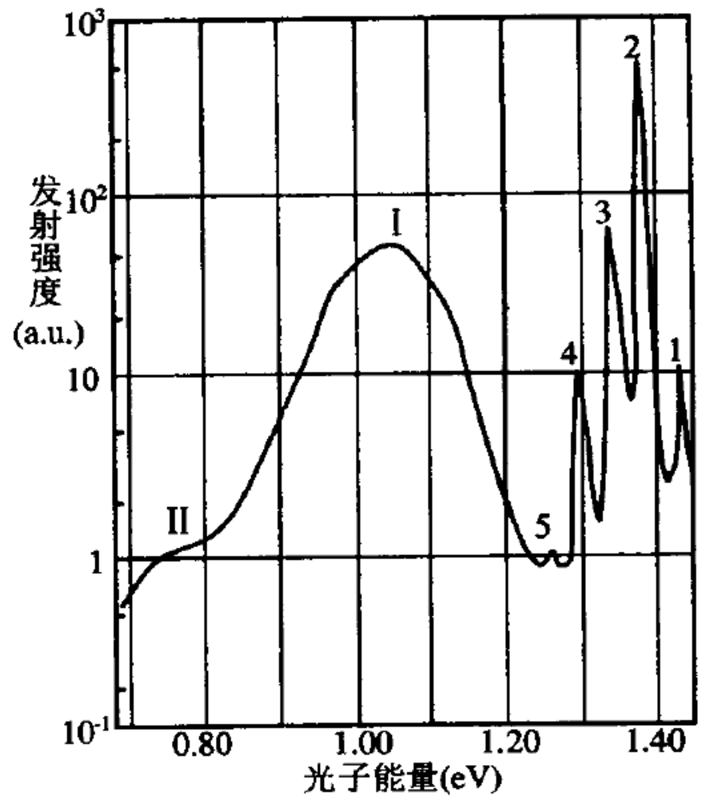
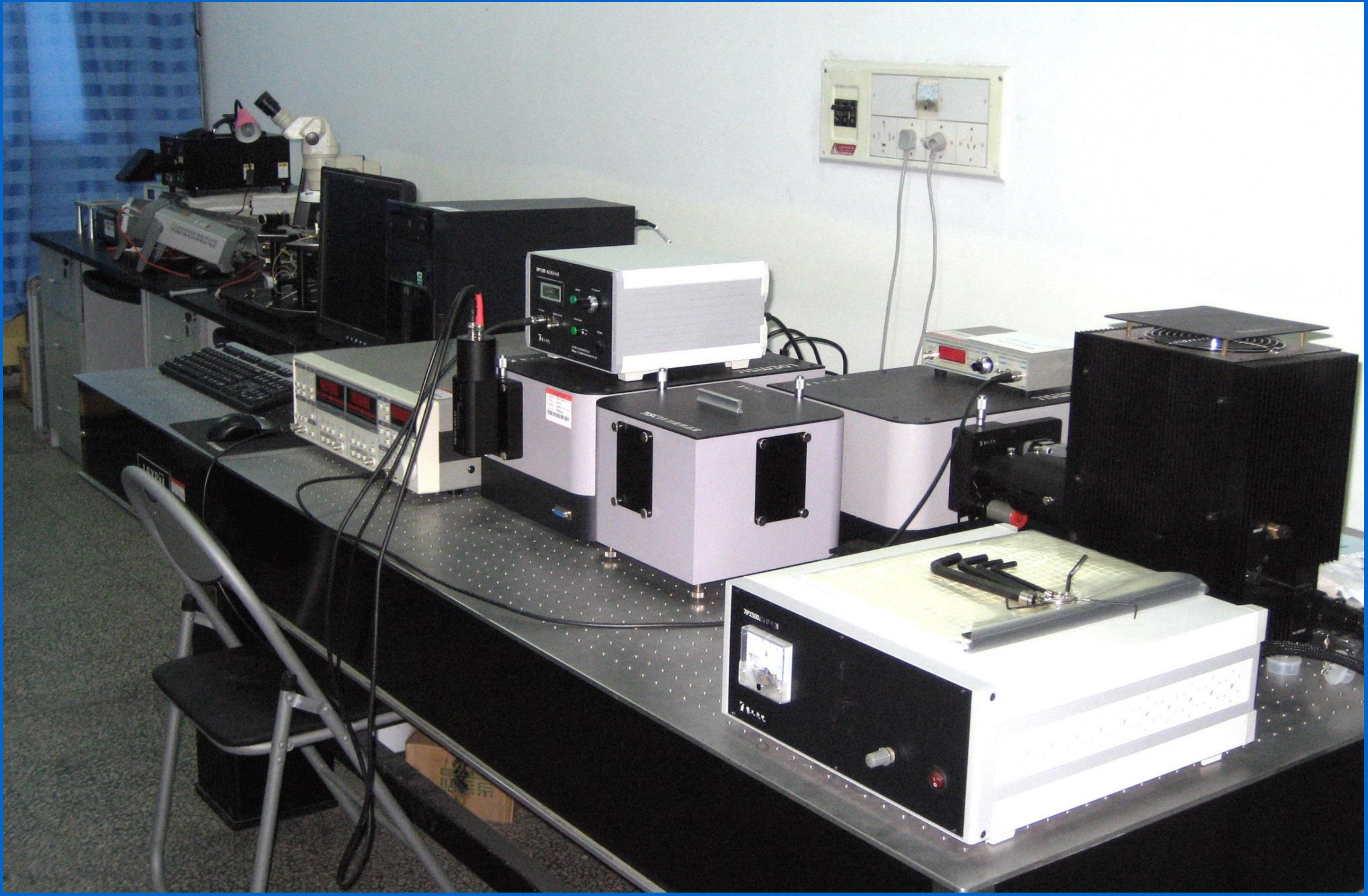


