

Extrinsic Semiconductors

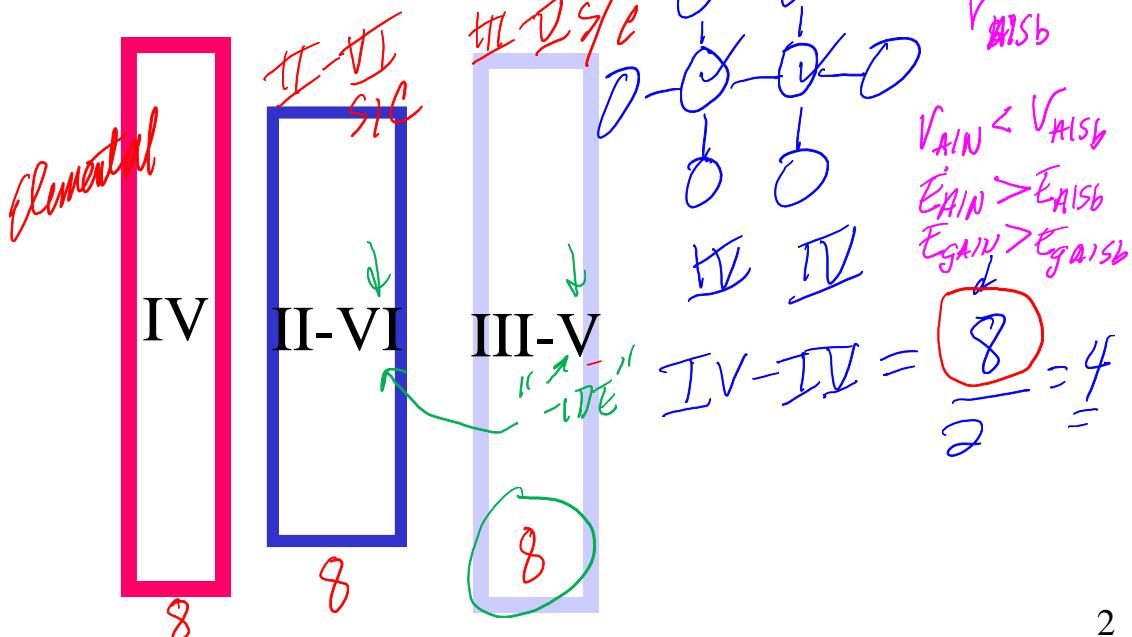
Bill Knowlton

- Octet Rule – S/C Categories
- Doping
- Hydrogenic Model or Effective Mass Theory
- Free Carrier Statistics – find n and p for doped S/Cs

Groups: IV, III-V, II-VI

Octet Rule: 2xIV & III+V & II+VI all add to 8!

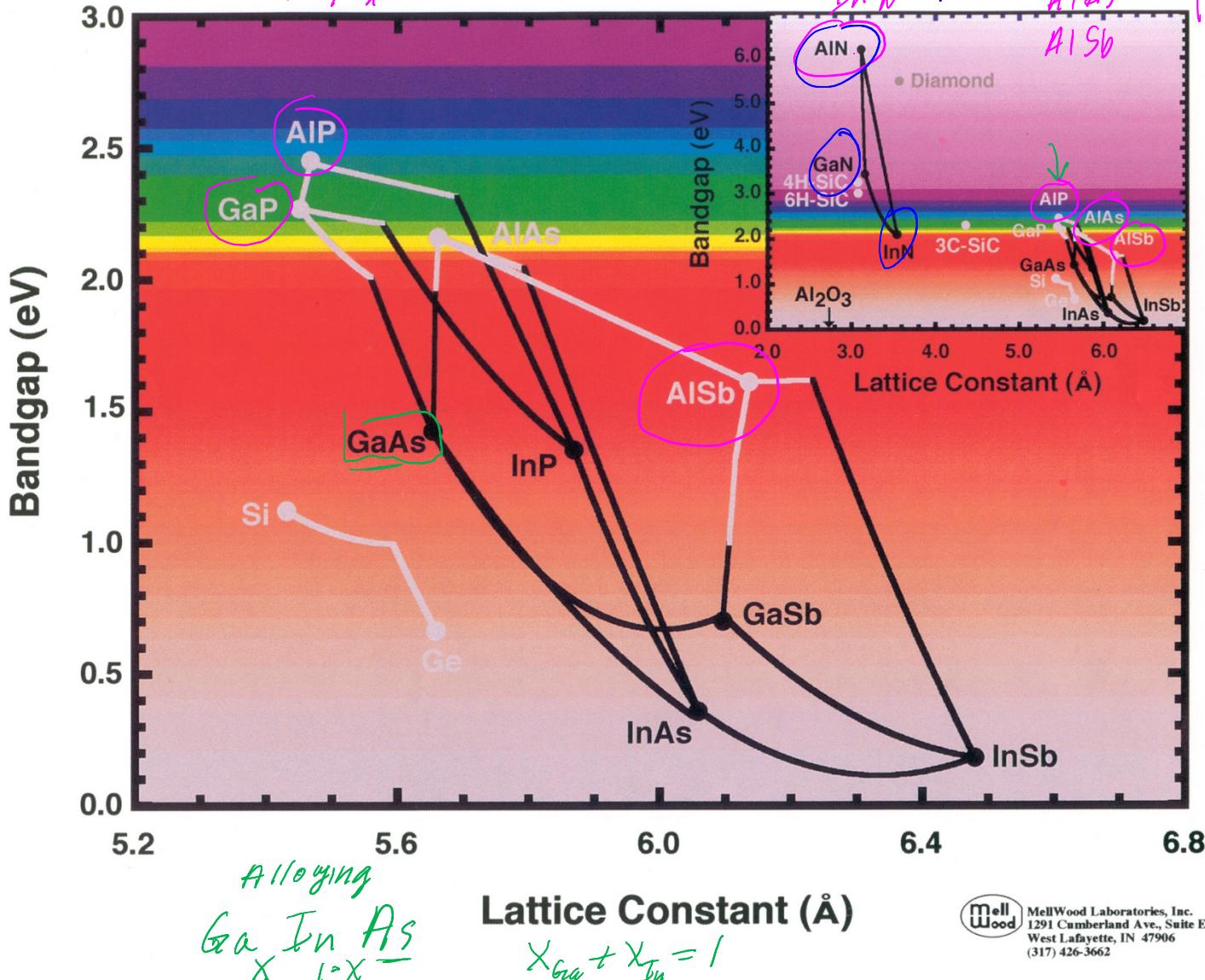
structures		VIII A																	
Cubic, body centered												VII A							
Monoclinic												VII A							
Rhombohedral												VII A							
IB												VII A							
IIB												VII A							
29	63.546	30	65.39	31	69.72	2	72.6	3	74.922	16	32.066	7	35.453	18	39.948	3	54.938	19	83.80
Cu	Copper	Zn	Zinc	Ga	Gallium	Ge	Germanium	As	Arsenic	S	Sulfur	Cl	Chlorine	Ar	Argon	Se	Selenide	Br	Bromine
8.96		7.14		5.91		3.2		3.72		2.07		1.71		1.784		4.80		1.12	
47	107.86	48	112.41	49	114.82	50	118.7	51	121.76	52	127.60	53	126.905	54	131.29	55	131.3	56	131.9
Ag	Silver	Cd	Cadmium	In	Indium	Sn	Tin	Sb	Antimony	Te	Tellurium	I	Iodine	Xe	Xenon	At	Astatine	Rn	Radon
10.5		8.65		7.31		3.0		1.62		1.62		1.92		3.74		4.80		1.92	
79	196.96	80	200.59	81	204.38	2	207.2	83	208.980	84	(209)	85	(210)	86	(222)	87	(223)	88	(224)
Au	Gold	Hg	Mercury	Tl	Thallium	Pb	Lead	Bi	Bismuth	Po	Polonium	At	Astatine	Rn	Radon	Fr	Francium	Ra	Radium
19.3		13.53		11.85		1.4		1.8		1.8		9.4		9.91		22.9		22.9	



Groups: IV, III-V, II-VI

□ Some Band Gaps and Lattice Constants

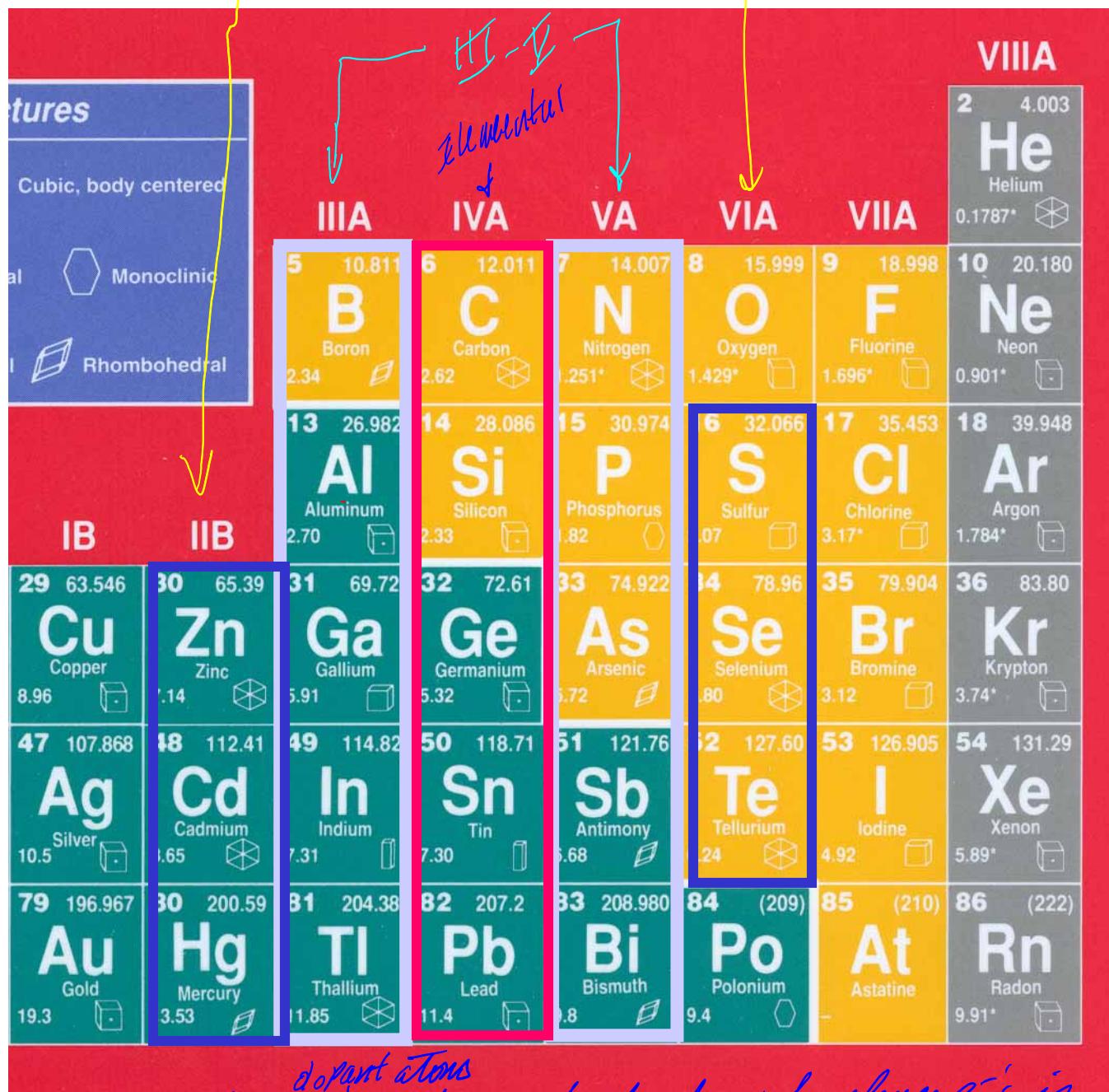
Alloying \rightarrow Eg Bandgap Engineering
 $\text{GaAs}_x \text{P}_{1-x}$



