APPLIED
PHYSICS
297

SEMI-
CONDUCTORS

AP 297

APPLIED PHYSICS 297 - 1961

Books and References

This list will include all of the books on reserve in the Gordon McKay Laboratory, and a few additional ones, but will not include references to original papers that are not general reviews. Books and articles marked with a + are on reserve in the library. The order of presentation is arbitrary.

(1)+ Shockley; Electrons and Holes in Semiconductors. The basic early reference to semiconductors contains three sections presented at different levels. Not recommended as text for this course, but should be consulted for early work and for "physical" discussions of phenomena bearing on semiconductor devices.

(2)+ Brooks; Advances in Electronics, Volume 7 This was essentially the text for previous version of the course that did not have Applied Physics 295 as prerequisite, and dealt more with the lore of semiconductors, and less with the rigorous treatment of the foundations of the subject. Should be read in its entirety in parallel with the course. All general material, i.e. not pertaining to detail results on Ge or Si should be assimilated.

(3)+ Proceedings of the IRE - November 1952. Contains a series of articles on semiconductors. Shows the state of knowledge at the time, and the topics of particular interest. These have now changed. Not particularly useful for course, but should be regarded as general education.

(4)+ Proceedings of the IRE December 1955. Ditto, except that some of the articles have more permanent value. Note Herman's article which sets down succinctly the elements of band theory and reduced Brillouin zone theory.

(5)+ Proceedings of the IRE Transistor Issue 1958. Ditto.

(6)+ Physics - Volume 20 Proceedings of the Amsterdam Conference. This was the second of a series of international conferences held at Reading (1; 1952); Garmisch (3, 1956); Rochester (4, 1958); Prague (5, 1960). The conference proceedings provide a sort of history of semiconductors, but also contain many articles of value for this course. The Reading Proceedings will not be put on reserve. The Amsterdam Proceedings contain, inter alia, many articles on band structure and on cyclotron resonance. They should be examined for articles aiding study, but caution is required regarding the use of results from such early work.

(7)+ The +Garmisch and +Rochester Proceedings. Similar comment.

The Rochester Conference proceedings contain theoretical articles that examine the one-electron theory in its relation to a many electron theory. Also, discussion of low mobility semiconductors such as the transition metal oxides. Wealth of papers on optical properties. This is the most up-to-date general reference work and should certainly be examined. It will not be suitable for a text, but references will undoubtedly be made to it during the course.

(8)+ Proceedings of the Photoconductivity Conference at Atlantic City.

The same comments apply. This volume is particularly interesting in that it contains some longer review articles that are well worth reading for background. It also has the first reported work on the detailed nature of absorption in semiconductors.

(9)+ Photoconductivity in the Elements; Moss Relatively elementary. Use as reference for data on specific semiconductors.

(10)+ Introduction to Semiconductors; Dunlap. Clear elementary text, written largely from an experimental point of view.

(11)+ Electronic Semiconductors; Spenke. A text of medium difficulty. Goes to great pains to explain the meaning of the mathematics, whenever possible.

(12)+ Semiconductors; R.A. Smith. Of medium difficulty. Treats things phenomenologically for the most part, uses particle concepts whenever possible. Clearly written from experimental standpoint, and should be read in parallel with the course.

(13)+ Theory of Brillouin Zones; Jones. A short new text of particular use in the first parts of the course. First chapters review the solutions to the one electron problem. Latter chapters discuss the complications of the point group symmetry for the classification of electronic states.

(14)+ Electrons and Phonons; Ziman. Probably could be regarded as text for most of the course, since it has about the same level of difficulty, and deals with largely the same subjects.

(15)+ Metals and Alloys; Mott and Jones. Older text, still used. Very clearly written.

(16)+ Wave Propagation; Brillouin. Early text of special interest to students of electrical engineering background. Develops properties of waves in periodic structures from a general viewpoint and so derives results of significance in several fields. The same general method of attack is used in an article by Slater, Rev. Mod. Phys. 30, 197 (1958)

(17)+ Handb der Physik Volume 19; Articles by Slater and Jones. These articles, particularly the first, could be used as a single text for one part of the course. Slater's article is an authoritative and comprehensive review of the band theory of solids and contains all we need to know, except perhaps for the recent developments due to Phillips.

(18)+ Elements of Solid State Theory; Wannier. A compact and advanced text, which the reader well versed in quantum mechanics will find stimulating. It is not, however, recommended as a starting textbook.

(19)+ Theory of Metals; Wilson. See comment under 14.

(20)+ The New Electronics; Lark Horowitz. Trace the early developments of semiconductors and transistors. Background reading.

(21)$^{+}$ Advances in Solid State Physics

Vol. 1: Reitz	Article on band theory. Same comments as on article by Slater under 17.
Vol. 1: Fan	General review article on semiconductors up to 1955. Most of material found elsewhere.
Vol. 3: Welker and Weiss	General article on group 3-5 compounds. Not needed for general theory: use as early reference on 3-5 compounds.
Vol. 4: Blatt	Article on theory of mobility of electrons in solids, paying particular attention to scattering mechanisms. Could be used as parallel reading for section of course dealing with transport.
Vol. 5: Koster	Articles on Group Theory.
Vol. 5: Kohn	Basic reference for section of course dealing with impurities in semiconductors, although this formulation will not necessarily be used.
Vol. 7: Callaway	Electron energy bands in solids.
Vol. 8: Newman and Tyler	Photoconductivity in germanium. Probably not required for the course, but may be needed for particular references.
Vol. 9: Scanlon	Review article on the polar semiconductors Pbs, PbSe, PbTe. Not needed for "general" part of the course.
Vol. 11: Lax and Marrorides:	Review article on cyclotron resonance.

(22) Rev. Mod. Physics Vol 30, p 102: Herman Review article on band structure, to be read in parallel with Chap. I of present course.

Rev. Mod. Physics Vol. 30, p. 122; Lax. Review article on experimental methods of determining band structure, also to be read in parallel with Chap. I of course.

(23) Reports on progress in Physics Articles that may be found helpful, but probably duplicate those already recommended

(a) Infrared absorption in semiconductors (Fan 1956)

(b) Physical problems in the thermoelectricity. (Joffe and Stilbans 1959)

(c) Group theory in solid state physics (Johnston 1960)

(d) Band structure calculations in solids. (Pincherle 1960)

(24) Progress in Theoretical Physics There are many pertinent articles in this journal, too many to list individually.

(25) Progress in Semiconductors; a series of review books edited by Gibson, Aigrain and Burgess.

APPLIED PHYSICS 297
SEMICONDUCTORS

LECTURE I 2-7-61

Background:
References: Smith " Semiconductors "
Pearson & Brattain " Proc. IRE Dec. 1955 "
Lark-Horowitz " The New Electronics -
Present State of Physics 1934 "

A good definition of a semiconductor is a material whose $\sigma \to 0$ as $T \to 0$.

Two main divisions into intrinsic and impurity types.

Donor level: state in which the impurity center becomes positive when ionized.
Acceptor level: impurity center becomes negative when ionized.

Band theory assumes scattering is low over a few lattice spaces so that they will feel the effect of the periodic lattice which will produce band structures.

Transition Metal Oxides (low mobility)
References:
Wannier, p. 169
JCPS Vol. 8, 531 (Brookhal
Joffe
Slater

I. 1 General Problem of Electronic Motion

The general Hamiltonian is:

$$H_{tot} = \underbrace{-\frac{\hbar^2}{2m}\sum_i \nabla_i^2}_{\text{electrons}} \underbrace{- \frac{\hbar^2}{2}\sum_n \frac{1}{M_n}\nabla_n^2}_{\text{nuclei}} + \underbrace{\frac{1}{2}\sum_{ij}{}' \frac{e^2}{r_{ij}}}_{\text{electrons}}$$

$$+ \underbrace{\frac{1}{2}\sum_{n,p}{}' \frac{Z_n Z_p e^2}{r_{np}}}_{\text{nuclei}} \pm \underbrace{\sum_{in} \frac{Z_n e^2}{r_{ni}}}_{\text{electrons - nuclei}}$$

Spin has been neglected. We can make the Born-Oppenhiemer approximation, that is:

$$\Psi_{Tot} = \psi_{el}\,\psi_{nuc}$$

The nuclear motion governs the electronic motion in an adiabatic sense. The nuclei wave function satisfy:

$$-\frac{\hbar^2}{2}\sum_n \frac{1}{M_n}\nabla_n^2 \psi_{nuc} + \frac{1}{2}\sum_{np}{}' \frac{Z_n Z_p e^2}{r_{np}}\psi_{nuc}$$

$$+ E(\cdots r_n \cdots)\psi_{nuc} = -\frac{\hbar}{i}\frac{\partial \psi_{nuc}}{\partial t}$$

and the electrons satisfy:

$$\left\{ -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 \psi_{el} + \frac{1}{2}\sum_{ij}{}' \frac{e^2}{r_{ij}} + \sum_{in}\frac{Z_n e^2}{r_{ni}} \right\}\psi_{el} = E\,\psi_{el}$$

The first order solution of the nuclear problem gives the lattice point position of the atoms. Therefore, $\sum_{in} \frac{Z_n e^2}{r_{ni}}$ gives rise to a periodic potential as expected, and can be written:

$$\sum_i V(r_i)$$

where $V(r_i) = V(r_i + R)$

The total wave function for the many electron equation must be written as an infinite series of $N_e \times N_e$ determinants. However, we choose a particular determinant composed of wave functions variationally chosen to minimize the energy. That is, we solve the HF equation for the wave functions (best possible).

$$\Psi_{el} = \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_{ne}(r_1) \\ \vdots & & & \\ \vdots & & & \\ \psi_1(r_{ne}) & & & \end{vmatrix}$$

The HF equations are:

$$-\frac{\hbar^2}{2m}\nabla_i^2\psi_i(r_1) + V(r_1)\psi_i(r_1) + \underbrace{\left[\sum_j{}'\int\psi_j^*(r_2)\frac{e^2}{r_{12}}\psi_j(r_2)\,dr_2\right]\psi_i(r_1)}_{\text{electron interaction term}}$$

$$\underbrace{-\sum_j{}'\left[\int\psi_j^*(r_2)\frac{e^2}{r_{12}}\psi_i(r_2)\,dr_2\right]\psi_j(r_1)}_{\text{exchange term and correlation}} = E_i\psi_i(r_1)$$

We can rewrite the Hamiltonian again as:

$$H\psi_i(r_1) = \left\{-\frac{\hbar^2}{2m}\nabla_1^2 + V(r_1) + \sum_j\int\psi_j^*(r_2)\frac{e^2}{r_{12}}\psi_j(r_2)\,dr_2\right.$$

$$\left. - \sum_j\frac{\int\psi_j^*(r_2)\psi_i(r_2)\psi_j(r_1)}{\psi_i(r_1)}\frac{e^2}{r_{12}}\,dr_2\right\}\psi_i(r_1) = E_i\psi_i(r_1)$$

The advantage of this form is that all terms are periodic in the lattice and general conclusions can be drawn without explicit solution of the equation.

LECTURE II 2-9-61

Recapitulation of One-Electron Results: (AP295)

(a) Bloch Theorem: $\psi(r) = b(k,r) = e^{ik\cdot r} u(k,r)$

Now k is a vector in reciprocal space where the reciprocal space definition is $a_i b_j = \delta_{ij}$.

$u(k,r)$ is defined as:

$$u(k,r) = \sum_K X_K(k)\, e^{iK\cdot r}$$

where K is a reciprocal lattice vector:

$$K = 2\pi(n_1 b_1 + n_2 b_2 + n_3 b_3)$$

It is seen that $u(k,r) = u(k, r+R)$

(b) Recall $\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(r) \right\}\psi = E\psi$, $p = -i\hbar\nabla$

Substituting B functions:

$$\left\{ -\frac{\hbar^2}{2m}(\nabla + ik)^2 + V(r) \right\} u(k,r) = E\, u(k,r)$$

whose solutions are: $u_n(k,r)$; $E_n(k)$

(c) Properties: $E_n(k) = E_n(-k)$
$u_n^*(-k) = u_n(k)$

Define the following expansions on the lattice.

$$b_n(k,r) = \sum_K X_n(k,K)\, e^{i(k+K)\cdot r}$$

$$u_n(k,r) = \sum_K X_n(k,K)\, e^{iK\cdot r}$$

$$V(r) = \sum_K V(K)\, e^{-iK\cdot r}$$

Result of substitution in (6) is:

$$\frac{\hbar^2}{2m}(k+K)^2 \chi_n(k,K) + \sum_{K'} V(K')\, \chi_n(k, K+K') = E_n(k)\, \chi_n(k,K)$$

This forms an infinite set of equations because of an infinite number of lattice vectors.