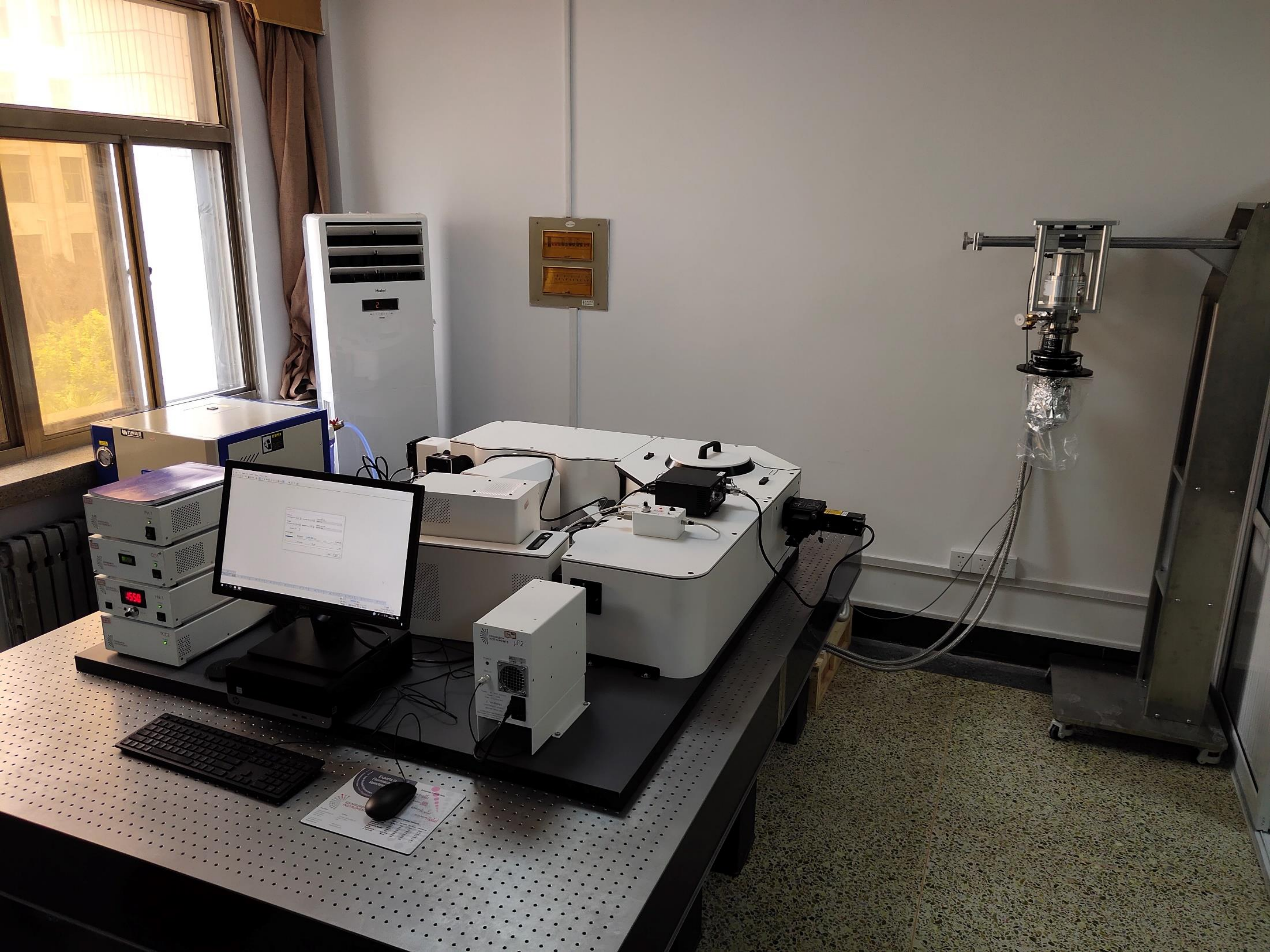
图 4.10 低温下(6K)InP半导体的光致发光光谱[4.12]

测试内容

- 光致发光谱（PL）
- 光致发光激发谱（PLE）
- 低温/变温PL谱
- PL寿命谱
- micro_PL

三、 PL谱测量技术




Haier
EDINBURGH INSTRUMENTS
µF2

荧光光谱技术的优点

- Sensitive (compared to absorption)
- Nondestructive
- Simple to perform
- Considerable analysis may be required to reach the physical mechanism

Refs./Textbooks

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