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Extrinsic S/C Prop.: Free Carrier Statistics

Donor and Acceptor Atoms for Group IV

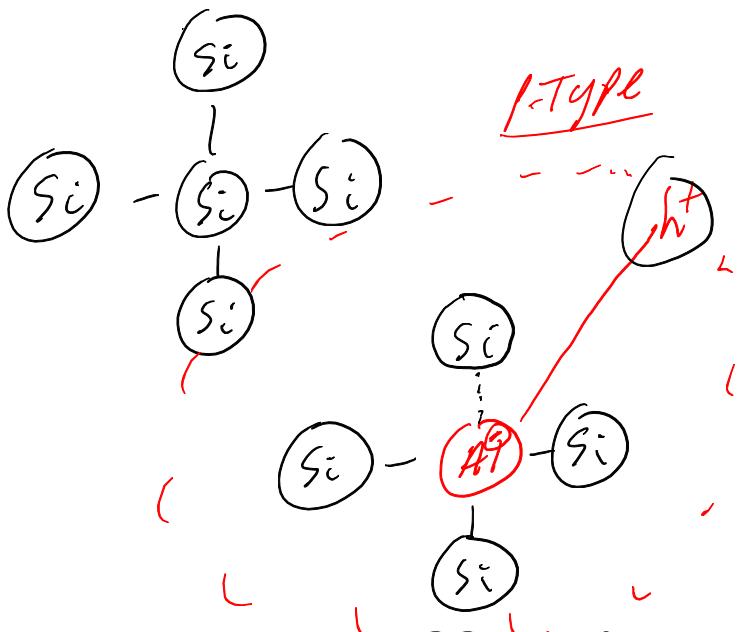
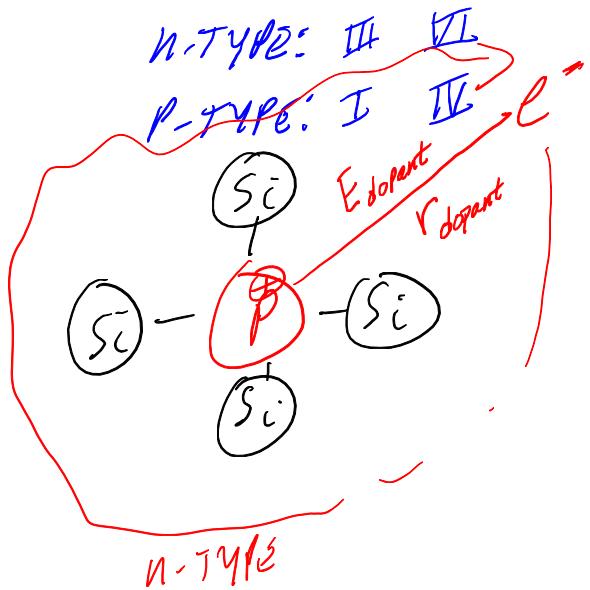


		Elements								
		Metals		Semiconductors				Non-metals		
		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	
Structures		Cubic, body centered								
I	Monoclinic									
II	Rhombohedral									
5	10.811	B	12.011	C	14.007	N	15.999	O	4.003	
		Boron		Carbon		Nitrogen		Oxygen	He	
2.34		2.62		2.51*		1.429*		1.696*	Helium	
13	26.982	Al	28.086	Si	30.974	P	32.066	S	0.1787*	
		Aluminum		Silicon		Phosphorus		Sulfur	Ne	
2.70		2.33		1.82		1.82		0.7	Neon	
29	63.546	Cu	30	Zn	31	Ga	32	Ge	10	20.180
		Copper		Zinc		Gallium		Germanium		
8.96		14		5.91		5.32		5.72		
47	107.868	Ag	48	Cd	49	In	50	Sn	18	39.948
		Silver		Cadmium		Indium		Tin		
10.5		16.5		1.65		7.31		7.30		
79	196.967	Au	80	Hg	81	Tl	82	Pb	53	83.80
		Gold		Mercury		Thallium		Lead		
19.3		3.53		11.85		11.4		11.4		

donor atoms

N-Type: add an impurity in which the # of valence e⁻'s is one greater than the matrix atom that is replaced
 IV → II provides one additional e⁻

P-Type: add an impurity in which # of valence e⁻'s is one less than the matrix atom it replaces
 IV → III provides one less e⁻ or one more h⁺

II-IV

Hydrogenic Model or Effective Mass Theory

Bohr Model $\Rightarrow H$

Mass Theory

$$E_H = \frac{e^4}{2(4\pi\hbar)^2} \cdot \frac{m_0}{\epsilon_0^2} = 13.6 \text{ eV}$$

$$r_H = \frac{4\pi\hbar^2}{e^2} \cdot \frac{\epsilon_0}{m_0} \approx 0.5 \text{ \AA}$$

SiC is not impurity

$$E_{\text{dopant}} = E_H \frac{m^*}{\epsilon_r^2}$$

$$r_{\text{dopant}} = r_H \cdot \frac{\epsilon_r}{m^*}$$

$$\frac{m^*}{\epsilon} = \frac{m_0 \cdot m^*}{\epsilon_0 \epsilon_r} = \epsilon_0 K$$

Hydrogenic

Guidelines

Extrinsic S/C Prop.: Effective Mass Model

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• The model: Effective Mass Theory

- a shallow impurity is compared to a hydrogen model atom embedded in a homogeneous medium with:
 - ↳ relative dielectric constant, ϵ .
 - ↳ an e^- or h^+ mass, which corresponds to the effective mass of the particular band extrema. Let's call this mass m^* .
- We can estimate the binding energy between a shallow donor δ atom (or ion in this case) and its ~~its~~ 5th valence e^- w/ the equation for the binding energy between a H^+ and its valence e^- modified by ϵ & m^* :

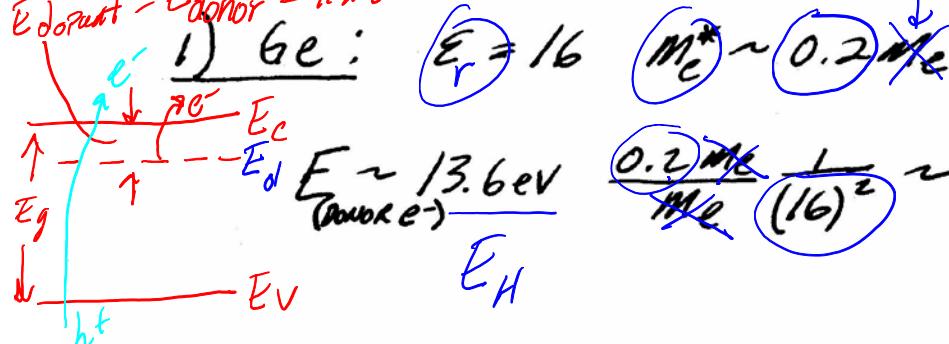
$$E = E_H \frac{m^*}{m_e} \frac{1}{\epsilon^2} = \frac{e^4 m_e}{2(4\pi\epsilon_0 h^2)} \frac{m^*}{m_e} \frac{1}{\epsilon^2} = 13.6 \text{ eV} \frac{m^*}{m_e} \frac{1}{\epsilon^2}$$

$$E_{\text{shallow-level}} = E_H \frac{m_{\text{eff}}}{\epsilon_r^2}$$

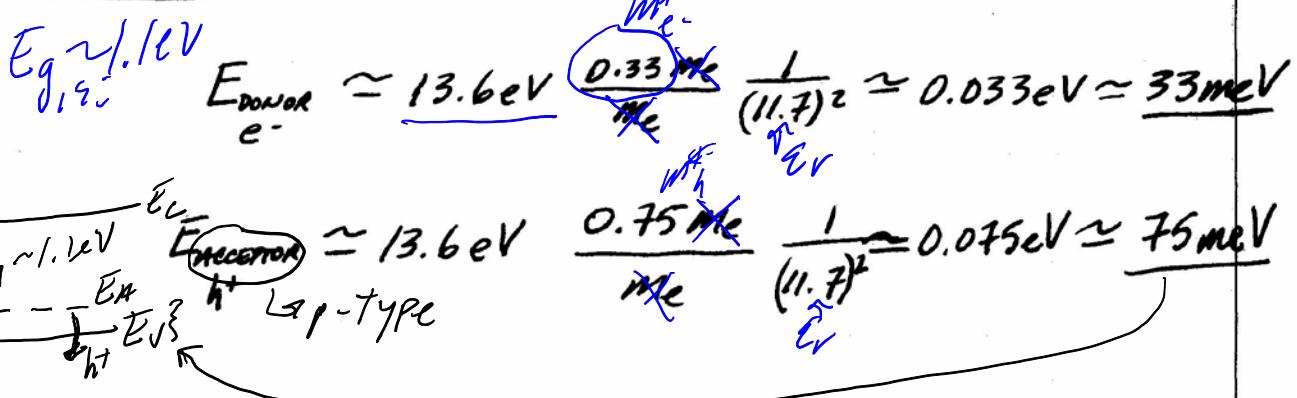
$$E_H = \frac{e^4 m_{\text{eff}}}{2(4\pi\epsilon_0 h^2)}$$

EXAMPLES:

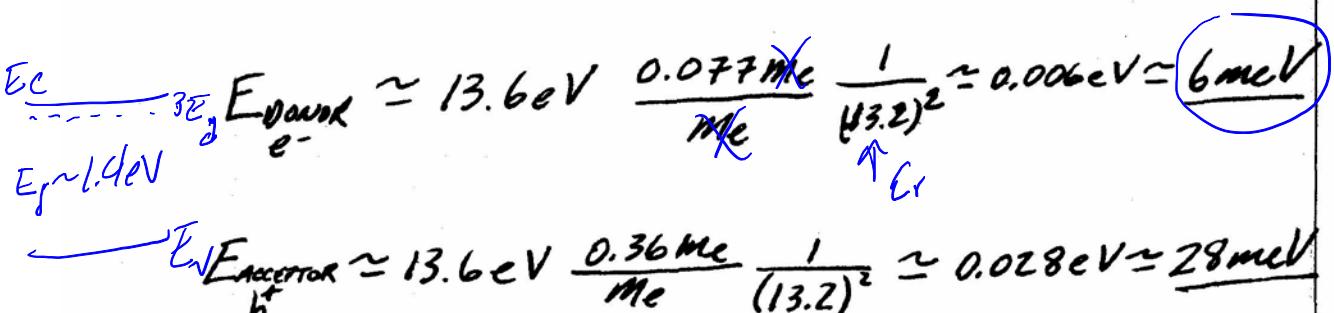
$$E_{\text{donor}} = E_{\text{donor}} = 11 \text{ meV} \quad E_{\text{Ge}} = 0.67 \text{ eV}$$



2) Si: $E = 11.7$ $m_e^* \approx 0.33 m_e$ $m_h^* \approx 0.75 m_e$



3) GaAs: $E = 13.2$ $m_e^* \approx 0.077 m_e$ $m_h^* \approx 0.36 m_e$



$E_{\text{Ge:P}} = 12 \text{ meV}$; $E_{\text{Si:P}} = 45 \text{ meV}$; $E_{\text{GaAs:Si}} = 58 \text{ meV}$

- As you can see, Effective Mass Theory (EMT) works well. This is strongly related to the very large Bohr radius for e⁻s & h⁺s bound to shallow-level impurity
- The Bohr Radius for e⁻s & h⁺s bound to shallow-level impurities can be approximated by modifying the eqn of the Bohr Radius for the e⁻ of a hydrogen atom using m^* and ϵ .

$$r_{\text{Bohr}} = r_{\text{Bohr}_{\text{H}-e^-}} \cdot \frac{m_e}{m^*} \epsilon = \frac{4\pi\epsilon_0 h^2}{m_e e^2} \cdot \frac{m_e}{m^*} \epsilon \approx 0.5 \text{ \AA} \frac{m_e}{m^*} \epsilon$$

$$r_{\text{Bohr-shallow-level}} = r_H \frac{\epsilon_r}{m_{\text{eff}}}$$

$$r_H = \frac{4\pi\epsilon_0 h^2}{m_{\text{eff}} e^2}$$

EXAMPLES:

1) Ge: $\epsilon = 16$ $m_e^* \approx 0.2 m_e$

$$R_{e^-}^{\text{Imp.}} \approx 0.5 \text{ \AA} \frac{m_e}{0.2 m_e} 16 \approx \underline{40 \text{ \AA}}$$

$\frac{m_e}{0.2 m_e}$

2) Si: $\epsilon = 11.7$ $m_e^* \approx 0.33 m_e$ $m_h^* \approx 0.75 m_e$

$$R_{e^-}^{\text{Imp.}} \approx 0.5 \text{ \AA} \frac{m_e}{0.33 m_e} 11.7 \approx \underline{17.7 \text{ \AA}}$$

$$R_{h^+}^{\text{Imp.}} \approx 0.5 \text{ \AA} \frac{m_e}{0.75 m_e} 11.7 \approx \underline{8 \text{ \AA}}$$

3) GeAs: $\epsilon = 13.2$ $m_e^* \approx 0.077 m_e$ $m_h^* \approx 0.36 m_e$

$$R_{e^-}^{\text{Imp.}} \approx 0.5 \text{ \AA} \frac{m_e}{0.077 m_e} 13.2 \approx \underline{86 \text{ \AA}}$$

$$R_{e^-}^{\text{Imp.}} \approx 0.5 \text{ \AA} \frac{m_e}{0.36 m_e} 13.2 \approx \underline{18 \text{ \AA}}$$

- In a sphere of $r_{\text{Bohr}} \sim 85\text{\AA}$, over 10^5 lattice points are contained within.
- Such large Bohr radii of e^- & h^+ of shallow-level impurities indicates how strongly delocalized in real space.
 - That is, the wavefunctions of these e^- & h^+ are spread over a very large volume relative to the volume of the impurity atom.
- The averaging over so many lattice points allows the use of an average dielectric constant, $\bar{\epsilon}$ (b/c e^- "sees" a continuous medium).
- Such a large r_{Bohr} , giving rise to extended wavefunctions in real space, means that the wavefunction is strongly localized in k -space.
- This inverse relationship between real-space and k -space originates from where?

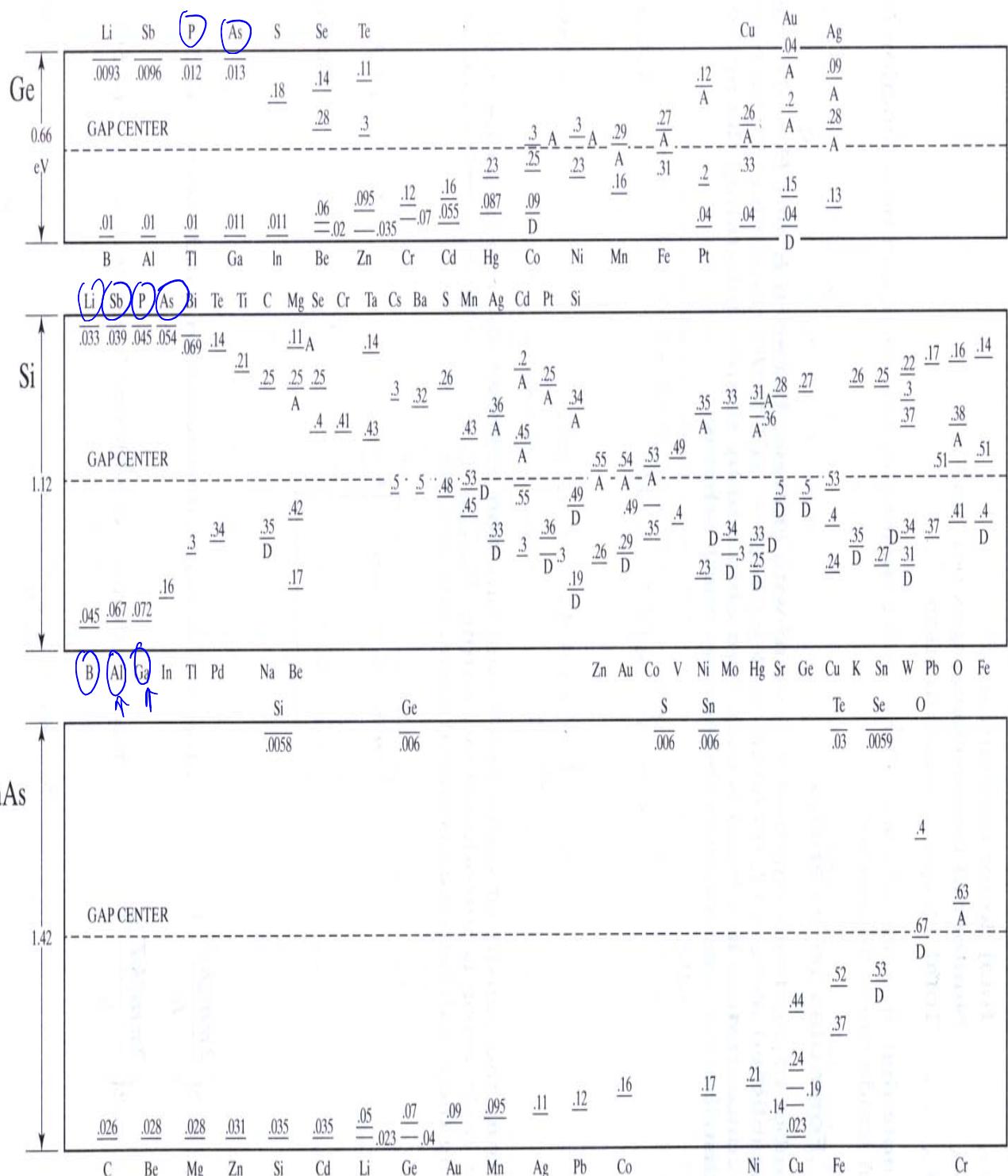
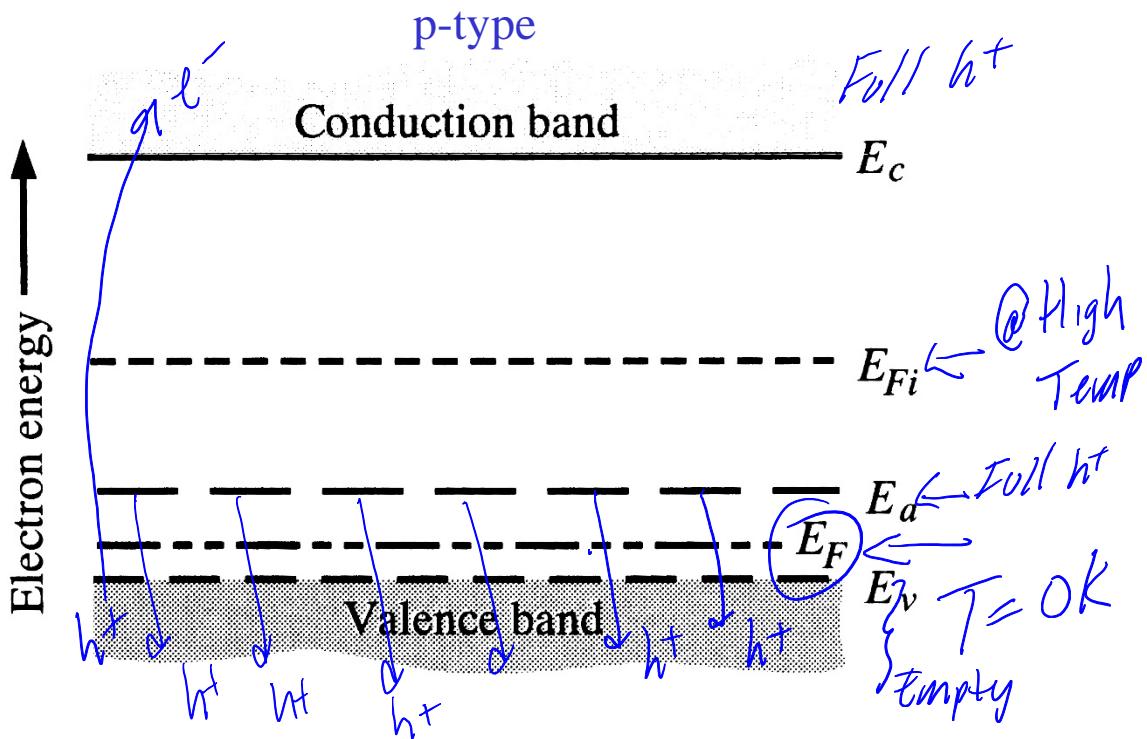
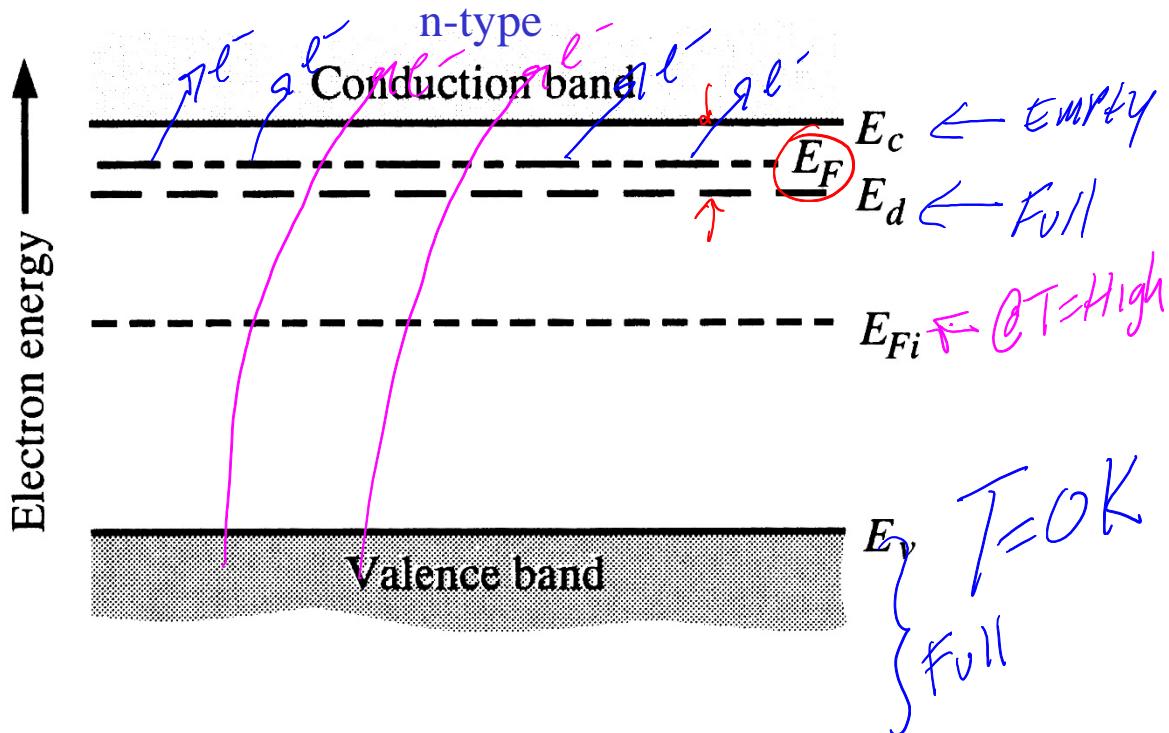


