Lecture contents

- Effective mass approximation
- Impurities

Effective mass approximation

Let's introduce small perturbation of periodicity

One-electron Schrödinger equation with weak and slowly (in space) varying perturbation V_i :

$$\left[\frac{p^2}{2m_0}+V(r)+V_i(r)\right]\psi(r)=E_i\psi(r)$$

And as usual build a solution as a wave packet of Bloch wavefunctions :

$$\psi(r)=\sum_{n,k}c_n(k)e^{ikr}u_{nk}(r)$$

Weak and slowly varying perturbation, such as screened Coulomb potential:

$$V_i(r)=-\frac{e^2}{\varepsilon r}$$

Closest band considered only (conduction band)

Packet localized in the *k*-space (close to minimum)

For non-degenerate, isotropic, parabolic minimum at $k = 0$

~1

Wave packet

$$\psi(r)\approx\left[\sum_k c(k)e^{ikr}\right]u_0(r)=F(r)u_0(r)$$

With *F(r)* - slow varying envelope function:

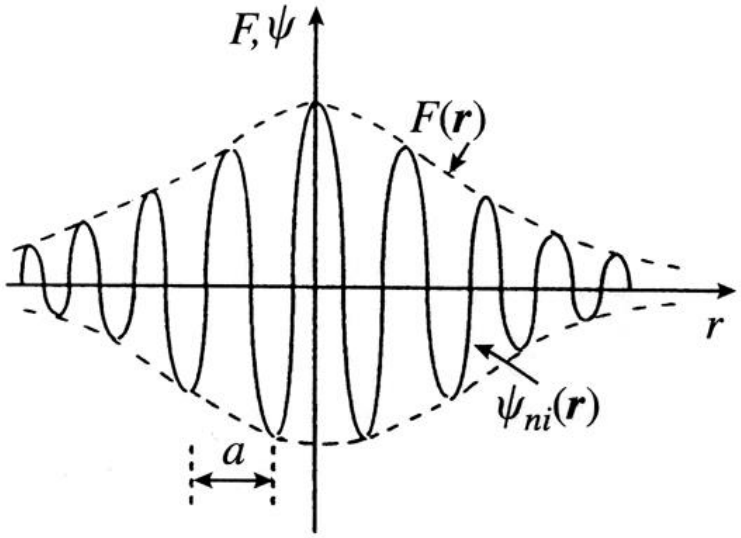
It is possible [Luttinger and Kohn, 1955] to substitute the effect of periodic potential into the effective Hamiltonian:

$$\left[\frac{p^2}{2m^*}+V_i(r)\right]F(r)=(E-E_C)F(r)$$

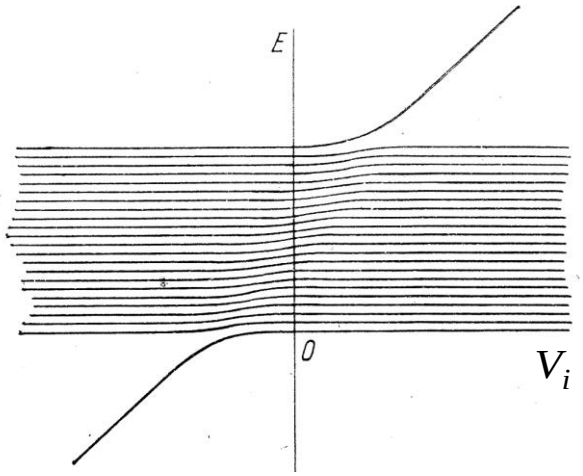
Effective mass approximation

Bloch wave packet: $\psi(r) \approx F(r)u_0(r)$

With dimensions in real and k-space $\Delta r \approx \frac{1}{\Delta k} >> a_0$

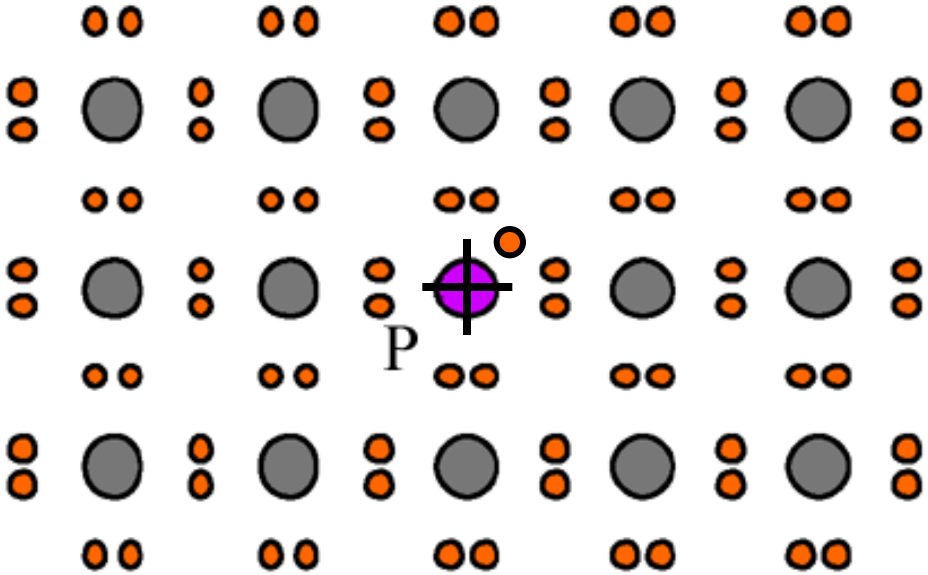


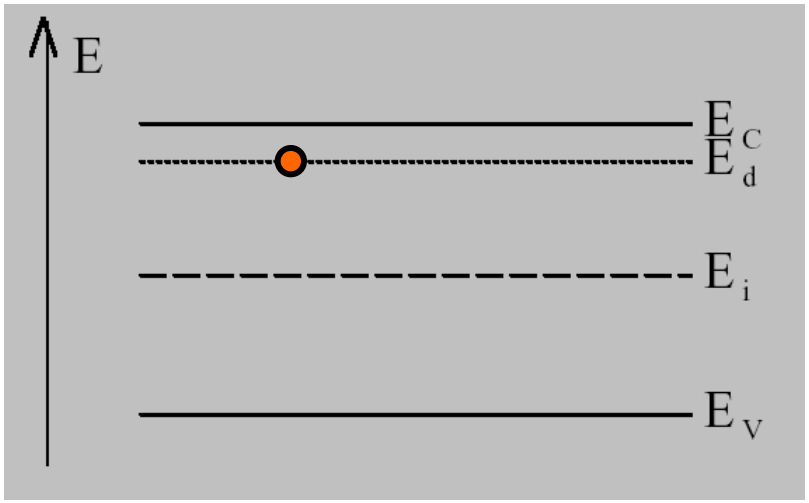
Depending on sign of the perturbation, the top-most or bottom-most state splits from the band :



Donors

Shallow donors:
- usually group V elements in Si and Ge (P, As, Sb)
- group IV elements on group III sublattice in III-V's (Si, Sn in GaAs)
- group VI elements on group V sublattice in III-V's (S, Te, Se in GaAs)