If we set $k, K \rightarrow k+K$, then $k \rightarrow k+K''$ and $K+K'' = K'''$, we get an identical equation to above which shows the following properties:

$$E_n(k) = E_n(k+K)$$

$$b_n(k,r) = b_n(k+K, r)$$

The justification of changing $k, K \rightarrow k+K$ is in the eigenvalues of the translation operator $e^{i(k+K)\cdot r}$ and then the solution as:

$$\psi = \sum_{k+K} A(k+K)\, e^{i(k+K)\cdot r} = \sum_{K} A(k+K)\, e^{i(k+K)\cdot r}$$

(d) Recall state densities:

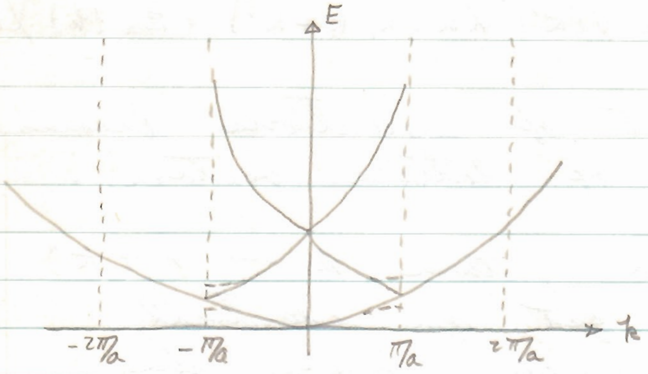
$$n(k) = \frac{2\Omega}{8\pi^3} d^3k \quad , \quad \rho(E) = \frac{2\Omega}{8\pi^3}\int \frac{dS}{|\nabla_k E|}$$

(e) Brillouin Zones: all properties of reciprocal lattice are represented in first BZ. Allowed values of k are determined by boundary conditions. This gives, from BVK conditions:

$$b_n(k, r+R_G) = e^{ik\cdot R_G}\, b_n(k,r)$$

$k \cdot R_G = 2\pi n$, spacing of k is inversely proportional to G, the number of atoms in the BVK cell. Spacing assumed so close that k is continuous.

(f) Free Electron on the Empty Lattice



We can now turn on the periodic potential and treat it as a perturbation:

The result is:

$$E = V(0) + \frac{\hbar^2 k^2}{2m} + \sum_K{}' \frac{|V(K)|^2}{E^{(0)}(k) - E^{(0)}(k+K)}$$

$$b(k,r) = \frac{1}{\sqrt{\Omega}} e^{ik\cdot r}\left[1 + \sum_K{}' \frac{V(-K)\, e^{iK\cdot r}}{E^{(0)}(k) - E^{(0)}(k+K)}\right]$$

However, must use second order because of difficulty at the BZ faces caused by degeneracy. We get:

$$E = V(0) + \frac{\hbar^2 k^2}{2m} \pm |V(K)|$$

thus splitting occours at BZ faces. Recall the various zone schemes.

LECTURE III   2-11-61

Degeneracy at BZ faces corresponds to Bragg scattering. When $V(K)=0$, no discontinuity. We then define Jones zone which is always larger than BZ or equal to it in simple cases.

I.1.4 Properties of $E_n(k)$ inside the reduced zone.

Conventions: if $E_n(k) < E_{n'}(k)$ for any one k
then $E_n(k) \leq E_{n'}(k)$ for all k

This convention precludes crossing bands, and is needed in labeling them.

Suppose Q is an operator of the point group such that $Q\,V(r) = V(r)$. Q could be a reflection or rotation operator. The condition for orthogonality transformation of coordinates:

$$x_i' = \sum_j a_{ij} x_j \quad ; \; i,j = 1,2,3$$

$$\det |a_{ij}| = 1 \;, \quad \sum_i a_{ij} a_{il} = \delta_{jl}$$

Now take:

$$\left[-\frac{\hbar^2}{2m} (\nabla + ik)^2 + V(r) \right] u(k,r) = E\, u(k,r)$$

and perform transformation, getting same thing except for:

$$k_i' = \sum_j a_{ij} k_j$$

We find:

$$\nabla^2 = \nabla'^2$$
$$k'^2 = k^2$$
$$k \cdot \nabla = k' \cdot \nabla'$$

with the result:

$$E_n(k) = E_n(k')$$
$$E_n(Qk) = E_n(k)$$

thus $E_n(k)$ possesses all the symmetries of the point group.

k-space has symmetries of r-space:

Assume: r-space lattice bases vectors:

$$\bar{a}_1, \bar{a}_2, \bar{a}_3 \quad \text{with} \quad \bar{a}_1 = a_{1x} \bar{i} + a_{1y} \bar{j} + a_{1z} \bar{k}$$

$$R = n_1 \bar{a}_1 + n_2 \bar{a}_2 + n_3 \bar{a}_3 = \begin{bmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & \vdots & \vdots \\ \vdots & \vdots & \vdots \end{bmatrix} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix} \equiv An$$

Let us perform an orthogonal transformation SA, but first consider the reciprocal lattice defined by:

$$\bar{a}_i \cdot \bar{b}_j = \delta_{ij}$$

then: $\bar{K} = [l_1\ l_2\ l_3] \underbrace{\begin{bmatrix} x & x & x \\ x & x & x \\ x & x & x \end{bmatrix}}_{B}$

and $BA = 1$

Now after the transformation, the new set of coefficients should satisfy the above relation. We assert, then, that:

$$SABS^{-1} = 1$$

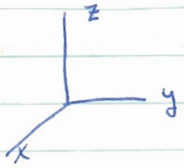
with $S^{-1} = \hat{S}$ for orthogonality.
We will find later that S is a symmetry operation. R on SR, $k \rightarrow k\hat{S}$

Cases:

1) Plane of symmetry: $x = y$

$$S = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \hat{S} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

then $k_x = k_y$ is a plane of symmetry

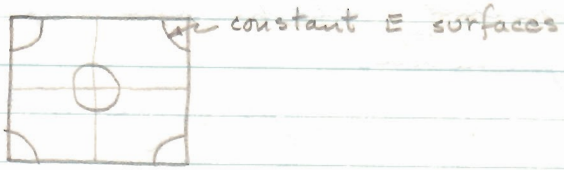
2) 

$$S = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \hat{S} = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$ Rotation symmetry

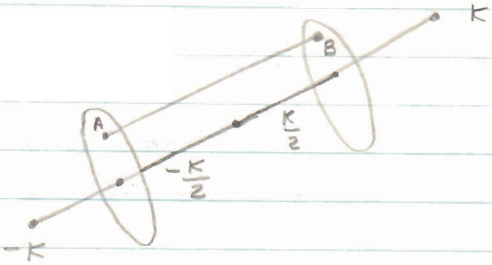
We will often refer to k-space having some symmetry of r-space.

Examination of $E(k)$ in reduced BZ:
Two ways, constant energy surfaces, or E vs. k in important directions which will usually display the extrema. Will find $E_n(k)$ will have symmetries of the point group.

Now across a symmetry plane, $\hat{n} \cdot \nabla_k E = 0$. However $\nabla_k E$ is normal to constant energy surfaces, thus constant energy surfaces cut $\perp$ to symmetry planes. For square lattice:



Now consider BZ faces:



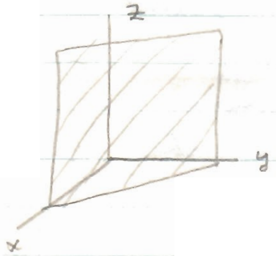
Suppose point group of xtal has a reflection plane parallel to these faces.

$$(K \cdot \nabla E)_A = -(K \cdot \nabla E)_B$$

Now A, B are the same point. $\nabla E_A = \nabla E_B$, $\therefore (K \cdot \nabla E)_{A,B} = 0$

1) sc

2) For bcc, reciprocal lattice is fcc, with first BZ a regular dodecahedron, formed by $\{110\}$ planes.



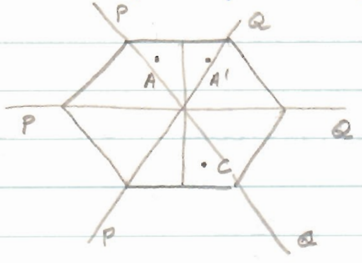
This is a plane of reflection, thus ∇E vanishes on this plane.

3) fcc has bcc for reciprocal lattice

Result is a truncated octahedron. The square faces are planes of reflection symmetry so that the normal derivative vanishes. However, the {111} planes are not planes of reflection, so in general ∇E does not vanish except along lines of trigonal symmetry, because of the hexagonal faces.

LECTURE IV   2-14-61

BZ for fcc is truncated octahedron of which we now discuss symmetries:



hex face of BZ

For inversion symmetry:

$$(\hat{K}\cdot\nabla_k E)_A = (\hat{K}\,\nabla_k E)_B = -(\hat{K}\cdot\nabla_k E)_C$$

$$(\hat{K}\cdot\nabla_k E)_A = (\hat{K}\cdot\nabla_k E)_{A'} = -(\hat{K}\cdot\nabla_k E)_C$$

Applications of Group Theory to Calculation of Band Structures.

Reference: Jones, The Theory of BZ and Electronic States in Crystals, Interscience.

A point group is the set of operations of reflection and rotations that leave the crystal invariant.

A space group is the set of operations of translation and rotation which leave the crystal invariant.

In Bravais lattices (one atom per unit cell), it is a geometric fact that there are:

32 point groups,

230 space groups

Rotation Operation:

Thru angle φ with direction cosines l, m, n, $c = \cos\frac{\varphi}{2}$, $s = \sin\frac{\varphi}{2}$, we have the following matrix:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} c^2 + (2l^2-1)s^2 & 2(lms - nc)s & 2(lns + mc)s \\ 2(lms + nc)s & c^2 + (2m^2-1)s^2 & 2(mns - lc)s \\ 2(lns - mc)s & 2(mns + lc)s & c^2 + (2n^2-1)s^2 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

which operates on the coordinates as shown.

Spin Translation:

$$V_R = \pm \begin{pmatrix} c + ins & (m - il)s \\ -(m + il)s & c - ins \end{pmatrix} \begin{pmatrix} f_1(r) \\ f_2(r) \end{pmatrix}$$

Denoting spin by $\underset{(up)}{\alpha}$ and $\underset{(down)}{\beta}$: $f_1(r)\alpha + f_2(r)\beta$

Apply R and get:

The operation then is: $f_1(Rr)V_R\alpha + f_2(Rr)V_R\beta$

See Jones, p. 90, Table 10.

Tabulation of Operations in the Cubic Case:

First, define a class. The elements of a group do not commute. If all the elements of a group commute, it is called an <u>Abelian</u> group. Example is translation in cubic. If A is an element,

$A' = X^{-1}AX$ is another element of the group and is said to belong to the same class. That is, if $B = X^{-1}AX$, A and B belong to the same class.

If we have finite group such as a point group, there is a finite number of classes.

Class Label	φ	c	s	Typical lmn	# of axis
E (identity)	0	1	0	—	—
$8\,C_3$ element pure rotation 3 fold axis	120°	$\frac{1}{2}$	$\frac{\sqrt{3}}{2}$	111	4
$3\,C_2$ or $3\,C_4^2$	180°	0	1	100	3
$6\,\sigma_c$ or $6\,C_2'J$	180°	0	1	110	6
$6\,S_4$	90°	$1/\sqrt{2}$	$\frac{1}{\sqrt{2}}$	100	3
or $6C_4J$	$-90°$	$1/\sqrt{2}$	$-1/\sqrt{2}$	100	3

All the cubic operations can be expressed by taking xyz into some permutation of $\pm x \pm y \pm z$ or there are 48 operations. The other classes of the cubic are:

$J,\ 8S_6 = 8C_3J,\ 3C_4^2J,\ 6C_2',\ 6C_4$

Representations of Groups:

Irreducible representation: the matrix representing the group has off-diagonal elements hence it irreducible. Number of irreducibles = classes.