Figure 4.14 Measured ionization energies for the most commonly encountered impurities in Ge, Si, and GaAs. The levels above midgap are referenced to E_c and are donor-like or multiply charged donors, unless marked with an A which identifies an acceptor level. The levels below midgap are referenced to E_v and are acceptor-like or multiply charged acceptors, unless marked with a D for donor level. (From Sze.^[3] Reprinted with permission.)

Extrinsic S/C Prop.: Doping

Doping



Extrinsic S/C Prop.:

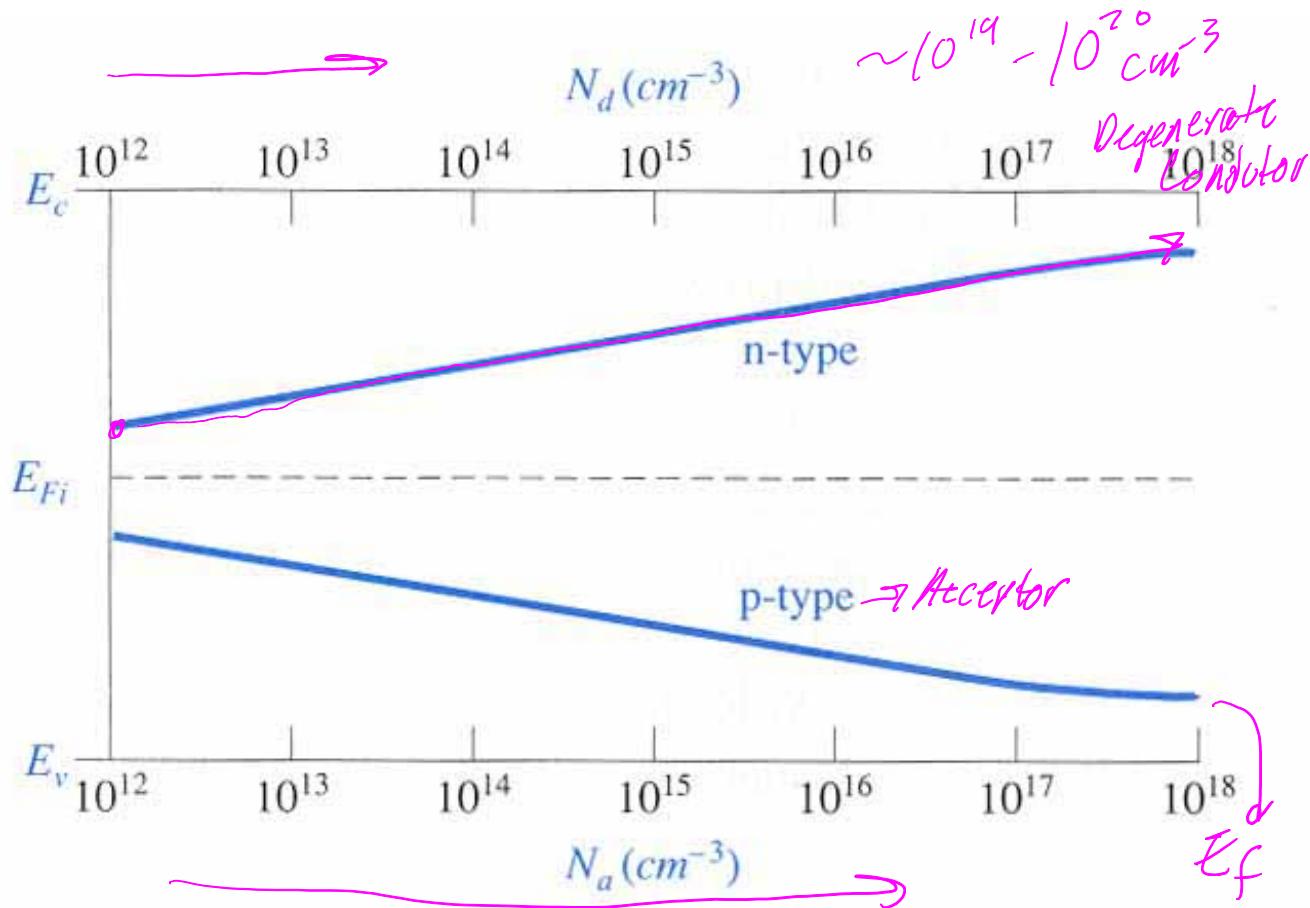
Doping & Temp Effects on Fermi Energy Level

Figure 3.18 Position of Fermi level as a function of donor concentration (n-type) and acceptor concentration (p-type)

$$E_i = \frac{E_g}{2} + \frac{3}{4} kT \ln \frac{m_{eff,h^+}}{m_{eff,e^-}}$$

As $N \uparrow$,
 $E_f \rightarrow$ band edge

Extrinsic S/C Prop.:

Doping & Temp Effects on Fermi Energy Level

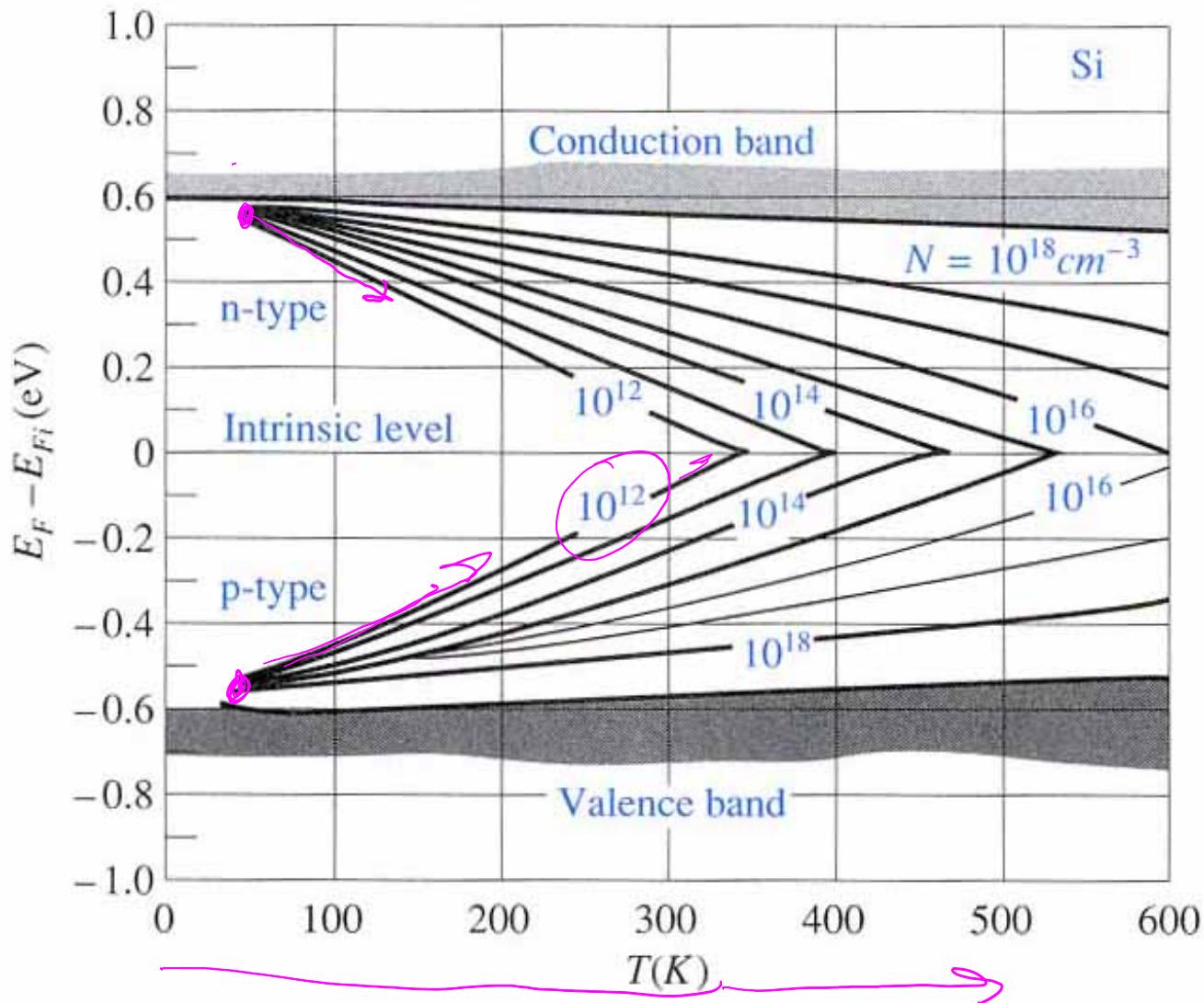


Figure 3.19 Position of Fermi level as a function of temperature for various doping concentrations (From Sze [11])