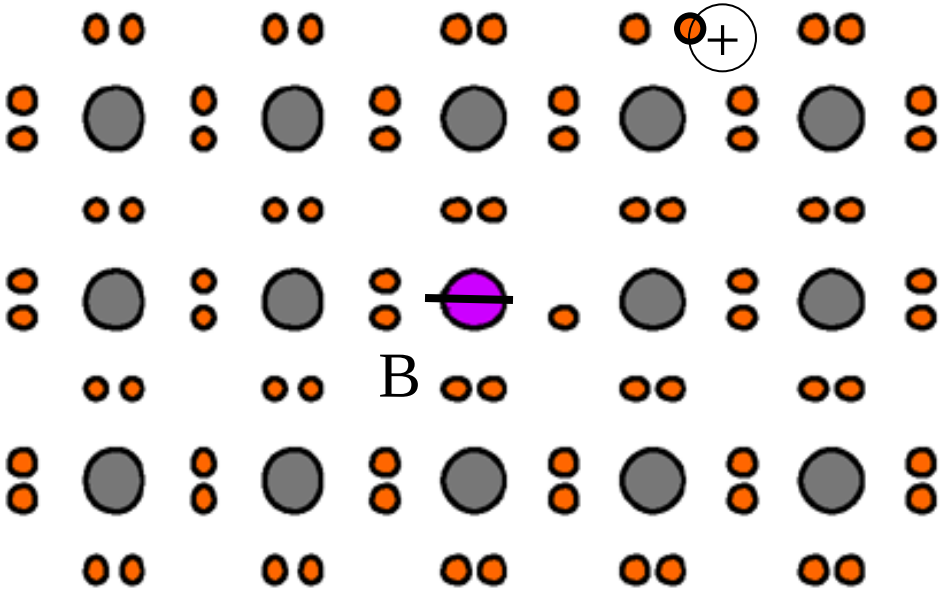


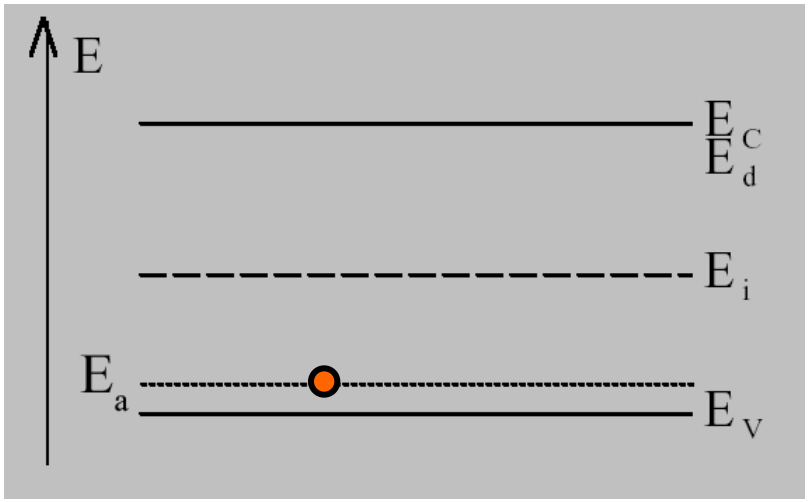


Acceptors

Shallow acceptors: - usually group III elements in Si and Ge (B, Al, Ga, In)
- group II elements on group III sublattice in III-V's (Be, Mg, Zn in GaAs)
- group IV elements on group V sublattice in III-V's (C, Si, Ge in GaAs)

Group IV impurities in III-V's are often amphoteric.





Hydrogen-like impurity (donor)

Hydrogen-like impurity = shallow impurity

Schrödinger equation for Hydrogen atom with effective mass and screened Coulomb potential:

$$V_i(r) = -\frac{e^2}{\varepsilon r}$$

$$\left[\frac{p^2}{2m^*} - \frac{e^2}{\varepsilon r}\right] F(r) = (E - E_C) F(r)$$

Solution for energy :

$$E_d = \frac{e^4 m^*}{2\varepsilon^2 \hbar^2}\frac{1}{n^2} = Ry\frac{m^*}{m}\frac{1}{\varepsilon^2}\frac{1}{n^2}$$

Effective Ry* :

Envelope function of the ground state :

$$F(r) = \frac{1}{\left(\pi a_B^3\right)^{1/2}} \exp\left(-\frac{r}{a_B}\right)$$

Semiconductor	Binding energy from (4.24) [meV]	Experimental binding energy of common donors [meV]
GaAs	5.72	Si_{Ga}(5.84); Ge_{Ga}(5.88) S_{As}(5.87); Se_{As}(5.79)
InP	7.14	7.14
InSb	0.6	Te_{Sb}(0.6)
CdTe	11.6	In_{Cd}(14); Al_{Cd}(14)
ZnSe	25.7	Al_{Zn}(26.3); Ga_{Zn}(27.9) F_{Se}(29.3); Cl_{Se}(26.9)

From Yu and Cordona, 2003

$$a_B = \frac{\hbar^2}{m_0 e^2}\frac{m_0}{m^*}\varepsilon$$

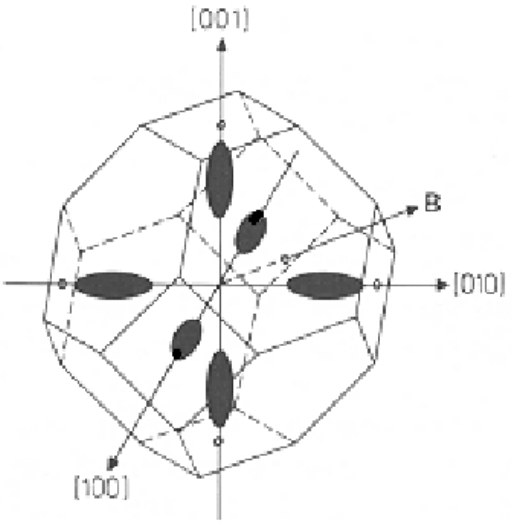
For donors in GaAs (m^*=0.07m: and ε = 12.6):