Character:

Suppose $M' = S^{-1}MS$

Then $\mathrm{Tr}\,M' = \mathrm{Tr}\,M$

All matrix of a given class have equal traces. Thus the trace is an invariant property. Properties represented are called character.

LECTURE V   2-16-61

The group operations obey:

$$D(a)\,D(b) = D(ab)$$

$$D(a^{-1}) = D^{-1}(a)$$

$$D^{-1} = D^{*\dagger}$$

The elements of the group obey orthogonality rules:

$$\sum_R \chi^*_\lambda(R)\,\chi_\mu(R) = g\,\delta_{\lambda\mu}$$

R = element of group ; χ_λ = character of irreducible representation

Example from Character Table for O_h:

$1+8+3-6-6+1+8+3-6-6$

We could also write these in terms of classes:

$$\sum_k \left(\frac{h_k}{g}\right)^{1/2} \chi^*_{\lambda,k} \left(\frac{h_k}{g}\right)^{1/2} \chi_{\mu,k} = \delta_{\lambda\mu}$$

or, still get:

$$\sum_\lambda \left(\frac{h_j}{g}\right)^{\frac{1}{2}} \chi^*_{\lambda,j} \left(\frac{h_k}{g}\right) \chi_{\lambda,k} = \delta_{jk}$$

We can use the following that will find the irreducibles of a group:

$$\chi(R) = \sum_\lambda C_\lambda\,\chi_\lambda(R) \quad , \quad C_\lambda = \frac{1}{g}\sum_R \chi^*_\lambda(R)\,\chi(R)$$

We could also devise a geometry to represent the groups, and will find in the regular representation: $C_\lambda = n_\lambda = \chi_\lambda(E)$, $\sum_\lambda n_\lambda^2 = g = E$

n_λ is dimensionality of representation λ.

The irreducibles of the rotation group are infinite in number. The irreducible representation of this group can be represented by the spherical harmonics of order l.

no rotation changes the order of a spherical harmonic. The classes are given by:

$$\chi_l(\phi) = \frac{\sin(l+\frac{1}{2})\phi}{\sin\frac{1}{2}\phi}$$

Example: d state, $l = 2$

5   −1   1   −1   1   5   −1   1   −1

$\Gamma_{12} + \Gamma_{25}$

In general:

state	l	
s	0	Γ_1
p	1	Γ_{15}
d	2	$\Gamma_{12} + \Gamma_{25}$
f	3	$\Gamma_{15} + \Gamma_{25} + \Gamma_2'$
g	4	$\Gamma_1 + \Gamma_{12} + \Gamma_{25}' + \Gamma_{15}'$

If we have two representation, their matrices multiply as:

$$\left(D^{(\lambda)} \times D^{(\mu)}\right)_{\alpha\beta,ij} = D^{(\lambda)}_{\alpha i}\, D^{(\mu)}_{\beta j}$$

If we take $\alpha = i$, $\beta = j$, then:

$$\sum_{\alpha,\beta} \left(D^{(\lambda)} \times D^{(\mu)}\right)_{\alpha\beta,\alpha\beta} = \sum_{\alpha,\beta} D^{(\lambda)}_{\alpha\alpha}\, D^{(\mu)}_{\beta\beta} .$$

Consider the matrix element of Q:

$$M_{ij} = \int \psi_i^{(\lambda)*}\, Q_k^{(\mu)}\, \psi_j^{(\nu)}\, d\tau$$

now $M_{ij} = 0$ unless:

$$D^{(\mu)} \times D^{(\nu)} \text{ contains } D^{(\lambda)}$$

Example: Dipole Matrix of Optical Transition

For cubic group: $\Gamma_v = \Gamma_{15}$

Γ_i	$\Gamma_i \times \Gamma_v$
Γ_1	Γ_{15}
Γ_2	Γ_{25}
Γ_{12}	$\Gamma_{15} + \Gamma_{25}$
Γ_{12}'	$\Gamma_{15}' + \Gamma_{25}'$
$\vdots$	
Γ_{15}	$\Gamma_1 + \Gamma_{12} + \Gamma_{15}' + \Gamma_{25}'$

There is a correspondence between rotation groups and spin groups. There is a double group (spin) corresponding to each vector group. We can obtain a representation of the double group: $\Gamma_i \times D_{\frac{1}{2}}$ which introduces 6 new classes for the O_h group.

Kramer's Degeneracy: If odd number of electrons (no magnetic field) there is always a two fold degeneracy that is not removable.

We have been talking about point groups and only rotations.

Space Groups

These are Abelian. We can always put these groups into the representation:

$$\bar{t}_n \psi(\bar{k}) = e^{i\bar{k}\cdot\bar{t}_n} \psi(\bar{k}) \qquad \text{(Bloch waves)}$$

However, there is always point group symmetry present too. These operations are denoted (Seitz): $\{R \mid t_n\}$

It was shown that $R\,\psi(\bar{k}) \rightarrow \psi(R^{-1}\bar{k})$

48 $\bar{k}$'s are generated from point group operations. These vectors are the star of k.

Interesting case occurs when the star of k is irreducible (degenerate).

LECTURE VI 2-18-61

Recapitulation: summary of one-electron methods, translational and point symmetry of lattice, introduction to group theory.

Calculation of Bands: group theory combined with perturbation theory and making crude calculations. Usually done at band extrema.

Calculate Bands by choosing suitable starting wave function

Uses of Group Theory: If know symmetries of wave functions can use a proper choice of wave functions to simplify calculations. Detection of degeneracies at points of high symmetry. Classification of eigenstates in terms of directions of high symmetry in the BZ. Group theory also tells us how symmetries change under E and H fields and how degeneracies are removed. Group theory does not tell magnitude and direction of splitting degeneracies.

k·p Perturbation Method

Band extrema at k = 0, where we assume En and the wave function are known.

(a) $H_0 \psi(r) = E \psi(r)$, $H_0 = \frac{p^2}{2m} + V(r)$

Solution: $\psi(r) = e^{ikr} u(k,r)$

$$u(k,r) = u(k, r+R)$$

$$\left\{ \frac{1}{2m} (p + \hbar k)^2 + V(r) \right\} u_n(k,r) = E_n(k)\, u_n(k,r)$$

Define: $\epsilon_n(k) = E_n(k) - \frac{\hbar^2 k^2}{2m}$

Then we have:

$$H_0' u_n(k,r) = \epsilon_n(k)\, u_n(k,r) \; ; \quad H_0' = \frac{p^2}{2m} + V(r) + \frac{\hbar}{m} k \cdot p$$

Now apply q to k: $\epsilon_n(k+q)$; $u_n(k+q, r)$

then: $(H_0' + H^{(1)})\, u_n(k+q, r) = \epsilon_n(k+q)\, u_n(k+q, r)$

$$H^{(1)} = \frac{\hbar}{m} q \cdot p$$

Perturbation methods give:

$$\epsilon_n(k+q) = \epsilon_n(k) + \frac{\hbar}{m} q \cdot P_{nn} + \frac{\hbar^2}{m^2} \sum_{n'}{}' \frac{(q \cdot P_{nn'})(P_{n'n} \cdot q)}{E_n - E_{n'}}$$

$$= \epsilon_n(k) + q \cdot \nabla_k \epsilon_n(k) + \frac{1}{2} \left(q \cdot \nabla_k \nabla_k \epsilon_n(k) \cdot q \right)$$

by Taylor series expansion.

Now: $\frac{\hbar}{m} q \cdot P_{n'n} = \frac{1}{\Omega} \int u_{n'}^* \frac{\hbar q \cdot p}{m} u_n \, d^3 r$

$$= \langle n' | H^{(1)} | n \rangle$$

For the wave function:

$$u_n(k+q, r) = u_n(k,r) + \sum_{n'}{}' \frac{\frac{\hbar}{m} q \cdot P_{n'n}\, u_{n'}(k,r)}{E_n - E_{n'}}$$

the perturbation term is weighted in favor of adjacent bands. Also, the bands tend to repel each other because of change in sign of $E_n - E_{n'}$ when one goes above or below band (n) of interest.

(b) Simple Band Edge: $k = 0$, BZ Center.
At BZ center, or energy minimum:

$$\nabla_k E_n(k) = 0, \quad \nabla_u E_n(k) = 0, \quad \therefore \quad P_{nn} = 0$$

Putting $k = 0$, we have from before:

$$E_n(q) = E_n(0) + \frac{\hbar^2 q^2}{2m} + \frac{\hbar^2 q^2}{m} \sum_{n'}{}' \frac{|P^u_{n'n}|^2}{E_n - E_{n'}}$$

$$= E_n(0) + \frac{\hbar^2 q^2}{2 m_n^*}$$

where m_n^* is the effective mass and is obviously equal to:

$$\left(\frac{m_n^*}{m}\right)^{-1} = 1 + \frac{2}{m} \sum_{n'}{}' \frac{|P^u_{n'n}|^2}{E_n - E_{n'}}$$

positive and negative values of m_n^* greater and less than one are seen to possible. From the Taylor series:

$$\frac{1}{m_n^*} = \frac{1}{\hbar^2} \frac{\delta^2 E_n(0)}{\partial q^2}$$

If adjacent bands are close, band curve sharply and m_n^* is small, and conversely. In InSb, $m_n^* < .04$. In Ge, $m_n^* \approx .14$

(c) Band Edge not at $k = 0$: We take the minimum at $k = k_0$ and make $k_0 = 0$ for simplicity. NB: Inversion symmetry no longer exists in the BZ and equation cannot be applied directly.

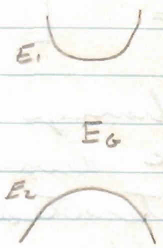
$$E_n(0) = E_n(0) + \frac{1}{2}\hbar^2 [k \cdot \mathbb{M}^{-1} \cdot k]$$

$$\mathbb{M}^{-1} = \hbar^{-2} \nabla_k \nabla_k E = \frac{1}{m}\left[\mathbb{I} - \frac{2}{m} \sum_{n'}{}' \frac{P_{nn'} P_{n'n}}{E_{n'} - E_n} \right.$$

(d) Two Adjacent Simple Bands:

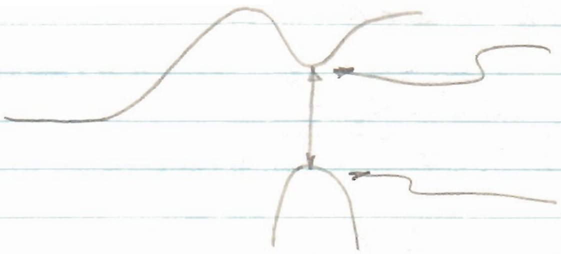
$$\frac{m}{m_1^*} = 1 - \frac{2}{m}\frac{P^2}{E_G} \longrightarrow -\frac{2P^2}{mE_G}$$

$$\frac{m}{m_2^*} = 1 + \frac{2}{m}\frac{P^2}{E_G} \longrightarrow \frac{2P^2}{mE_G}$$



assuming that $\left|\frac{2P^2}{mE_G}\right| >> 1$

note that the masses are equal and behave the same except opposite in direction. Sometimes parameters in one band can be measured and in other cannot:



{ Cannot use conductivity data to measure band structure here

{ Can be done here

However, information is desired because of optical transitions, therefore, if only these bands interact, we can measure m_n^* in valence band and know it will equal m_n in conduction band right above. Example of above model.

(e) $u_1(0,r)$, $u_2(0,r)$, $k=0$: Exact Solution

$$E_n(k) = \frac{E_1(0) + E_2(0)}{2} \pm \frac{1}{2}\left\{ E_G^2 + \frac{4\hbar^2 k^2}{m^2} P^2 \right\}^{1/2} + \frac{\hbar^2 k^2}{2m}$$

$$u_1(k,r) = \frac{1}{\sqrt{2\eta}}\left[\sqrt{\eta+E_G}\; u_1(0,r) + \sqrt{\eta-E_G}\; u_2(0,r)\right]$$

$$u_2(k,r) = \frac{1}{\sqrt{2\eta}}\left[\sqrt{\eta-E_G}\; u_1(0,r) + \sqrt{\eta+E_G}\; u_2(0,r)\right]$$

$$\eta = \left[E_G^2 + \frac{4\hbar^2 k^2 P^2}{m^2}\right]^{1/2}$$

Change of wave function occurs as we move away from $k=0$. Wave functions become adulterated.