$$E_i = \frac{E_g}{2} + \frac{3}{4} kT \ln \frac{m_{eff,h^+}}{m_{eff,e^-}}$$

As $T \uparrow$,
 $E_f \rightarrow \text{mid gap}$

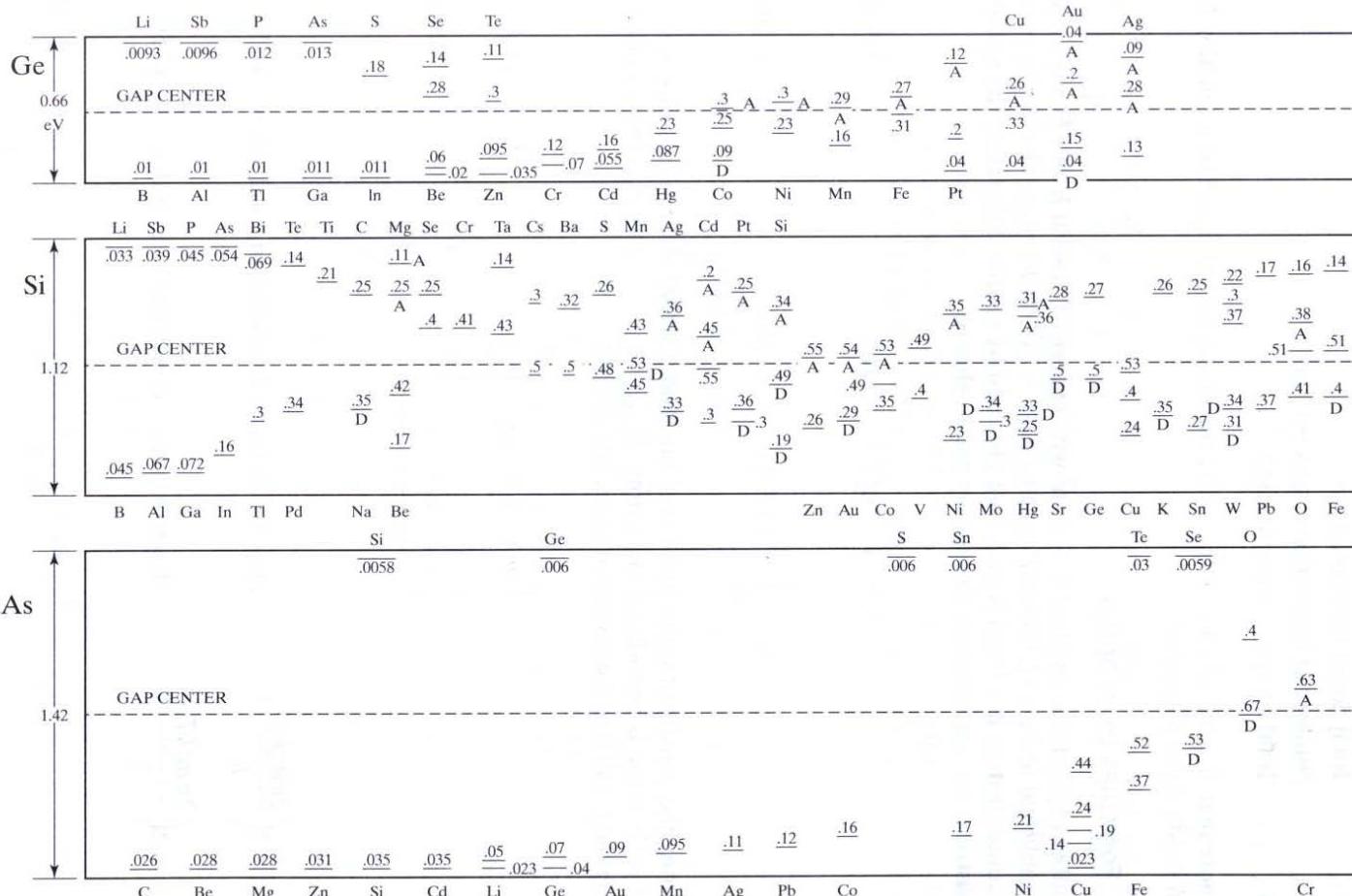


Figure 4.14 Measured ionization energies for the most commonly encountered impurities in Ge, Si, and GaAs. The levels above midgap are referenced to E_c and are donor-like or multiply charged donors, unless marked with an A which identifies an acceptor level. The levels below midgap are referenced to E_v and are acceptor-like or multiply charged acceptors, unless marked with a D for donor level. (From Sze.^[3] Reprinted with permission.)

Table 5.1 Selected typical properties of Ge, Si and GaAs at 300 K. Effective mass related to conductivity (labeled a) is different than that for density of states (labeled b).

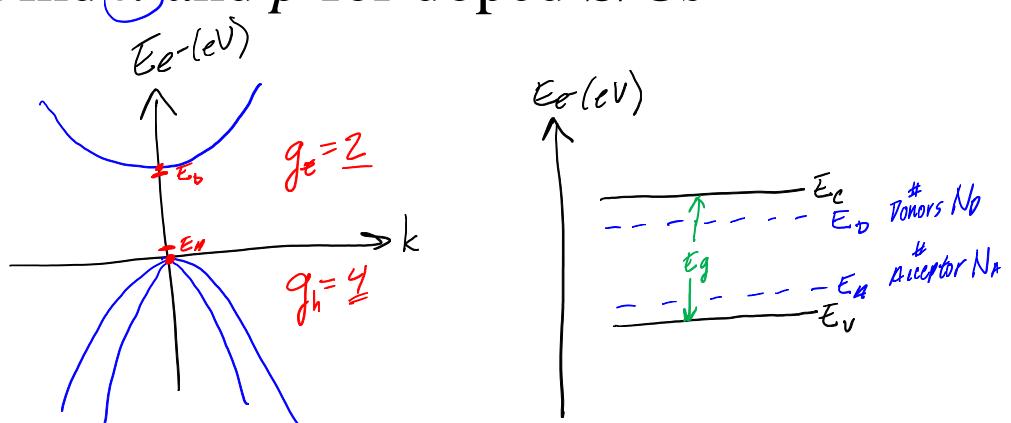
	E _g (eV)	χ (eV)	N _c (cm ⁻³)	N _v (cm ⁻³)	n _i (cm ⁻³)	μ _e (cm ² V ⁻¹ s ⁻¹)	μ _h (cm ² V ⁻¹ s ⁻¹)	m _e */m _e	m _h */m _e	ε _r
Ge	0.66	4.13	1.04×10 ¹⁹	6.0×10 ¹⁸	2.4×10 ¹³	3900	1900	0.12 a	0.23 a	16
								0.56 b	0.40 b	
Si	1.10	4.01	2.8×10 ¹⁹	1.04×10 ¹⁹	1.45×10 ¹⁰	1350	450	0.26 a	0.38 a	11.9
								1.08 b	0.56 b	
GaAs	1.42	4.07	4.7×10 ¹⁷	7×10 ¹⁸	1.8×10 ⁶	8500	400	0.067 a,b	0.40 a	13.1
								0.50 b		

Note: Effective mass related to conductivity (labeled a) is different for density of states (labeled b). From Principles of Electronic Materials and Devices, Second Edition, S.O. Kasap (© McGraw-Hill, 2002)

<http://Materials.Uask.Ca>

Extrinsic Free Carrier Statistics

Find n and p for doped S/Cs



Extrinsic S/C Prop.: Free Carrier Statistics

□ Free Carrier Statistics:

- ✓ Previously, we determined the eqns:

- o $n = f(T)$

- o $p = f(T)$

- ✓ Carrier concentrations as a function of temperature in intrinsic S/C's.

- ✓ We found that:

$$n_i^2 = N_c N_v e^{-E_g / kT}$$

- ✓ Since we have been discussing impurities in S/Cs (extrinsic S/Cs), we would like to find n and p for the extrinsic case.

- ✓ That is, we want to determine how many free e⁻'s and h⁺'s exist near their respective band edges as a function of:

- o Impurity concentration $n = f(N_{h,p}, T)$

- o Temperature

- ✓ Called “Free Carrier Statistics”, this is again performed using:

- o Statistical Mechanics ✓ $f_{FD}(E)$

- o Quantum Mechanics ✓ $g(E)$

❑ Let's define our extrinsic S/C system:

- ✓ One type of donor (when I say “donor” or “acceptor”, I mean shallow-level donor or acceptor):
 - o The donor has energy, E_D ✓
 - o The donor concentration, N_D ✓
- ✓ One type of acceptor
 - o The acceptor has energy, E_A ✓
 - o The acceptor concentration, N_A ✓
- ✓ The position of the Fermi energy level, E_f , will be determined self-consistently by the:
 - o Temperature, T
 - o Impurity concentrations, N_D & N_A
 - o Band gap energy, E_g
- ✓ One additional factor to introduce: Degeneracy, g , in k -space:
 - o Donors:
 - $g = 2$, (spin $1/2$) $m_j = \pm 1/2$ (2 spin states)
 - o Acceptors:
 - $g = 4$, (spin $3/2$) $m_j = \pm 3/2$ (4 spin states)
 - » m_j is the total angular momentum

Extrinsic S/C Prop.: Free Carrier Statistics

Derive $N \therefore \underline{N_D > N_A}$

- We now can ask: “What is the probability that a donor level at energy E_D with degeneracy g is occupied?”
- In order to answer this question, we need to use a distribution statistics of e^- 's & h^+ 's
- What distribution function would you suggest?

Extrinsic S/C Prop.: Free Carrier Statistics

- The Fermi-Dirac distribution function is (w/degeneracy g):

$$F(E) = \frac{1}{1 + g e^{\frac{(E-E_f)}{kT}}}$$

- The probability for occupancy of a donor level at energy E_D is:

$$F(E_D) = \frac{1}{1 + g_D e^{\frac{(E_D-E_f)}{kT}}}$$

- The fraction of donor levels, N^* , which are occupied by e⁻s is:

$$\underline{N^*} = \underline{N_D} \cdot F(E_D) = \frac{N_D}{1 + g_D e^{\frac{(E_D-E_f)}{kT}}}$$

- Let's choose a specific case in which:

$$\underline{N_D > N_A} \quad \text{*n-Type*}$$

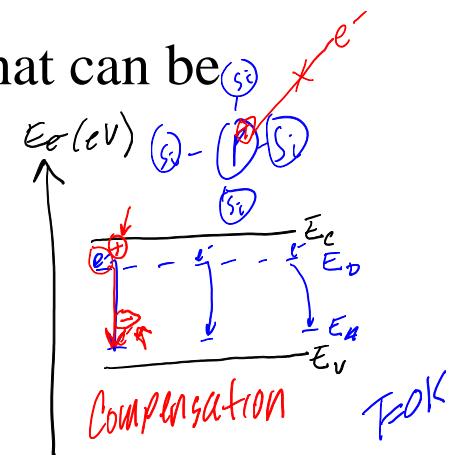
- What “type” of extrinsic S/C do we have?