Ry* =6.6 meV, a_B = 91 A

Valley-orbit coupling (donors in indirect-gap semiconductors)

In indirect gap semiconductors the conduction band is degenerate

In Si, 6 valleys are along {100} directions in k-space :



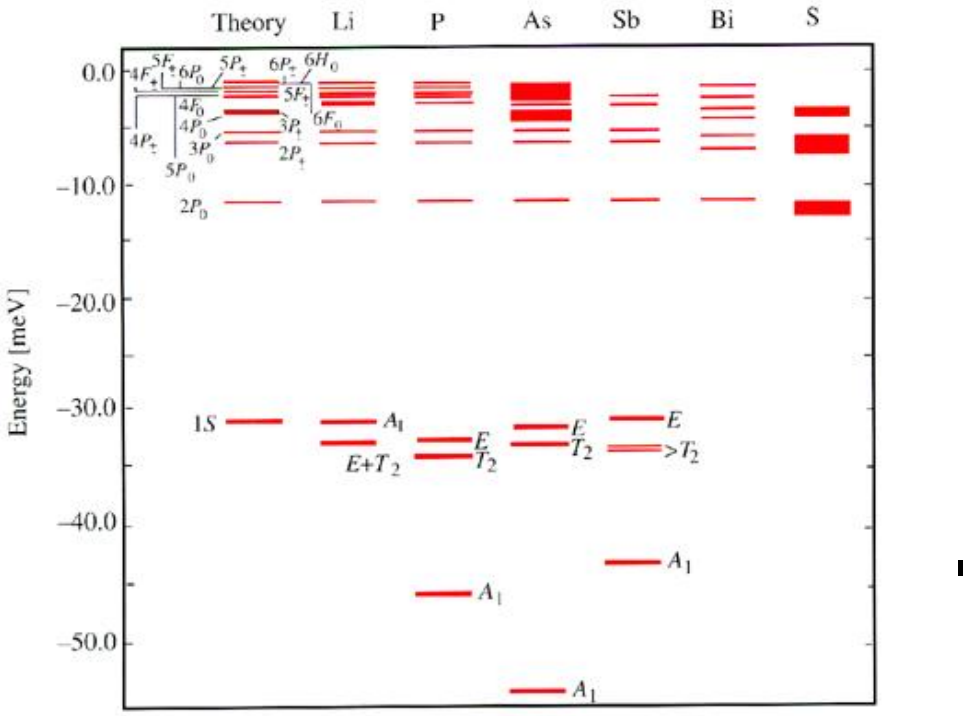
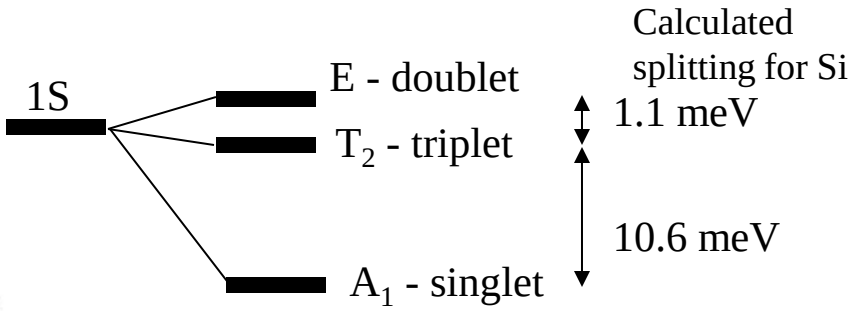


Fig. 4.3. Calculated and measured shallow donor energy levels in Si. (From [4.10])

From Yu and Cordona, 2003

6-fold ground state s-level splits into 3 levels due to valley-orbit interaction in the spherically symmetric potential:



Acceptors

- No splitting of the hydrogen-like ground state (1S) in acceptors
- Energies are calculated using degenerate and non-parabolic hole effective masses