LECTURE VII   2-21-61

Recall: $t_n \psi(k) = e^{ik\cdot t_n}\psi(k)$ t_n can be primitive or non-primitive translation.

We also introduced the notation $\{R|t_n\}$.

Star of the k-vector: $\beta k = k + K$
subgroup $\mathcal{K}$ which leaves k invariant, β.
Group is $\mathcal{G}$ with elements α_i.
Representation: $D(\{\beta|t_n\}) = e^{ik\cdot t_n} D(\beta)$

$$\mathcal{G} = \mathcal{K} + \underbrace{\{\alpha_2|a_2\}\mathcal{K}}_{\text{coset}} + \{\ \}\mathcal{K}$$

$$D_{nl}(\{\alpha|a\}) = D_{11}(\{\beta|b\})$$

$$\{\alpha|a\} = \{\alpha_l|a_l\}\{\beta|b\}$$

The only matrices involved are the irreducible representations.

$$\text{Number of cosets} = \frac{\text{order of group}}{\text{order of subgroup}}$$

Refer to BZ on p. 198 in Koster. (Face Centered Cubic)

Symmetry Element	Group	Classes	# Elements	Koster Single	D. Group Extra Classes	C.T. Double Group
Γ	O_h	10	48	p 194	6	p 247
Δ	C_{4v}	5	8	185	2	242
Λ	C_{3v}	3	6	187	3	243
Σ	C_{2v}	4	4	182	1	241
Q	C_2	2	2	181	2	240
S, Z, U, K	C_{2v}	4	4	182	1	241
W	D_{2d}	5	8	185	2	242
L	D_{3d}	6	12	188	6	243
X	D_{4h}	10	16	186	4	242

For diamond, take classes which are commonn between Td and O_h and those not common and combine with non-primitive operations. The cases where different from fcc. are the irreducible representations at the three points Z, W, X and the representation are doubly degenerate. See Koster, p. 232, 233.

Use of character table to find irreducible representation: Character Generation: Given any arbitrary function ϕ, can generate basis functions by:

$$\underset{\text{basis function}}{\phi_\lambda} = \sum_R \chi_\lambda^*(R)\, R\, \underset{\text{arbitrary function}}{\phi}$$

Example: Take fcc: representations Γ_{25}', Γ_{15}, and $\phi = x\, f(r)$ (p state)

For Γ_{25}': $(3x) - 1(-x) - 1(2x) + 1(-2x) = 0$

$\therefore$ no p-like functions

For Γ_{15}: $2\left\{3x - 1(-x) + 1(2x) - 1(-2x)\right\} = 16x$

Take $\phi = xy\, f(r)$: can be shown as basis function for Γ_{25}'.
For Γ_{25}' we have $16\, xy\, f(r)$, $\therefore$ $xy\, f(r)$ is basis function.

For diamond: $\left\{3x - 1(-x) - 1(2x) - 1(2x)\right\} f_1$ $\qquad \Gamma_{25}'$

$\left\{-3(-x) + 1(x) + 1(-2x) + 1(-2x)\right\} f_2$

$$8x\, f(|r|) - 8\,|x\hat{r} - \bar{\tau}|\, f(|r-\tau|)$$

$$[8xy f_1] + [8xy f_2]$$

Γ_{25}' represents d-like functions for cubic group.

For plane waves in various directions:

$\phi = (000) \rightarrow \Gamma_1$ is generated for ϕ_λ

$\phi = (111) \rightarrow \Gamma_1, \Gamma_2', \Gamma_{25}', \Gamma_{15}$,

by using $\phi_\lambda = \sum_R \chi_\lambda^*(R) R\phi$

Linear combination of plane waves can form a basis function

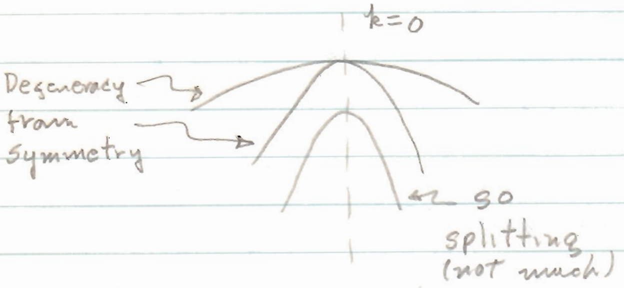
LECTURE VIII 2-23-61

(f) $P_{n'n} = \frac{1}{\Omega} \int u_{n'}^* \, p \, u_n \, d^3r$

This matrix element corresponds to optical transitions between bands. In two band case, m.e. leads to masses.

I.2.4 k·p Perturbation Methods Applied to Degenerate Bands.

Conduction band is usually non-degenerate. However, valence band is degenerate.



In Ge there are 4 valence bands, but one is so deep, we neglect it.

First attempts on this Problem:

Shockley, PR 78, 173 (1950)

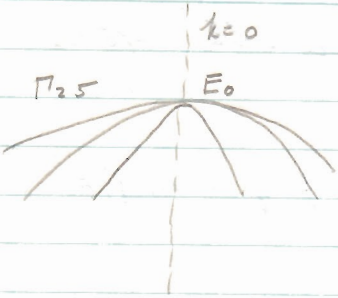
p bands in cubic xtals, without so.

Kane, JPCS 1, 82, 249. Also Vol. 8 which is the basic reference in the field.

Dresselhaus, Kip & Kittel, PR 98, 368 (1955)

(a) k·p Method for Degenerate Bands in Diamond, without SO Interactions.

This will hold (no SO) for diamond, but not for Ge or Si



We take the wave functions to have Γ_{25} or p symmetry at $k=0$.

We have: X, Y, Z, φ_α

$$\left.\begin{aligned} &(1)\quad H_0\psi = E_0\psi \\ &H_0\varphi_\alpha = E_\alpha\varphi_\alpha \\ &H_0 = \frac{p^2}{2m} + U(r) \end{aligned}\right\} \quad \begin{aligned} &\psi = (X, Y, Z) \\ &\varphi_{\alpha} = \varphi_{\alpha_1}, \varphi_{\alpha_2}, \varphi_{\alpha_3} \end{aligned}$$

f(r) is understood

From previous results:

$$(2)\quad \left\{H_0 + \frac{\hbar}{m} k\cdot p\right\} v_k(r) = E(k)\, v_k(r)$$

from $\Phi = e^{ik\cdot r} v_k(r)$. We work in one band. Using perturbation theory:

$$v_k(r) = a_x X + a_y Y + a_z Z + \sum_\alpha \left(\lambda b_\alpha^{(1)} + \lambda^2 b_\alpha^{(2)}\right)\varphi_\alpha$$

$$(3)\quad E(k) = E_0 + \lambda\omega_1 + \lambda^2\omega_2$$

Take: $\lambda \frac{\hbar}{m} k\cdot p$ as perturbation

Substituting:

$$(4)\quad \left\{-(\lambda\omega_1 + \lambda^2\omega_2) + \lambda\frac{\hbar}{m} k\cdot p\right\}\left\{a_x X + a_y Y + a_z Z\right\}$$

$$+ \sum_\alpha (E_\alpha - E_0)\left(\lambda b_\alpha^{(1)} + \lambda^2 b_\alpha^{(2)}\right)\varphi_\alpha$$

$$- \lambda^2\omega_1 \sum_\alpha b_\alpha^{(1)}\varphi_\alpha + \lambda^2\frac{\hbar}{m} k\cdot p \sum_\alpha b_\alpha^{(1)}\varphi_\alpha = 0$$

Multiply by X^*, Y^*, Z^* and integrate to get three equations.

(5) $$-(\lambda\omega_1+\lambda^2\omega_2)\,a_x + \lambda\frac{\hbar}{m}\Big\{a_x\langle x|k\cdot p|x\rangle$$

$$+\,a_y\langle x|k\cdot p|y\rangle + a_z\langle x|k\cdot p|z\rangle\Big\}$$

$$+\,\lambda^2\,\frac{\hbar}{m}\sum_\alpha b_\alpha^{(1)}\langle x|k\cdot p|\alpha\rangle = 0$$

We get three such equations with ME's of the form:

$$\langle\xi|k\cdot p|\eta\rangle = \int \xi^*\,k\cdot p\,\eta\,d^3r \quad,\quad \xi,\eta = x,y,z$$

Consider:

$$\langle x|k\cdot p|y\rangle = k_x\langle x|p_x|y\rangle + k_y\langle x|p_y|y\rangle + k_z\langle x|p_z|y\rangle$$

Applying the operation $(C_4^2)_z$, we see that ME's of this type vanish.

The first order correction gives nothing. Equating the coefficients of λ^2 to zero:

$$-\omega_2 a_x + \frac{\hbar}{m}\sum_\alpha b_\alpha^{(1)}\langle x|k\cdot p|\alpha\rangle = 0$$

$$-\omega_2 a_y + \frac{\hbar}{m}\sum_\alpha b_\alpha^{(1)}\langle y|k\cdot p|\alpha\rangle = 0$$

$$-\omega_2 a_z + \frac{\hbar}{m}\sum_\alpha b_\alpha^{(1)}\langle z|k\cdot p|\alpha\rangle = 0$$

from (5).

Multiply (4) by φ_α^* and integrate, omit $b_\alpha^{(2)}$ and get equation for $b_\alpha^{(1)}$:

$$b_\alpha^{(1)} = \frac{\hbar}{m(E_0-E_\alpha)}\Big\{a_x\langle\alpha|k\cdot p|x\rangle + a_y\langle\alpha|k\cdot p|y\rangle$$

$$+\,a_z\langle\alpha|k\cdot p|z\rangle\Big\}$$

Resubstituting:

$$\begin{pmatrix} A k_x^2 + B(k_y^2 + k_z^2) & C k_y k_x & C k_x k_z \\ C k_x k_y & A k_y^2 + B(k_x^2 + k_z^2) & C k_y k_z \\ C k_z k_x & C k_z k_y & A k_z^2 + B(k_y^2 + k_x^2) \end{pmatrix} \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} = \omega_2 \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$$

$$A = \frac{\hbar^2}{m^2} \sum_\alpha \frac{1}{E_0 - E_\alpha} \langle \xi | p_\xi | \alpha \rangle \langle \alpha | p_\xi | \xi \rangle$$

$$B = \frac{\hbar^2}{m^2} \sum_\alpha \frac{1}{E_0 - E_\alpha} \langle \xi | p_\eta | \alpha \rangle \langle \alpha | p_\eta | \xi \rangle$$

$$C = \frac{\hbar^2}{m^2} \sum_\alpha \frac{1}{E_0 - E_\alpha} \left\{ \langle \xi | p_\eta | \alpha \rangle \langle \alpha | p_\xi | \eta \rangle + \langle \xi | p_\xi | \alpha \rangle \langle \alpha | p_\eta | \eta \rangle \right\}$$

Usually A, B, C are found experimentally.
(Dresselhaus, Kip, Kittel)

LECTURE IX 2-25-61

Errata: Recall $\phi_\lambda = \sum_R \chi_\lambda(R) R \phi$

For Diamond: $\Gamma'_{25} = \{3x - 1(-x) - 1(-2x) + 1(-2x)\} f_1$

$+ \{-3x - 1(x) - 1(+2x) + 1(+2x)\} f_2 = 8x f(r) - 8\,|x\hat{r} - \bar{\tau}|\, f(|r - \tau|)$

If we move out from Γ to say Δ we obtain a subgroup of the group. There are 48 elements of the cubic group at Γ and 8 at Δ. Can obtain compatability relations. Example from Jones:

Γ_1	Γ_2	Γ_{12}	Γ'_{15}	Γ'_{25}	Γ'_1	Γ'_2	Γ'_{12}	Γ_{15}	Γ_{25}
Δ_1	Δ_2	$\Delta_1 + \Delta_2$	$\Delta'_1 + \Delta_5$	$\Delta'_2 + \Delta_5$	Δ'_1	Δ'_2	$\Delta'_1 + \Delta'_2$	$\Delta_1 + \Delta_5$	$\Delta_2 + \Delta_5$

See diagrams in Herman's paper in Rev Mod Phys. to see compatibility relations. Look for crossings which give accidental degeneracies. Order of levels in free electron diagram are taken to be those known experimentally.