Extrinsic S/C Prop.: Free Carrier Statistics

- The maximum number of e^- 's that can be promoted to the CB is:

$$N = N_D - N_A$$

Majority dopants (S_D) Minority dopants (S_A)



- There are N_A e^- 's compensated by acceptors.

- Since the acceptor states lie very close to the VB, the compensated e^- 's in the acceptor states need nearly the E_g to be promoted to the CB.

- Therefore, they can be safely neglected at low temperatures: $T <$ room temperature

- Let: n = number or concentration of e^- 's in CB

$N = N_D - N_A = N^* + n$

$\uparrow \text{at } T \rightarrow N_D$
 $\uparrow \text{at } T \rightarrow N_A$

- Thus: $N = N_D - N_A = N^* + n$
- ✓ Where N^* is concentration of donor states occupied by e^- 's

Extrinsic S/C Prop.: Free Carrier Statistics

□ Since:

$$\underline{N^*} = \underline{N_D} \cdot \underline{F(E_D)}$$

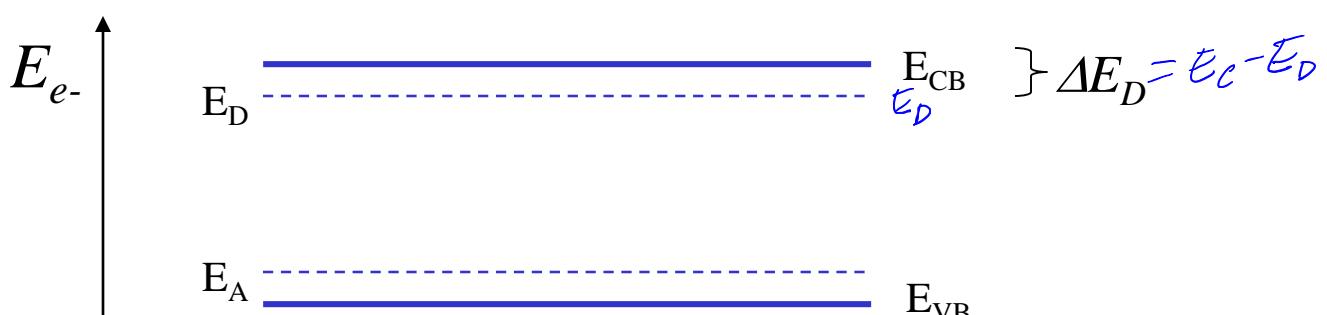
□ Substituting N^* in the previous equation:

$$\begin{aligned} N &= \frac{N_D}{1 + g_D e^{\frac{(E_D - E_f)}{kT}}} + n \\ &= \frac{N_D}{1 + g_D e^{\frac{E_D}{kT}} e^{\frac{-E_f}{kT}}} + n \end{aligned}$$

□ Thus:

$$\frac{N - n}{N_D} = \frac{1}{1 + g_D e^{\frac{E_D}{kT}} e^{\frac{-E_f}{kT}}}$$

□ Let's draw the energy band diagram when the S/C is compensated and define certain energy levels.



Extrinsic S/C Prop.: Free Carrier Statistics

- Continuing with our previous equation and taking the reciprocal of both sides, we have:

$$\frac{N_D}{N-n} = 1 + g_D e^{\frac{E_D}{kT}} e^{-\frac{E_f}{kT}}$$

$$\frac{N_D}{N-n} - 1 = g_D e^{\frac{E_D}{kT}} e^{-\frac{E_f}{kT}}$$

$$\frac{N_D - N + n}{N-n} = g_D e^{\frac{E_D}{kT}} e^{-\frac{E_f}{kT}} \quad (i)$$

- From our earlier determination of the number of e⁻'s in the CB, we found that:

$$\underline{n} = N_C e^{-\frac{(E_c - E_f)}{kT}}$$

\cdot Intrinsic Case
 \cdot Solve For $E_f \rightarrow$ Substitute

- Where we assumed the *Boltzmann Approximation*.
- Thus, we are assuming that the S/C is nondegenerate.

Extrinsic S/C Prop.: Free Carrier Statistics

- Solving for E_f , we have:

$$E_f = E_c + kT \ln \left(\frac{n}{N_C} \right)$$

- Substituting E_f into equation. (i), we obtain:

n.
$$\frac{N_D - N + n}{N - n} = g_D e^{-(E_C - E_D)/kT} \frac{N_C}{n} \cdot n$$

Let: $\Delta E_D = E_C - E_D$ & $\Theta = N_C g_D e^{-\Delta E_D/kT}$

So:
$$\frac{n(N_D - N + n)}{N - n} = \Theta \quad (\text{ii})$$

LHS = RHS \rightarrow Arrhenius Behavior

- With some algebra, we obtain a quadratic equation in n :

$$n^2 + (N_D + \Theta - N)n - N\Theta = 0$$

Extrinsic S/C Prop.: Free Carrier Statistics

- ❑ To determine the number of e⁻'s in CB, solve for n .
- ❑ Using the Quadratic equation, solve for n :

$$\begin{aligned}
 n &= \frac{1}{2} \left\{ - (N_D + \Theta - N) \pm \sqrt{(N_D + \Theta - N)^2 + 4\Theta N} \right\} \\
 &= \frac{1}{2} \left\{ - (N_D + \Theta - N) \pm (N_D + \Theta - N) \sqrt{1 + \frac{4\Theta N}{(N_D + \Theta - N)^2}} \right\} \\
 &= \frac{1}{2} (N_D + \Theta - N) \left\{ \pm \sqrt{1 + \frac{4\Theta N}{(N_D + \Theta - N)^2}} - 1 \right\}
 \end{aligned}$$

- ❑ Since $n \geq 0$, we take only the positive solution.

$N = N_D - N_{A_F}$

$$n = \frac{1}{2} (N_D + \Theta - N) \left\{ \sqrt{1 + \frac{4\Theta N}{(N_D + \Theta - N)^2}} - 1 \right\}$$

Where: $\Theta = N_C g_D e^{-\Delta E_D / kT}$

ARRHENIUS

- ❑ This last expression is good to within several kT of the CB b/c the *Boltzmann Approximation* was used. $n = \frac{1}{2} (\Theta + N_A) \left[\sqrt{1 + \frac{4\Theta(N_D - N_A)}{(\Theta + N_A)^2}} - 1 \right]$ (i i i)

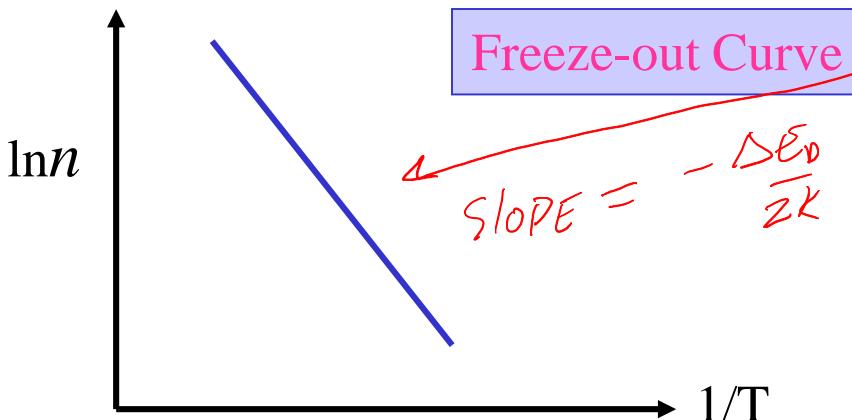
Extrinsic S/C Prop.: Free Carrier Statistics

We can use equation (ii) to examine several *Cases*:

- ❑ Case 1: $N_A = 0$ therefore $N = N_D$.
 - ✓ @ low T, $n \ll N_D$.
 - ✓ n = concentration of CB e⁻'s, a.k.a. the free carrier concentration

$$n \approx \sqrt{g_D N_D N_C e^{-\Delta E_D / kT}} = (g_D N_D N_C)^{1/2} e^{-\Delta E_D / 2kT}$$

- ✓ Plot of $\ln(n)$ vs $1/T$

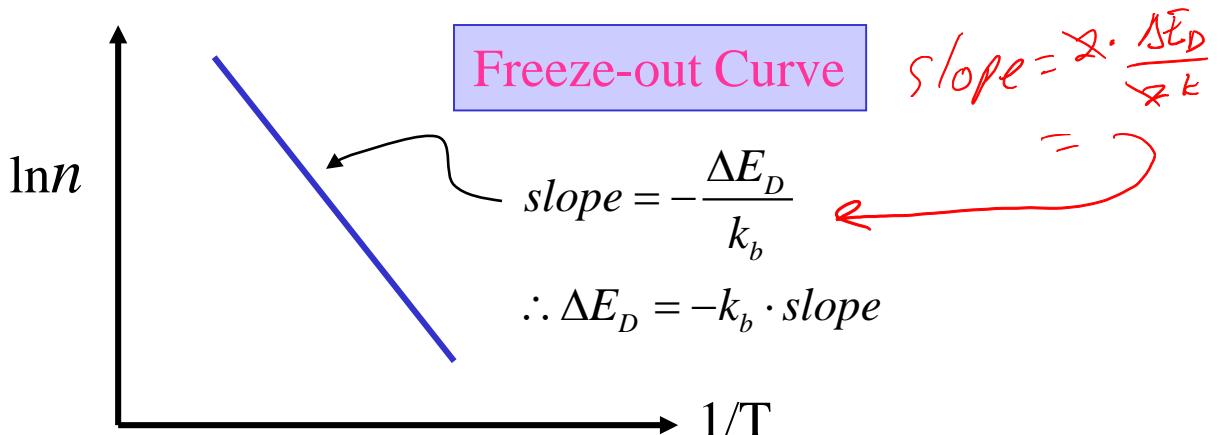


Extrinsic S/C Prop.: Free Carrier Statistics

❑ Case 2: $N_A \neq 0$, $T \sim \text{low}$, thus $n \ll N_A \ll N_D$

$$n \approx g_D N_C \frac{N_D - N_A}{N_A} e^{-\Delta E_D / kT}$$

✓ Plot of $\ln(n)$ vs $1/T$



✓ This region is also known as the "Full-slope regime".