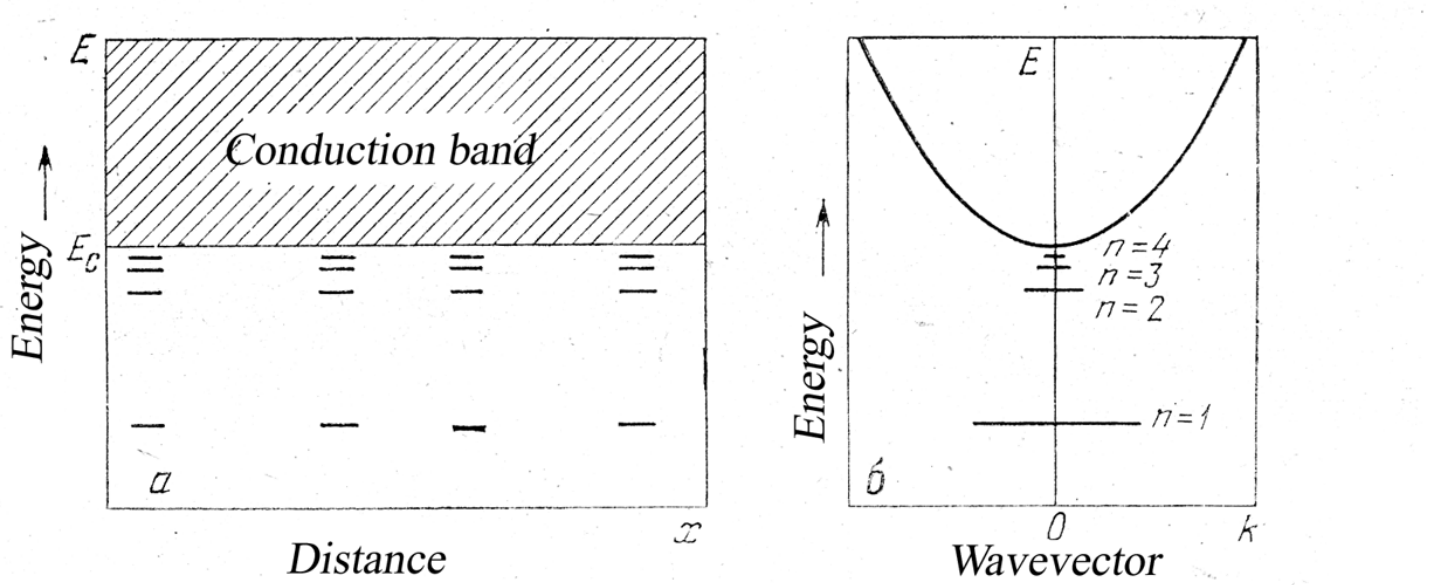
Table 4.4. Comparison between the values of the lowest-energy bound states of acceptors for various semiconductors with the diamond or zinc-blende structures calculated by *Baldereschi* and *Lipari* [4.14, 16, 17] using (4.47) with available experimental values (values in italics represent measurements after 1973). All energies are in meV

	Experiment	$1S_{3/2}$	$2S_{3/2}$	$2P_{1/2}$	$2P_{3/2}$	$2P_{5/2}$
Si	*45*, 68.9	31.6	8.6	4.2	11.2	7.6
Ge	10.8	9.8	2.9	0.6	4.2	2.5
GaP	*57–64*	47.5	13.7	4.2	19.1	11.7
GaAs	*31*	25.6	7.6	1.6	11.1	6.5
GaSb	13–15	12.5	3.8	0.65	5.6	3.2
InP	*31*, 56.3	35.2	10.5	2	15.5	8.9
InAs	10–*20*	16.6	5.1	0.4	7.9	4.4
InSb	≈10	8.6	2.7	0.2	4.2	2.3
ZnS		175.6	52	11.7	75.1	44.1
ZnSe	114	110.1	33	6.1	48.6	28
ZnTe	≈*30*	77.7	23	5.1	33.4	19.6
CdTe	≈*30*	87.4	26.5	3.7	39.9	22.6

From Yu and Cordona, 2003

Impurity levels in a band structure

- Energy levels of impurities are localized in real space
- Energy levels of impurities are localized in k- space close to band-edge: length of lines reflects the width of packet in the k-space



When effective mass approximation is applicable ?