If we have inversion symmetry, all one electron levels are doubly degenerate. For those that do not, there is not always degeneracy, but the Kramers degeneracy still exists $(E(k) = E(-k))$.

Band Calculation (Orthogonalized Plane Waves).

Would expect little resemblance between free electron approximation and actual band structure because of strong periodic potential. However, orthogonalizing atomic wave functions proves to give good correspondence.

We assume that the potential in the crystal can be written:

$$V(\bar{r}) + R'$$

where R' is an operator. Then operating on a symmeterized plane wave function:

$$\left[V(\bar{r}) + R'\right] S_i^0 = V S_i^0 + \sum_c \underset{\substack{\downarrow \\ \text{core wave function}}}{(\varphi_c, A S_i^0)}\, \varphi_c$$

Problem is to choose A. By introducing repulsive potential we make ME same as possible. Denote wave functions at other points by S_j. Take as criteria for A that

$$\sum_j{}' \left| (S_j, \{V + R'\} S_i^0) \right|^2 \quad \text{is a minimum}$$

by choosing R' suitably

Then problem is to find repulsive potential. Substituting:

$$\sum_j{}' \left| (S_j, V S_0') + \sum_c (S_j, \varphi_c)(\varphi_c, A S_i^0) \right|^2$$

Only unknown is A.

is a minimum. The S's are known so we minimize with respect to φ_c. We assume that S_0' along with S_j form a complete orthogonal set.

The result is:

$$(\psi_c, S_i^\circ)\left\{E_c - W_i^\circ - (S_i^\circ, V S_i^\circ)\right\} + (\psi_c, A S_i^\circ)$$
$$- \sum_{c'} (\psi_{c'}, A S_i^\circ)(\psi_c, S_i^\circ)(S_i^\circ, \psi_{c'}) = 0$$

where: E_c = energy of core-state c
W_i° = Free electron energy of S_i°

with the solution, defining first:

$$W_i' = (S_i^\circ, V S_i^\circ) + \sum_{c'} (S_i^\circ, \psi_{c'})(\psi_{c'}, A S_i^\circ)$$
$$= (S_i^\circ, (V+R') S_i^\circ)$$

then: $$(\psi_c, A S_i^\circ) = (W_i^\circ + W_i' - E_c)(\psi_c, S_i^\circ)$$

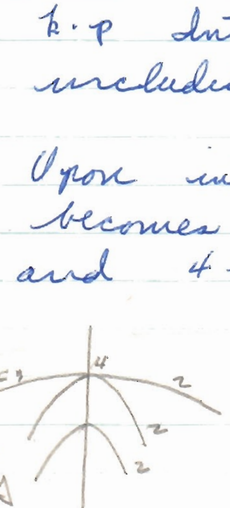
and: $$W_i' = \frac{(S_i^\circ, V S_i^\circ) + \sum_{c'} (W_i^\circ - E_{c'}) \, |\psi_{c'}, S_i^\circ|^2}{1 - \sum_{c'} |(\psi_{c'}, S_i^\circ)|^2}$$

LECTURE X 2-28-61

(b) k·p Interaction in Degenerate Valense Bands including Spin-Orbit Coupling.

Upon introducing spin, 3-fold degeneracy at $k=0$ becomes 6-fold. Interaction splits into 2-fold and 4-fold. We introduce a diagonal representation.

Two fold degeneracy from inversion symmetry



Transform from $(x\, y\, z\, m_s) \rightarrow (l\, s\, j\, m_j)$
A, B, C defined in VIII remain unchanged. Recall the operation of VIII:

$$S a = w a$$

Including spin: $$\mathcal{S} a = \begin{pmatrix} S & 0 \\ 0 & S \end{pmatrix} a = w a$$

Previously, a was a column vector with three components $a_x\ a_y\ a_z$. Now there are 6: $a_x^\alpha\ a_y^\alpha\ a_z^\alpha\ a_x^\beta\ a_y^\beta\ a_z^\beta$

The coordinates are: $x\alpha, y\alpha, z\alpha, x\beta, y\beta, z\beta$

Introduce the transformation: $\underset{(l,s,j,m_j)}{\Psi} = M \underset{(x\,y\,z\,m_s)}{\Theta}$

where $\Psi = \frac{3}{2}\frac{3}{2}, \frac{3}{2}\frac{1}{2}, \frac{3}{2}-\frac{1}{2}, \ldots$

$\Theta = x\alpha$, etc.

We state: $S' = M^* S \tilde{M}$, Then:

$$\begin{bmatrix} \omega & 0 & 0 & 0 & & \\ 0 & \omega & 0 & 0 & & 0 \\ 0 & 0 & \omega & 0 & & \\ 0 & 0 & 0 & \omega & & \\ & & & & \omega+\Delta & 0 \\ & 0 & & & 0 & \omega+\Delta \end{bmatrix} = S'$$

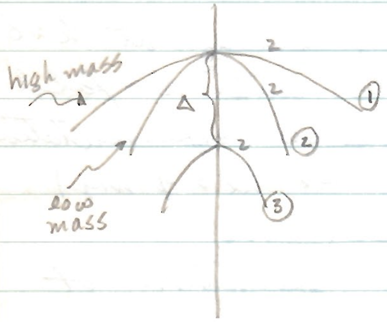
We factor the determinant assuming $\frac{\hbar^2 k^2}{2m} << \Delta$.
Not too good for silicon, OK for Ge.
We get; for the two 2-fold degenerate bands.

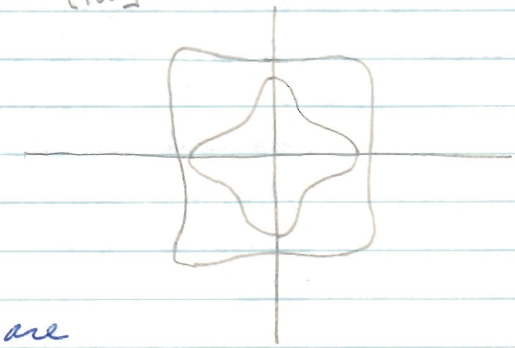
$$\begin{matrix} E_1(k) \\ E_2(k) \end{matrix} = \left(\frac{\hbar^2}{2m_0} + A'\right)k^2 \mp \left[B'^2 k^4 + C'^2\left(k_x^2 k_y^2 + k_y^2 k_z^2 + k_x^2 k_z^2\right)\right]^{1/2}$$

where $A' = \frac{1}{3}(A+2B)$, $B' = \frac{1}{3}(A-B)$, $C' = \frac{1}{3}\left(C^2 - (A-B)^2\right)$

and:

$$E_3(k) = -\Delta + \left(\frac{\hbar^2}{2m_0} + A'\right)k^2 = -\Delta + A''k^2$$





In practice, A, B, C are determined by cyclotron resonance.

We now try to find and fit spherical surface to fluted surfaces. Try:

$$\begin{matrix}E_1\\E_2\end{matrix} = A'' k^2 \mp \left[B'^2 + C'^2 S\right]^{1/2} k^2$$

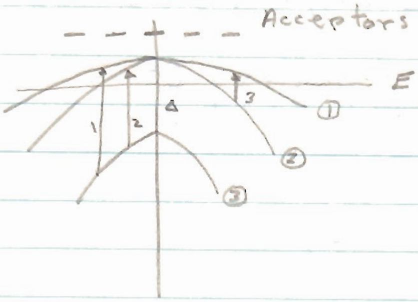
$$S = \left\langle \frac{1}{k^4}\left(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2\right)\right\rangle_{\theta,\varphi}$$

Now: $\begin{matrix}E_1\\E_2\end{matrix} = \frac{\hbar^2}{2m_p} k^2$ and we identify

$$\frac{1}{m_p} = \frac{2A''}{\hbar^2} \mp \frac{2}{\hbar^2}\left[B'^2 + C'^2 S\right]^{1/2}$$

We make this fit in order to talk about the mass of a single hole. By making the proper arguments, we assign the appropriate sign to the degenerate levels involved.

Splitting of valence band causes absorption (optical) that is non-phonon aided.

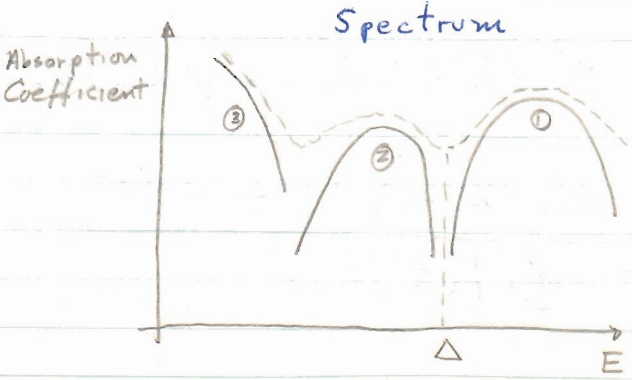


We show the allowed transitions between the three levels:

For ①: low energy cut off at Δ
high energy cut off by lack of holes in band 1.

For ②: high energy cut off at Δ, low energy cut-off due to lack of holes in band 2.

For ③: no low energy cut off, high energy cut off due to lack of holes in band 1.



This leads to determination of Δ.

References:

Kahn, PR 97, 1647 (1955)

Kane, JPCS 1, 82 (1956)

The m.e. of transition is $\propto \langle u_c | A\cdot p | u_v \rangle$. However, since we have symmetry, this is forbidden. But, mixing of other bands makes for finite m.e. which is now $\propto k$ since of admixture of wave functions is $\propto k$ and $(m.e.)^2 \propto k^2$. Thus the m.e. goes as $|\epsilon - \epsilon_v|$.

LECTURE XI 3-2-61

OPW method:

Notation: S_i^0 = particular SCPW under consideration
S_j = other SCPW
ψ_c = core states
V = lattice potential
A = operator to be determined
$V(r) + R'$ such that:

$$R' S_i^0 = \sum_c (\psi_c, A S_i^0)\, \psi_c$$

Minimize: $\sum_j \left\{ \left| (S_j, V S_i^0) + (S_j, R' S_i^0) \right| \right\}^2$

With the result:

$$(\psi_c, S_i^0)\left\{ E_c - W_i^0 - (S_i^0, V S_i^0)\right\} + (\psi_c, A S_i^0)$$
$$- \sum_{c'} (\psi_{c'}, A S_i^0)(\psi_c, S_i^0)(S_i^0, \psi_{c'}) = 0$$

where W_i^0 = KE of SCPW S_i^0 or $\frac{\hbar^2}{2m}|k|^2$

Use for definition of W_i':

$$W_i' = (S_i^0, [V+R']\, S_i^0) = (S_i^0, V S_i^0) + \sum_{c'} (\psi_{c'}, A S_i^0)(S_i^0, \psi_{c'})$$

Then:

$$W_i' = \frac{(S_i^0, V S_i^0) + \sum_{c'} (W_i^0 - E_{c'})\,|(\psi_{c'}, S_i^0)|^2}{1 - \sum_{c'} |(\psi_{c'}, S_i^0)|^2}$$

$$(\psi_c, A S_i^\circ) = (W_i^\circ + W_i' - E_c)(\psi_c, S_i^\circ)$$

We assume that core states are atomic states and do not overlap from cell to cell or atom to atom. E_c = energy of core states.

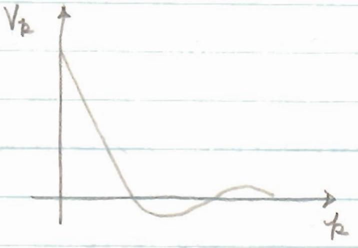
Reference: L. Kleinman & J. Phillips PR117, 460 (1960)
Application to Si PR118, 1153 (1960)

This procedure can be carried to second order by defining an effective potential:

$$V_{eff}(r)\, S_i^\circ = V(r)\, S_i^\circ + \sum_{c'} (\psi_{c'}, A S_i^\circ)\, \psi_{c'}$$

or $$V_{eff}(r) = V(r) + \frac{\sum_{c'} (\psi_{c'}, A S_i^\circ)\, \psi_{c'}}{S_i^\circ}$$

We take Fourier components of V:



Effect of making SCPW orthogonal to core states has effect of eliminating higher order matrix elements. Works better for s-states than for p or higher states.