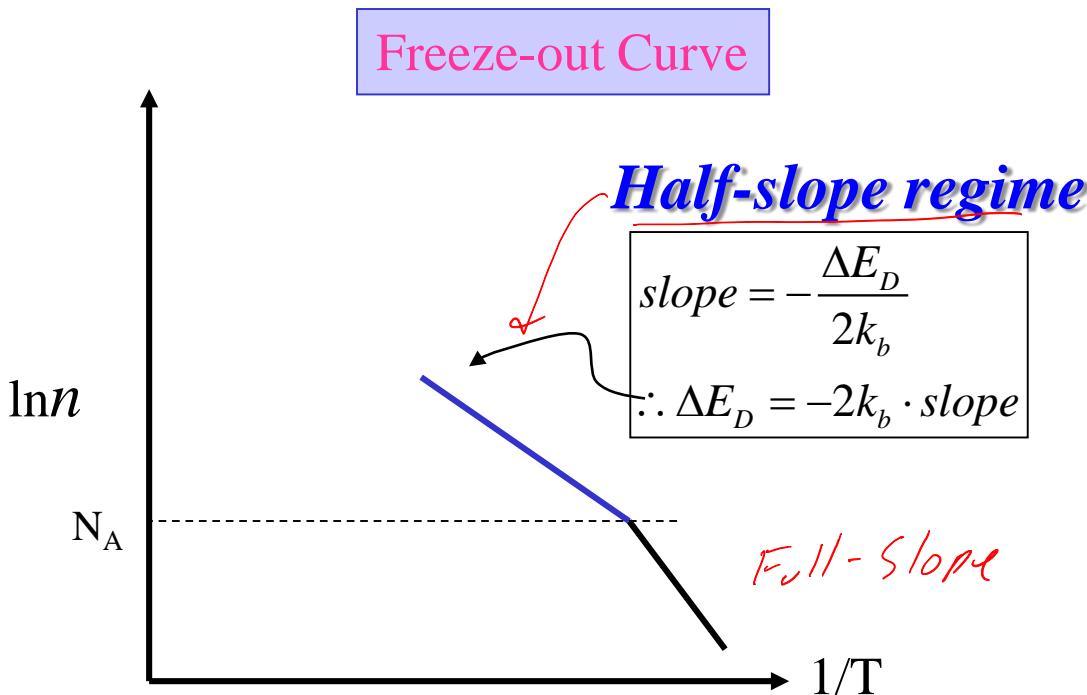
Full-slope regime

Extrinsic S/C Prop.: Free Carrier Statistics

□ Case 3: Increase T such that $\frac{N_A}{r} \ll n \ll \frac{N_D}{r}$

$$n \approx (g_D N_C N_D)^{1/2} e^{-\Delta E_D / 2kT}$$

- ✓ Similar to case 1, we find that the slope is $E_D/2k$ or “half-slope”.
- ✓ Hence, the region in blue below is known as the “**half-slope regime**”.

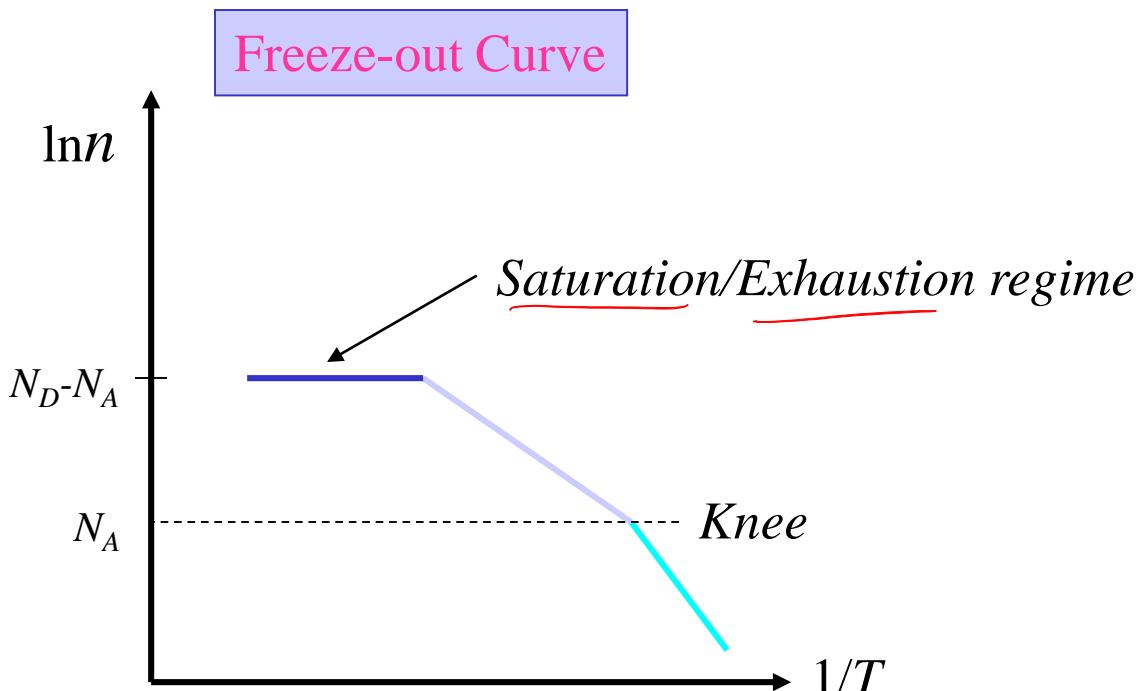


Extrinsic S/C Prop.: Free Carrier Statistics

□ Case 4:

- ✓ As T continues to increase, a region is attained in which the free e^- concentration, n , remains constant.
- ✓ This is known as the
 - o Exhaustion regime
 - o Saturation regime
- ✓ In this condition, n is given by:

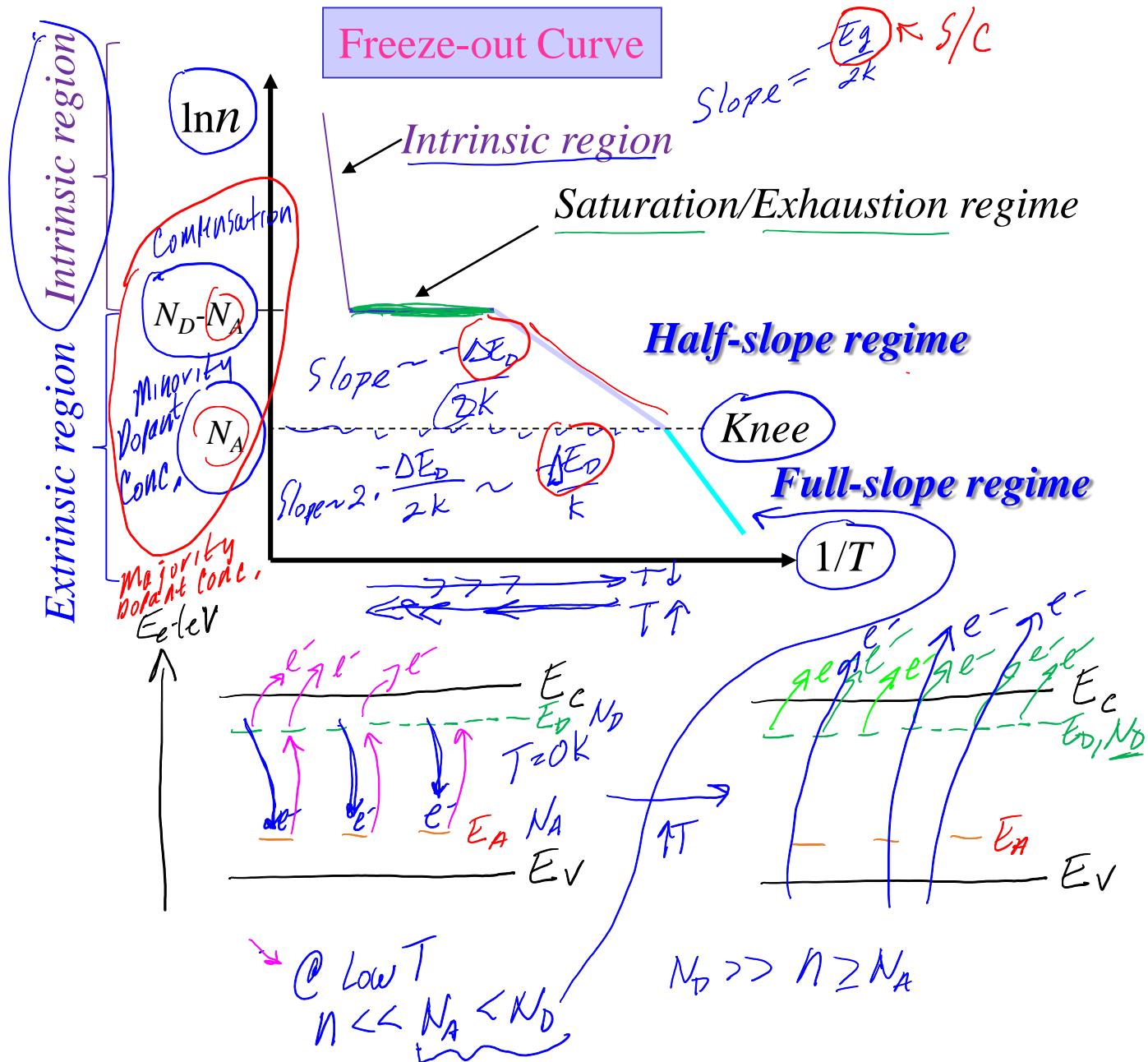
$$n = N_D - N_A$$



- ✓ Question: What happens at higher temps beyond the saturation regime?

Extrinsic S/C Prop.: Free Carrier Statistics

- ## □ Putting it all together:



Extrinsic S/C Prop.: Free Carrier Statistics

❑ Fermi Energy Level of a Doped S/C as a Function of Temperature

- ✓ Assume equilibrium
- ✓ At temperatures sufficiently high for the S/C to be intrinsic, E_f lies near mid-gap.
- ✓ As T decreases E_f moves either toward the:
 - o CB for n-type
 - o VB for p-type
- ✓ E_f coincides with the majority dopant energy level at the T for which 50% of the majority dopants are frozen out (i.e., neutral).