Width of the band

$$V_{pert} \ll \langle \psi_0(r) | \Delta V | \psi_0(r-R) \rangle = -\gamma$$

$$\Delta r \approx \frac{1}{\Delta k} >> a_0$$

EMP works fine when perturbation of crystal periodic potential is small in value and large in scale:

- Potentials in device structures
  - Electrostatic potentials
  - Heterostructures
- "Shallow" impurities = Hydrogen-like impurities: those with similar covalent radius that do not disturb periodicity significantly and have similar valence states

When EMA works poorly:

- Impurities and defects with strong disturbance of crystal periodicity = deep levels or deep impurities: vacancies, group I, VII in III-V's, d-metals, low radius.

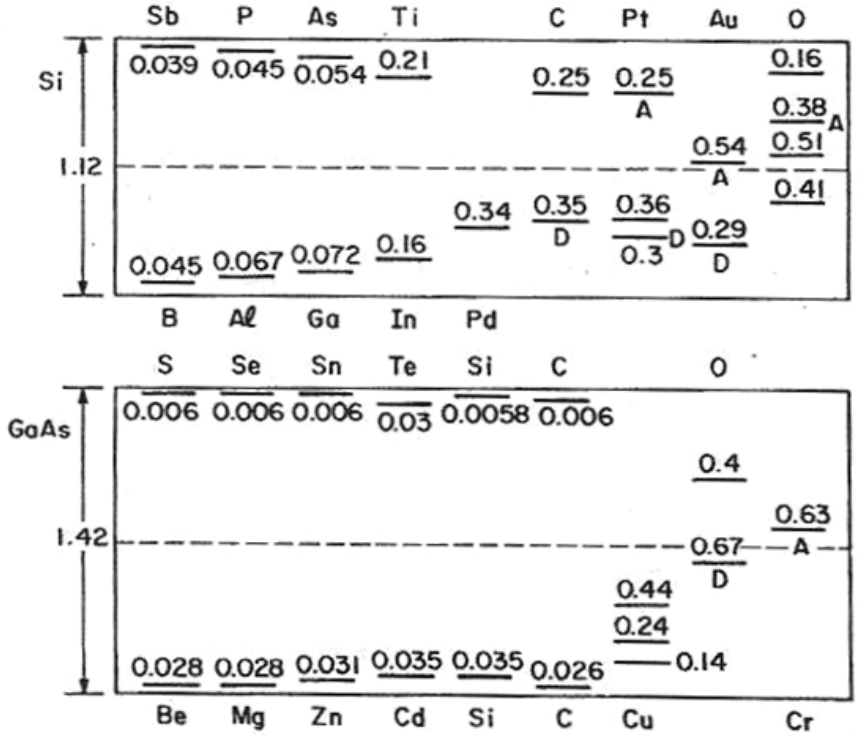


Fig. 18 Measured ionization energies for various impurities in Si and GaAs. The levels below the gap center are measured from the top of the valence band and are acceptor levels unless indicated by D for donor level. The levels above the gap center are measured from the bottom of the conduction band and are donor levels unless indicated by A for acceptor level.[5]

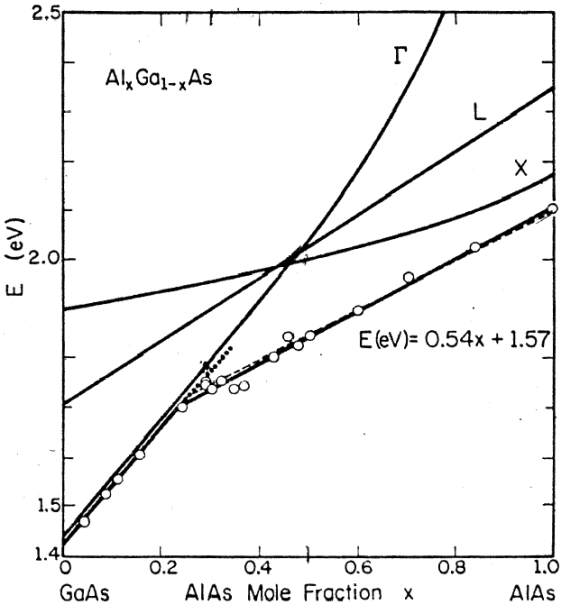
From Milnes, 1973

Central cell corrections and deep levels

- Ground state ionization energy depends on the nature of impurity
- Impurity potential tends to have short range component (on top of Coulomb potential) called "Central cell correction"
- Central cell correction violate the assumption that the defect potential is slowly varying in space
- Excited states due to larger radius are less effected by central cell. Excited p-states with zero at the impurity are almost unaffected by short range potential
- If an impurity level lies far from any band edge ("Deep levels") it cannot be described by effective mass / hydrogen-like approximations
- In many cases deep levels are associated with large lattice relaxations around the defect. This induces strongly localized potential (large central cell correction)
- In many cases a different charge leads to different lattice distortions is so-called "Jahn-Teller Effect"