What we have is first order correction. In second order perturbation approach, we get:

$$W_i'' = \sum_j{}' \frac{\left| (S_j, V S_i^\circ) + \sum_c (S_j, \psi_c)(W_i^\circ - E_c + W_i')(\psi_c, S_i^\circ) \right|^2}{W_i^\circ - W_j^\circ}$$

using Veff in second order perturbation treatment.

Another approach. Use:

$$e^{ik\cdot r} - \underbrace{\sum_c (\psi_c, e^{ik\cdot r})\, \psi_c}_{OPW} \qquad \text{(see Jones)}$$

using as the potential the original $V(r)$. This is the OPW method. More rigorous than above.

First treatment is more suitable for discussion of energies in Ge, Si and III-V compounds.

Problem of Form of $V(r)$:

Cannot use strictly electrostatic potential.

In HF approximation:

charge density due to core states

$$= \sum_c \sum_{R_{1,2}} g_c \left| \psi_c(r - R_{1,2}) \right|^2 = \rho(r)$$

from which we can calculate the Hartree potential due to cores alone (most important):

$$V(r) = \int \frac{\rho(r')}{|r - r'|} \, dr$$

Must include exchange terms which usually come in as operators:

$$\rho_{ex}(r, r') = \sum_c \sum_{R_{1,2}} g_c' \, \psi_c^*(r - R_{1,2}) \, \psi_c(r - R_{1,2})$$

This can be written as an exchange operator:

$$A \varphi_i(r) = - \sum_c \sum_{R_{1,2}} g_c' \left\{ \int \frac{\psi_c^*(r' - R_{1,2}) \, \varphi_i(r')}{|r - r'|} \, dr' \right\} \psi_c(r - R_{1,2})$$

Enables us to compute exchange matrix elements between states: $(\varphi_1, A\varphi_2)$.

Another term that appears in potential is correlation which is nearly always been neglected. Need not be taken into account for free electrons, but enters for cores.

No really complete self-consistent calculation have been made in semiconductors because of difficulty of handling inter-electron action in the valence band since we only know wave functions at symmetry points.

Slater Exchange Hole:

If have non-uniform charge density take exchange potential for free electrons at local points. Exchange potential is introduced as:

$$V_{ex} = -C\left[\rho_v(r)\right]^{1/3}$$

This gives more reasonable treatment of valence electron exchange than H-F methods. This is because H-F ignores correlation. Exchange hole, although it ignores correlation, still gives answer one would expect if correlation were included in H-F calculation.

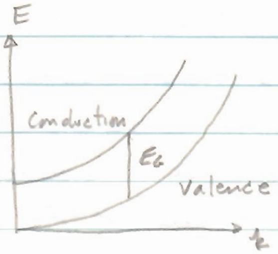
LECTURE XII 3-4-61

Energy band calculation by OPW method:

1) Coulomb potential of core } ion-core potential
2) Exchange "potential" of core } which could be
2') Polarization potential "Quasi-adiabatic" obtained from HF
Not important in semiconductor atomic treatment.
3) Coulomb potential of the other valence electrons
4) Exchange & correlation with other valence electrons.

Slater hole : $(\rho(r))^{1/3}$; HFS approximation.

Difficulty with HF method is that exchange operator A has not a diagonal matrix representation and has peculiar effect of only shifting energy. In the free electron case, HF gives too much energy because of neglect of correlation, an electron of spin up digs a hole in the distribution of down spin. Right way to do this is to consider hole dug in all distributions, up and down, but exclusion principle assign hole to other spin distribution. Other difficulties: HF gives infinite density of states near fermi surface. This will happen in semiconductor also, because top of valence band acts as fermi surface. Way to overcome difficulties is to use screening potential instead of pure coulomb potential, that is, use $\frac{1}{\epsilon r}$ instead of $1/r$. ϵ is dielectric constant. Can use HF methods except use $\frac{1}{\epsilon r}$ in the equations, using a simple model of the semiconductor to find ϵ.



$$E_k^v = \frac{\hbar^2 k^2}{2m}$$

$$E_k^c = \frac{\hbar^2 k^2}{2m} + \langle E_g \rangle$$

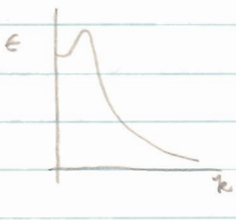
The dielectric constant for this model can be written:

$$\epsilon(0) = 1 + \left(\frac{\hbar \omega_p}{E_G}\right)^2$$

where E_G is an optical energy gap

$$= 16$$

using E_G = 5ev for Ge
4.4ev for Si



Can show for large distances, the force field goes as $\frac{1}{\epsilon(0) r}$, for small distances, it goes as $\frac{1}{r}$.

What one gets for exchange integral in HF equation is:

$$-\frac{e^2}{2} \sum_{\substack{k' \\ \text{occupied}}} \int dr_1 \int dr_2 \, \psi_{k'}^*(r_2) \frac{1}{\epsilon(r_{12}) r_{12}} \psi_{k,\alpha}^{n}(r_2) \psi_{k,\alpha}^{n'*}(r_1) \psi_{k'}(r_1)$$

α means same irreducible representation, n denotes different elements of class. Phillips has evaluated these integrals. Presence of ϵ at large distances reduces off diagonal elements of the exchange operator.

Phillip's Results: For Silicon

	HF	HFH	HSI	Exp.
E_g	.56	.10	.17	1.1 ev
E_d	.62	.22	.21	2.6 ev
E_v	1.38	.85	.76	no data

HFH can be seen to give good agreement with experimental values. This is complete "a priori" calculation. Phillips shows correction to k.p approximation is no more than 5% when screening is used (5% error in effective mass). Actually not completely a priori since we use experimentally value of dielectric constant, however, method can be made self-consistent by using results for band gap in dielectric calculation in a repetitive manner. Trouble with most band calculation methods is that they do not predict which compounds will be semi-conductors. Exact nature of gap cannot be predicted as to whether conduction band overlaps valence band.

References: G. Busch, Nuvo Cim. I, supp. 10 p 696-704 (1958)
Mooser & Pearson, J. Electronic 1, 629 (1956)
Goodman, JPCS 6, p 305-314 (1958)

LECTURE XIII 3-7-61

References: Rochester Conference, Papers A.4, P.5, P.6
T. Metal Oxides Paper B.2. Also in Rochester Conference.

Chemical Bonding in Semiconductors:

Band structure and BZ theory have failed to predict which elements and compounds would be semiconductors.

A use of Band Theory is that of expressing m.e. of R' in OPW method in Fourier components that become small in the off diagonal elements and can build up a semiempirical band theory. Can take two principle directions of $V(k)$ or $R'(k)$ such as (111) or (200) and construct general picture of bands.

The common semiconductors crystallize in the diamond structure and hence form tetrahedral bonds. One can form a set of wave functions having lobes in the tetrahedral bond directions, viz,

$$A f_s(r) + B_x x f_p(r) + C_y y f_p(y) + D_z z f_p(z)$$

When overlap occurs, depression of energy occurs and bonding takes place. If orbitals are symmetric, have bonding. If anti-symmetric, have anti-bonding.

In the band picture, the valence band corresponds to bonding electrons. The energy gap should correspond to that of the difference between symmetric and anti-symmetric.

$$\left.\begin{array}{lll} C & : & 6 \text{ ev} \\ Si & : & 1.12 \text{ ev} \\ Ge & : & .75 \text{ ev} \\ Sn & : & .1 \text{ ev} \end{array}\right\} \text{Decreasing } E_g \text{ corresponds to decreasing bond strength.}$$

III - V Compounds:

B	N
Al	P
Ga	As
In	Sb
Tl	Bi

Lattice constants of the permuted combinations of these ZnS structures are very close to the IV compounds. However, their ionic nature increases the band gap and hence the bond strength. Melting points are somewhat higher than those of IV.

Rule for semiconductors: electrons must add up to four per atom. Mooser - Pearson Rule:

$$\frac{n}{n_a} + b = 8$$

b is number of bonds between electronegative atoms, n_a = number of one type of atom per formula n = number of valences. In semiconductor, $b = 0$, $n_a = 1$, $n = 8$. In mixed structures, viz, GaS, GaSe, InS, $b = -1$ because of pair compensation of electropositive atoms. $n_a = 1$, $n = 9$.

Another type of semiconductor is of the form NaAu, or $NaKAu_2$. This is due to difference in energy between s and p levels. This compound is analogous to LiH. We get bonding between s electrons of Na and Au.

II - VI Diamond Compounds:

ZnS		
CdS	2.38	ev
CdSe	1.75	ev
CdTe	1.5	ev

Chalcopyrites I - III - VI_2

$CuInSe_2$
$AgInTe_2$ } related to II - VI

I - IV - V_2 : related to III - V

Possible non-existent case: III_2 - IV - VI

Another: I_2 - II - IV - VI_4 : $Ag_2CdSnTe_4$ (does not exist)

However: $Cu_2ZnGeSe_4$ may exist and
Cu_2FeSnS_4 is known to exist.

See article by Goodman, JPCS 6.

Goodman's Rule. Any compound is a semiconductor if its ionic formula can be written. Ex: $In^{3+}Sb^{5-}$. However, the bonding is just the opposite of this. Covalent bonding gives correct polarization but ionic does not.

Transition Metal Oxides: NiO, usually have some kind of magnetic properties. Band picture predicts insulator, band gap 5 ev. There are 8 3d electrons which produce an unfilled band. The d electrons are localized. But if d electrons are localized on Ni, get uncertainty in energy.

LECTURE XIV 3-9-61

I.2.4(c) k·p Perturbation with Spin-Orbit Interaction: InSb

$$\left\{ \frac{p^2}{2m} + V(r) + \frac{\hbar}{m}(k\cdot p) + \frac{\hbar}{4m^2c^2}(\nabla V \times p)\cdot\sigma + \frac{\hbar^2}{4m^2c^2}(\nabla V \times k)\cdot\sigma \right\}$$

$$\cdot\, u_n(k,r) = E'(k)\, u_n(k,r)$$

$$E'(k) = E(k) - \frac{\hbar^2 k^2}{2m}$$

The two extra terms come from $H_{so} = \frac{\hbar}{4m^2c^2}(\nabla V \times p)\cdot\sigma$ operating on Bloch functions. The k dependent s.o. term only amounts to 1% as most s.o. coupling occurs near the core. We assume that we know the solution to:

$$\left(\frac{p^2}{2m} + V(r)\right) u_n = E_n u_n$$

The conduction band is s-type, while the valence band is p-type.

Reference: Kane JPCS 1, 249 (1956)

We choose as basis functions:

$$|iS\uparrow\rangle, \; \left|\frac{X-iY}{\sqrt{2}}\uparrow\right\rangle, \; |Z\downarrow\rangle, \; \left|\frac{X+iY}{\sqrt{2}}\uparrow\right\rangle$$

$$|iS\downarrow\rangle, \; \left|-\frac{(X+iY)}{\sqrt{2}}\downarrow\right\rangle, \; |Z\uparrow\rangle, \; \left|\frac{X-iY}{\sqrt{2}}\downarrow\right\rangle$$

We arrive at the following secular equation by perturbation methods: wave vector in k_z direction:

$$\begin{bmatrix} H & 0 \\ 0 & H \end{bmatrix}$$

where:

$$H = \begin{bmatrix} E_s & 0 & k\cdot p & 0 \\ 0 & E_p - \frac{\Delta}{3} & \sqrt{2}\frac{\Delta}{3} & 0 \\ k\cdot p & \sqrt{2}\frac{\Delta}{3} & E_p & 0 \\ 0 & 0 & 0 & E_p + \frac{\Delta}{3} \end{bmatrix}$$

$$P = -i\frac{\hbar}{m}\langle S|p_z|Z\rangle$$

$$\Delta = \frac{3\hbar i}{4m^2c^2}\langle X|\frac{\partial V}{\partial x}p_y - \frac{\partial V}{\partial y}p_x|Y\rangle$$

The solutions are: $H - \lambda = 0$ redefine origin

$E' = 0$

Then: $E'(E'-E_G)(E'+\Delta) - k^2P^2\left(E' + \frac{2\Delta}{3}\right) = 0$

with $E_p = -\frac{\Delta}{3}$, $E_s = E_G$

(1) for small k:

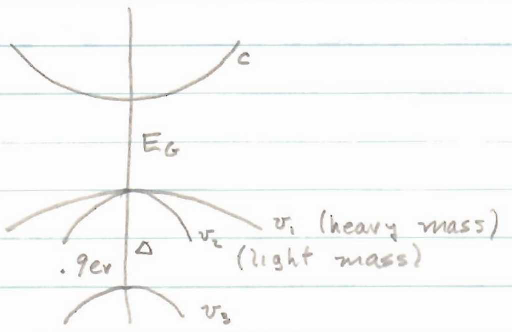
$$E_c = E_G + \frac{\hbar^2k^2}{2m} + \frac{P^2k^2}{3}\left(\frac{2}{E_G} + \frac{1}{E_G+\Delta}\right)$$

$$E_{v_1} = \frac{\hbar^2k^2}{2m}$$

$$E_{v_2} = \frac{\hbar^2k^2}{2m} - \frac{2P^2k^2}{3E_G}$$

$$E_{v_3} = -\Delta + \frac{\hbar^2 k^2}{2m} - \frac{P^2 k^2}{3(E_G+\Delta)}$$

This procedure only includes interaction between valence and conduction bands. Other interband coupling will cause surfaces not to be spherical.