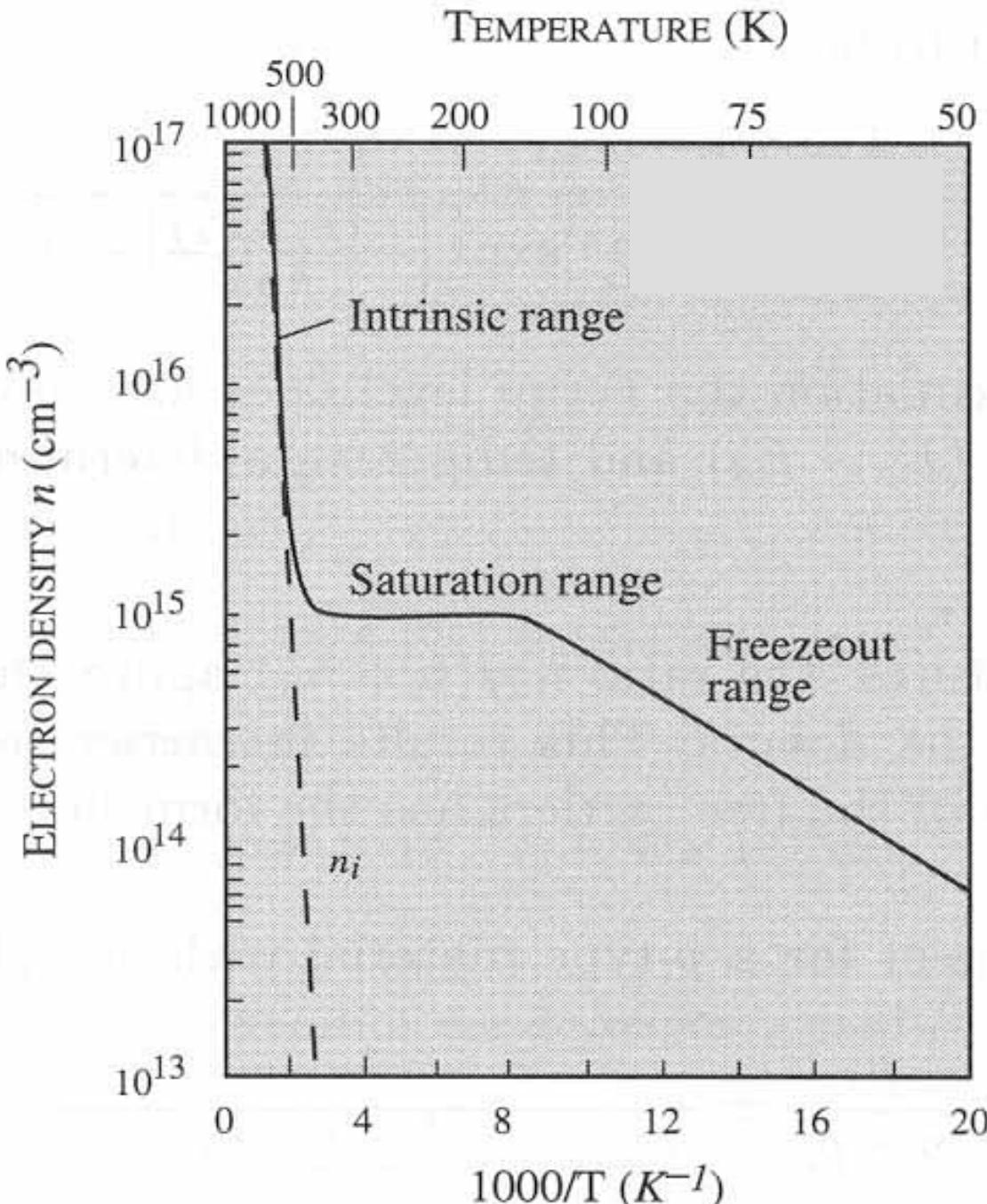
$$\therefore N_D = N_D^o - N_D^+$$

$$N_D^o = N_D^+$$

- ✓ For *uncompensated* S/C (ideal case), E_f would approach a position close to the mid-point between the dopant level and a band edge (CB or VB).
- ✓ For compensated S/Cs, a fraction of the majority dopants remain ionized at the lowest T and E_f will be very close to the majority dopant energy level.

In-class Exercise:

- ✓ Determine if n- or p-type?
- ✓ $|N_D - N_A|$?
- ✓ Minority dopant concentration?
- ✓ Full slope or half slope?
- ✓ E_g ? What is the S/C material?
- ✓ E_D or E_A ? What is the dopant?
- ✓ Show where intrinsic region and extrinsic region and saturation regimes are.



Extrinsic S/C Prop.: Free Carrier Statistics

□ Freezeout Curve

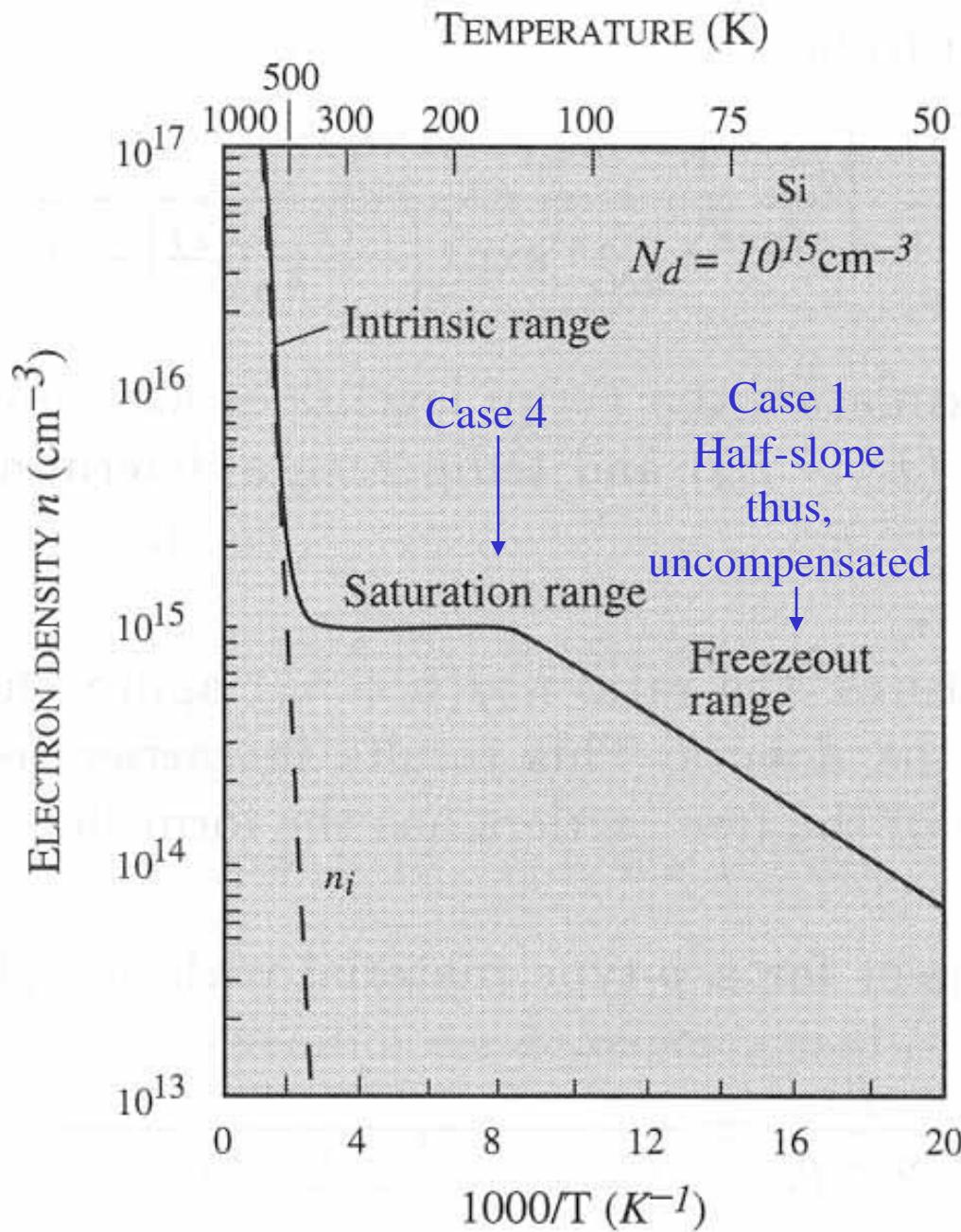


Figure 2.15: Electron density as a function of temperature for a Si sample with donor impurity concentration of 10^{15} cm^{-3} . It is preferable to operate devices in the saturation region where the free carrier density is approximately equal to the dopant density.

Extrinsic S/C Prop.: Free Carrier Statistics

□ Freezeout Curve

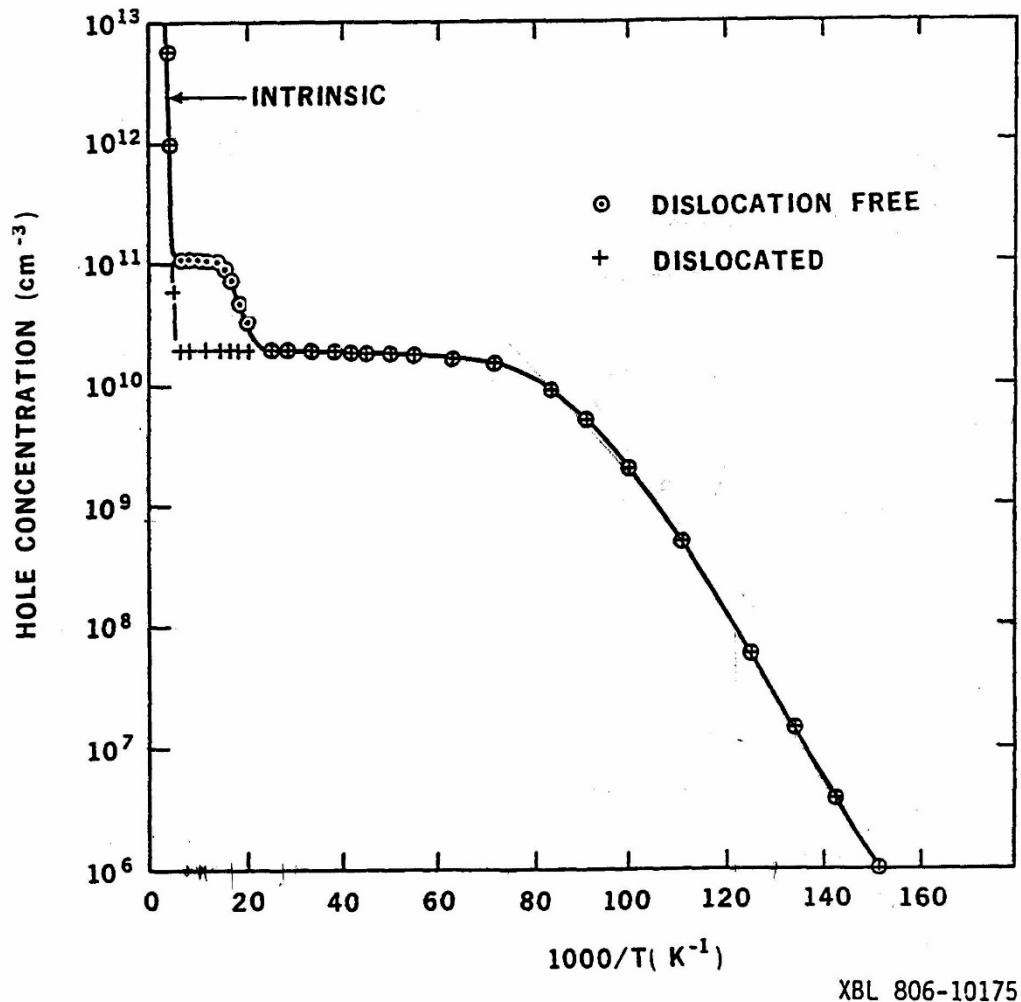


Fig. 21. Arrhenius plots of the free hole concentrations of a dislocation-free and a dislocated piece of single crystal high-purity Ge grown in a H_2 atmosphere.