Example: DX center

- $Al_xGa_{1-x}As$ at x >0.22 donors suddenly behave more like deep centers
- hydrogenic donor ionization energy in GaAs ~6 meV → >0.1 eV in $Al_xGa_{1-x}As$ (160 mev at x=0.4)
- Exhibit persistent photoconductivity ...
- Optical ionization energy ~ 1eV is much larger than thermal
- DX centers with negative-U metastable state



- 6 mev reaction
- Capture of free electron

$$d^0 \rightarrow d^+ + e$$
$$d^0 + e \rightarrow DX^-$$
$$\Rightarrow \quad 2d^0 \rightarrow d^+ + DX^-$$

Configurations of Si and S d^0 and DX^-

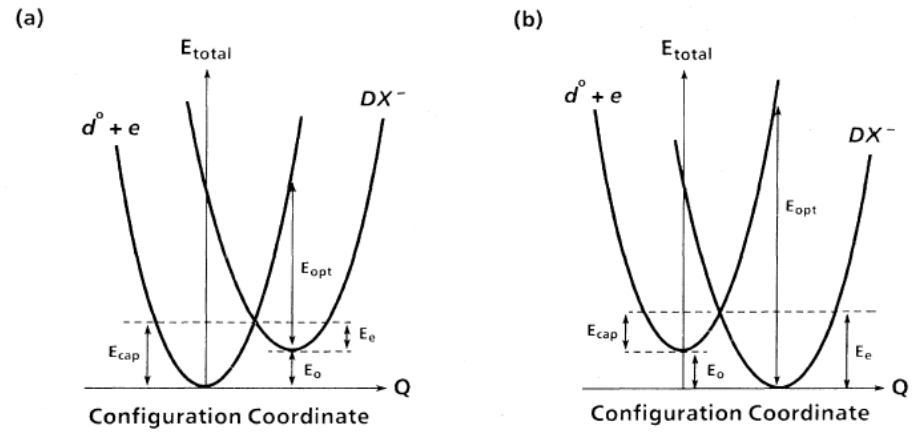
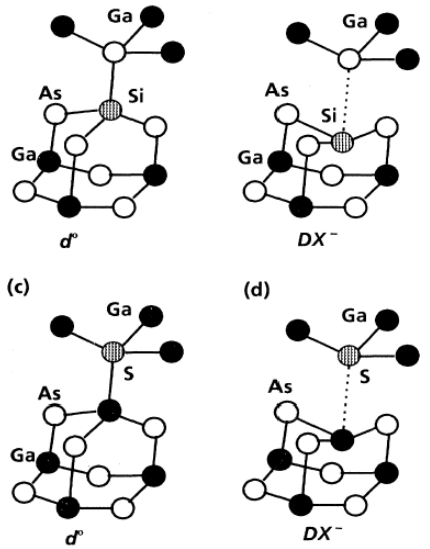


FIG. 1. Configuration-coordinate diagrams for *DX* centers in GaAs and typical $Al_xGa_{1-x}As$ alloys are shown in (a) and (b), respectively. The *DX* center is a metastable resonance in GaAs and has a higher energy than a shallow donor state (d^0). For $Al_xGa_{1-x}As$ alloys characterized by $x \geq 0.22$, *DX* centers are more stable than the shallow donors.



From Chadi and Cheng, 1989

Example: EL2 in GaAs

- Probably the most frequently studied point defect at all: EL2 in GaAs is deep donor with the level close to mid-gap (E_d ~ 0.8 eV)
- Used to obtain semi-insulating GaAs (compensation of unwanted impurities)
- Self-compensation works when [EL2] > [shallow acceptors] > [shallow donors]
- Exhibits metastability at T<100 K : illumination at low temperature → properties changes (e.g. no IR absorption any more)
- Dabrowski/Scheffler and Chadi/Chang: EL2 is isolated antisite defect As_{Ga} and in metastable state the antisite atom moves outward and leaves a V_{Ga}