(2) $\Delta >> kP, E_G$ gives:

$$E_c = \frac{\hbar^2 k^2}{2m} + \frac{E_G + (E_G + \frac{8P^2k^2}{3})^{1/2}}{2}$$

$$E_{v_1} = \frac{\hbar^2 k^2}{2m}$$

$$E_{v_2} = \frac{\hbar^2 k^2}{2m} + \frac{(E_G - \{E_G + \frac{8P^2k^2}{3}\}^{1/2})}{2}$$

$$E_{v_3} = -\Delta + \frac{\hbar^2 k^2}{2m} - \frac{P^2 k^2}{3(E_G+\Delta)}$$

This changes curvature of E_c and E_{v_2}.

Consider perturbation from higher bands using as a basis the wave functions of the above analysis. Several linear terms occur. Some from k dependent s.o. coupling which are negligible and some from k independent which dominate. This causes maxima to fall along one-one-one directions and are ellipsoids of revolution. Exactly how high and where these maxima are has not been observed.

In InSb, the s.o. splitting is in conflict with experiment. In Ge, s.o. splitting is almost that of the free atom. In InSb can guess:

$$\underbrace{\frac{29}{20}}_{\text{from Ge}} \left\{ \underbrace{.35 \times .28}_{In} + \underbrace{.65 \times .8}_{Sb} \right\} = .9 \text{ ev}$$

$\frac{29}{20}$ is ratio of experimental s.o. to that of free atom. Invariant to material.

Experimental Techniques: Reference: Lax, Rev. Mod. Phys.

We will take up:

(a) cyclotron resonance, microwave, infra-red
(b) galvanometric effect, elastoresistance effect vs T.
(c) ρ vs. T
(d) i.r. absorption, reflectivity, emission
(e) oscillatory magneto-absorption
(f) hot electron effects
(g) Tunneling effects
(h) high pressure effects, alloying
(i) e.s.r., Endorff technique

Lattice Vibrations:

(a) neutron diffraction
(b) optical absorption and emmission
(c) lattice vibration spectrum
(d) tunneling properties.

LECTURE XV   3-11-61

Cyclotron Resonance:

At this time, we will deal with quasi-classical approach. CR suggested by Schockley, first done by Dresselhaus, Kip and Kittel, and Lax and co-workers. See Lax in Rev. Mod. Phys. and article in Advances in SS Physics.

Assume that band edge is non-degenerate but not necessarily simple. The energy near the extremum is:

$$E_n(k) - E_n(k_0) = \frac{\hbar^2}{2m_1}(k_x - k_{x0})^2 + \frac{\hbar^2}{2m_2}(k_y - k_{y0})^2$$

$$+ \frac{\hbar^2}{2m_3}(k_z - k_{0z})^2$$

For simplicity, we write:

$$E = \frac{\hbar^2}{2m_1} k_1^2 + \dots$$

Applying a magnetic field:

$$\dot{v} = \frac{d}{dt}(\nabla_k E) = -\frac{1}{\hbar^2}(\nabla_k \nabla_k E)\left(\frac{e}{c} \nabla \times H\right)$$

Recall Ehrenreich has difficulty obtaining this.

$$\dot{v}_1 = \frac{1}{m_1}\left(-\frac{e}{c}\right)(v_2 H_3 - v_3 H_2), \text{ etc.}$$

Take for solution: $v_1, v_2, v_3 = v_{10}, v_{20}, v_{30}\, e^{i\omega t}$ and get a secular equation:

$$\begin{vmatrix} i\omega & \frac{eH_3}{m_1 c} & -\frac{eH_2}{m_1 c} \\ -\frac{eH_3}{m_2 c} & i\omega & \frac{eH_1}{m_2 c} \\ \frac{eH_2}{m_3 c} & -\frac{eH_1}{m_3 c} & i\omega \end{vmatrix} = 0$$

Result is: $\omega = 0$

$$\omega^2 = \frac{e^2H_1^2}{m_2m_3c^2} + \frac{e^2H_2^2}{m_3m_1c^2} + \frac{e^2H_3^2}{m_1m_2c^2}$$

The direction of the magnetic field is given by its direction cosines $\alpha_1, \alpha_2, \alpha_3 \to (H, xyz)$

Then: $\omega_1 = \frac{eH}{\sqrt{m_2m_3}\,c}$, etc.

$$\omega = \omega_1^2\alpha_1^2 + \omega_2^2\alpha_2^2 + \omega_3^2\alpha_3^2$$

Introduce the RF field:

$$\dot{v} = (\hbar^{-2}\nabla_k\nabla_k E)\left(-e\mathcal{E} - \frac{e}{c}v \times H\right) + \frac{v}{\tau}$$

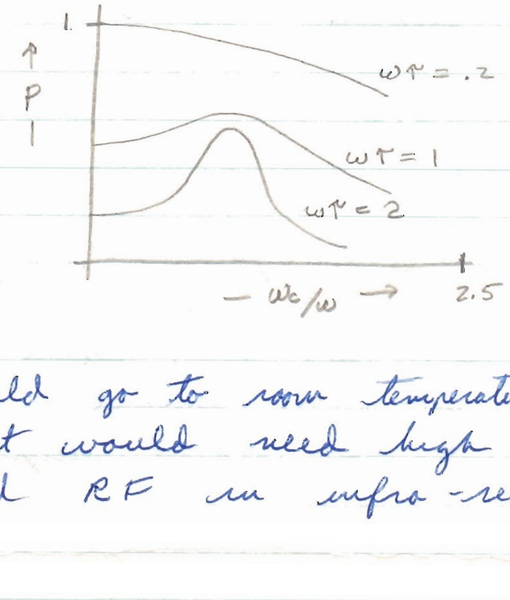
τ is a phenomenological scattering constant called relaxation time. Now:

$$J = nev = \sigma E$$

and the power absorbed is:

$$P = \mathrm{Re}\,(J\cdot E) = \mathrm{Re}\sum \sigma_{ij}E_iE_j$$

Power Absorbed vs. ω_c/ω



ω_c = cyclotron resonant frequency
ω = RF frequency

Note how resonance peaks depend on τ. $\omega\tau \geq 1$ for good peaks. τ is temperature dependent and to get good results must go to liquid He. Fields required are of a few thousand gauss, RF $\lambda = 1$ cm.

Could go to room temperature but would need high H and RF in infra-red.

At low temperatures, carriers must be excited by external means like optical transition caused by incident FR. Not many carriers needed to observe resonance.

By changing direction of field could obtain three effective masses. Must first determine of extrema direction in k space. Usually lies along symmetry axis or at $k = 0$. In Ge minima are along (111) and field applied in (100), will see equivalent components of minima and will get one peak. If H off a symmetry axis get more than one peak. In Si 111 direction gives one peak, so minima lies in 100 direction. See diagrams in DKK.

For information about holes in s.o. split valence band see Lax' review. Recall:

$$\begin{matrix} E_1(k) \\ E_2(k) \end{matrix} = A'' k^2 \mp \left\{ B'^2 k^4 + C'^2 \left(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_y^2 \right) \right\}$$

Recall from 295: $m_c^* = \frac{\hbar^2}{2\pi}\left(\frac{dA}{dE}\right)$

A = area in k space. Rewrite the energy:

$E = \alpha(\varphi)(k^2)$ in cylindrical coordinates with H in z direction. Assume $k_H = 0$

$$\frac{dA}{dE} = \oint \frac{k\,d\varphi}{\frac{dE}{dk}}$$

This treatment neglects the RF field.

For some materials hard to get $\omega\tau \gg 1$. Some experiments have been done in IR in pulsed magnetic fields. Find that carriers exist deep in band as well as at edge.

LECTURE XVI 3-14-61

Optical Properties of Solids:
Reference: Mott & Jones (semi-classical) p. 99

Introduce the vector potential:

$$\bar{A} = -\frac{c}{2i\omega}\bar{F}\left(e^{i\omega t} - e^{-i\omega t}\right)$$

$$\bar{F} = \frac{1}{c}\dot{A} = F\cos\omega t \quad , \quad \nabla\cdot A = 0$$

We assume that the system wave function is expressed in terms of Block functions:

$$\Psi(r,t) = \sum_n a_n(k,t)\, b_n(k,r) \qquad \{k \text{ is conserved}\}$$

Take $\frac{e}{m_0 c}\bar{A}\cdot\bar{p}$ as the perturbation in the Schroedinger equation:

$$-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = H\Psi = H_0\Psi + \frac{e}{m_0 c}\bar{A}\cdot\bar{p}\,\Psi$$

with: $H_0\, b_n(k,r) = \epsilon_n(k)\, b_n(k,r)$

Now:

$$-\frac{\hbar}{i}\dot{a}_n(k,t) = a_n(k,t)\,\epsilon_n(k) - \frac{e}{2i\omega m_0}e^{i\omega t}\sum_{n'}\langle n|F\cdot p|n'\rangle$$

$$\cdot\, a_{n'}(k,t) + \frac{e}{2i\omega m_0}e^{-i\omega t}\sum_{n'}\langle n|F\cdot p|n'\rangle\, a_{n'}(k,t)$$

Since: $a_n(k,t) = a_n^{(0)}(k,t) + a_n^{(1)}(k,t) + \dots$
we can use perturbation methods to order one, and write:

$$a_n^{(0)}(k,t) = \delta_{n0}\, e^{-\frac{i}{\hbar}\epsilon_0(k)t} \qquad (\text{Assume})$$

$$a_n^{(1)}(k,t) = C_n(k,t)\, e^{-\frac{i}{\hbar}\epsilon_n(k)t} \qquad (\text{Redefinition})$$

Thus: $-\frac{\hbar}{i}\dot{c}_n(k,t) = -\frac{e}{2i\omega m_0} e^{i(\omega_n+\omega)t}\langle n|F\cdot p|0\rangle$

$+\frac{e}{2i\omega m_0} e^{i(\omega_n-\omega)t}\langle n|F\cdot p|0\rangle$

defining $\omega_n(k) = \frac{\epsilon_n(k)-\epsilon_0(k)}{\hbar}$

We drop k as we take it to be conserved in the transition.

$$C_n(k,t) = \frac{e}{2m_0\hbar\omega}\left\{\frac{e^{i(\omega_n+\omega)t}-1}{i(\omega_n+\omega)} - \frac{e^{i(\omega_n-\omega)t}-1}{i(\omega_n-\omega)}\right\}\langle n|F\cdot p|0\rangle$$

At time 0, the a_n's are zero. We now write for the total wave function.

$$\Psi(r,t) = b_0(k,r)\,e^{-\frac{i}{\hbar}\epsilon_0(k)t} + \frac{e}{2m_0\hbar\omega}\,e^{-\frac{i}{\hbar}\epsilon_0(k,t)}$$

$$\cdot\left\{\sum_n \langle n|F\cdot p|0\rangle\, b_n(k,r)\cdot\left[\frac{e^{i\omega t}-e^{-i\omega_n t}}{i(\omega_n+\omega)} - \frac{e^{-i\omega t}-e^{i\omega_n t}}{i(\omega_n-\omega)}\right]\right\}$$

We will find that those terms that violate exclusion principle will drop out. The current is:

$$J = -\frac{e}{m_0}\langle p\rangle - \frac{e^2}{m_0 c}\langle A\rangle$$

When performing the averaging, we keep only terms to the first order. The result is:

$$J = -\frac{e^2\bar{F}}{2m_0^2\hbar\omega}\cdot\sum_n \langle 0|p|n\rangle\langle n|p|0\rangle\left\{\frac{e^{i\omega t}}{i(\omega_n+\omega)} + \frac{e^{i\omega t}}{i(\omega_n-\omega)}\right.$$

$$\left. - \frac{e^{-i\omega t}}{i(\omega_n+\omega)} - \frac{e^{-i\omega t}}{i(\omega_n-\omega)}\right\} + \frac{e^2}{m_0}\,\frac{\bar{F}}{2i\omega}\left(e^{i\omega t} - e^{-i\omega t}\right)$$

From $\bar{J} = \dot{\bar{P}}$, we can find the polarization:

$$\bar{P} = \frac{e^2 F}{m_0}\cdot\left\{ \sum_n{}' \frac{2}{m_0\hbar\omega_n}\langle 0|p|n\rangle\langle n|p|0\rangle \frac{1}{\omega_n^2-\omega^2} - \frac{1}{\omega^2}\left[1 - \sum_n{}' \frac{2}{m_0\hbar\omega_n}\langle 0|p|n\rangle\langle n|p|0\rangle\right]\right\}$$

Define: $\underset{\sim}{f}_{on}(k) = \frac{2}{m_0\hbar\omega_n}\langle 0|p|n\rangle\langle n|p|0\rangle$

Then:

$$P = \frac{e^2 F}{m_0}\cdot\left\{ \sum_n{}' \frac{\underset{\sim}{f}_{on}(k)}{\omega_n^2-\omega^2} - \frac{1}{\omega^2}\Big[\underbrace{\underset{\sim}{1} - \sum_n{}' \underset{\sim}{f}_{on}(k)}_{f_{oo}(k)}\Big]\right\}$$

From $\bar{D} = \bar{F} + 4\pi\bar{P}$, we can find the dielectric constant $\underset{\sim}{\epsilon}$:

$$\underset{\sim}{\epsilon} = \underset{\sim}{1} + \frac{4\pi e^2}{m_0}\left\{\quad\right\} = \underset{\sim}{1} + \frac{4\pi e^2}{m_0}\sum_n{}' \frac{\underset{\sim}{f}_{on}}{\omega_n^2-\omega^2} - \frac{4\pi e^2}{m_0\omega^2}\underset{\sim}{f}_{oo}$$

$$= \underset{\sim}{1} + \frac{4\pi e^2}{m_0}\sum_n \frac{\underset{\sim}{f}_{on}}{\omega_n^2-\omega^2}$$

All this is from a one-electron standpoint and does not include a Lorentz correction since this arises from the many body problem. See Pines in the Phys. Rev.

Recall the property of $\underset{\sim}{f}_{on}(k)$:

$$\sum_n \underset{\sim}{f}_{on}(k) = \underset{\sim}{1}$$

Then: $\sum_n{}' \underset{\sim}{f}_{on}(k) = \underset{\sim}{1} - f_{oo}(k) = \frac{m_0}{\hbar^2}\nabla_k\nabla_k E_0(k)$

so that effective mass can be related to optical properties of bands.

LECTURE XVII 3-16-61

Recall: $C_n(k,t) = a_n(k,t)\, e^{-\frac{i}{\hbar}E_n(k)t}$

$$|C_n(k,t)|^2 = \frac{e^2}{4m_0^2\hbar^2\omega^2}\,|\langle n|F\cdot p|0\rangle|^2 \left|\underbrace{\left\{\frac{e^{i(\omega_n+\omega)t}-1}{i(\omega_n+\omega)} - \frac{e^{-i(\omega_n-\omega)t}-1}{i(\omega_n-\omega)}\right\}}_{\text{rapidly oscillating.}}\right|^2$$

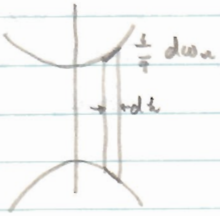
We integrate this transition probability over adjacent states:

$$\int \frac{\Omega}{8\pi^3}\, dk\, |C_n(k,t)|^2$$

We transform to an element in ω_n space via:

$$dk = \frac{dS_k\, d\omega_n}{|\nabla_k\omega_n(k)|}$$

where the surface is over constant frequencies rather than energies.



$$\int dk \to \rho(\omega_n)\int d\omega_n$$

The rapidly oscillating part squared is:

$$\left[\frac{\sin\frac{\omega_n-\omega}{2}t}{\frac{\omega_n-\omega}{2}t}\right]^2 t^2 \qquad x = \frac{\omega_n-\omega}{2}t\,;\quad d\omega_n = \frac{2\,dx}{t}$$

which gives $2t\underset{\uparrow}{\int_{-\infty}^{\infty}}\left[\frac{\sin x}{x}\right]^2 dx$ long time from start

$= 2\pi t$

Then:

$$2\cdot\int\frac{\Omega}{8\pi^3}\,dk\,|C_n(k,t)|^2 = \frac{2\pi e^2\rho(\omega)}{4m_0^2\hbar^2\omega^2}\,\frac{\Omega}{4\pi^3}\,|\langle n|F\cdot p|0\rangle|^2\, t \cdot \delta(E_n-E_0)$$

$$\int \frac{dS_k}{|\nabla_k \omega_n(k)|} \, |\langle n|F\cdot p|0\rangle|^2 = \langle |\langle n|F\cdot p|0\rangle|^2 \rangle_{av} \, \rho(\omega_n)$$

which is used to represent the average matrix element when it is k dependent.

Recall: $\underset{\sim}{f}_{0n}(k) = \frac{2}{m_0 \hbar \omega_n} \langle 0|p|n\rangle\langle n|p|0\rangle$

$$\frac{\pi e^2}{m_0^2 \hbar^2 \omega^2} |\langle n|F\cdot p|0\rangle|^2 \rho(\omega) = \frac{\pi e^2}{2 m_0 \hbar \omega} \left(F\cdot \underset{\sim}{f}_{0n} \cdot F\right) \rho(\omega_n)$$

which is proportional to the energy absorbed if the field F exists inside the material. The absorption coefficient is then:

$$\mu = \frac{4\pi^2 e^2}{m_0 c} \left(\hat{e}\cdot \underline{f_n} \cdot \hat{e}\right) \rho(\omega_n)$$

using that the power absorbed is $\sim \frac{c}{8\pi} F^2$.
$\underset{\sim}{e}$ is the direction of polarization.
Because of averaging of matrix element:

$$\underset{\sim}{f_n} = \langle f_{0n}(k) \rangle_{S_k}$$

In all above work, constants may not be correct. Final answer is: All of above concerns direct transitions of absorption.

Semi-classical: imagine oscillators in field with displacement y:

$$\ddot{y} + \gamma \dot{y} + \omega_0^2 y = \frac{-eF}{m_0} e^{i\omega t}$$

$$\therefore \quad P = \sum_{i=1}^{N} e y_i = \sum_{i=1}^{N} \frac{e^2 F}{m_0} e^{i\omega t} \frac{1}{(\omega_i^2 - \omega^2) + i\omega\gamma_i}$$

$$\bar{D} = \bar{F} + 4\pi \bar{P} \, ; \quad \underset{\sim}{\epsilon} = 1 + \sum_{i=1}^{N} \frac{4\pi e^2}{m_0} \frac{1}{(\omega_i^2 - \omega^2) + i\omega\gamma_i}$$

which is similar to QM result. The i's represent electrons.

The QM result is:

$$\epsilon = 1 + \frac{4\pi e^2}{m_0} \sum_{s,n} \sum{}' \left[\frac{f_{0n}}{\omega_{0n}^2 - \omega^2} - \frac{f_{00}}{\omega^2} \right]$$

where s corresponds to i. The SC result can be forced into states over n by splitting up the electrons into pieces which vibrate independently because $\sum_n f_{0n} = 1$. The sum over n is over the states over one electron. We can then include this in SC result by appending the subscript n to i:

$$\epsilon = 1 + \sum_{\substack{i=1 \\ n}}^{N} \frac{4\pi e^2}{m_0} \frac{f_{i,n}}{(\omega_{i,n}^2 - \omega^2) + i\omega\gamma_{i,n}}$$

which is now identical to QM result except for damping γ which is due to lattice vibrations. Writing:

$$\epsilon = \epsilon' + i\epsilon''$$

where: $$\epsilon' = 1 - \frac{4\pi e^2}{m_0} N_{eff} \frac{\tau^2}{1+\omega^2\tau^2} + \frac{4\pi e^2}{m_0} \sum_{m,n} \int \frac{f_{mn}(\omega_{m,n})\rho_{mn}(\omega_{mn})\, d\omega_{mn}}{\omega_{mn}^2 - \omega^2}$$

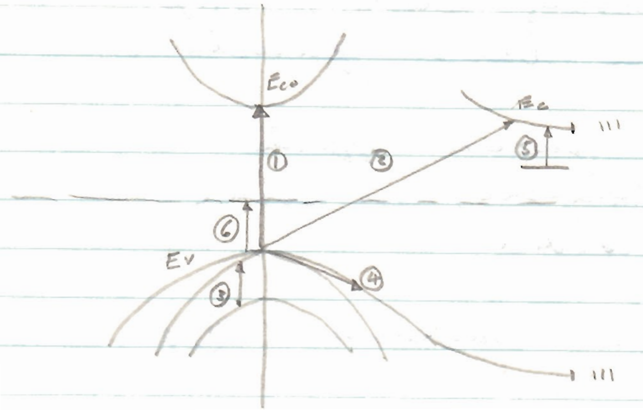
and:

$$\epsilon'' = \frac{4\pi e^2}{m_0 \omega^2} N_{eff} \frac{\tau}{1+\omega^2\tau^2} + \frac{4\pi e^2}{m_0} \sum_{m,n} \int \frac{f_{mn}(\omega_{mn})\rho_{mn}(\omega_{mn})\,\omega\,\gamma_{mn}\, d\omega_{mn}}{(\omega_{mn}^2 - \omega^2)^2 + \omega^2\gamma_{mn}^2}$$

where $$\rho_{mn}(\omega_{mn}) = \frac{1}{4\pi^3} \int f(E_n(k))\left[1 - f(E_n(k))\right] \frac{dS_k}{|\nabla_k \omega_{mn}(k)|}$$

LECTURE XVIII 3-18-61

Absorption Mechanisms Involving transitions:
Consider the band structure of Ge:



① direct transition
- a) allowed
- a') allowed, phonon cooperation, where photon has energy smaller than gap, rest provided by phonon.
- b) disallowed
- b') disallowed, phonon cooperation

①' Direct transition: exciton formation: hole-electron pair creation where hole and electron does not separate completely and we have hydrogenic levels.

② Indirect Transition: strictly disallowed, but occurs thru mechanism of intermediate state (usually phonon), that is, m.e. would be of form: $\langle i | A\cdot p | I \rangle \langle I | \text{phonon} | f \rangle$.

a) Intermediate state allowed, phonon absorption
b) " " " , " emmission
c) " " " , impurity interaction
d) " " forbidden, phonon absorption
e) " " " , " emission
f " " " , impurity interaction

②' Indirect transition: exciton formation: phonon emission and absorption.

③ Direct transition, parity disallowed at $k=0$, no phonons usually.

④ Free carrier absorption: analogous to ② in that it requires allowed intermediate states with phonon or impurities. Transition for one k state to another.

⑤ Impurity excitation, ionization, H energy levels.

⑥ Same as ⑤ except deep-lying impurity. Short line in ⑤ means small amount of band function needed for impurity state. Deep lying has many valence band functions.

Application of magnetic field causes effects in each of the transitions. However, in some cases it has not been absorbed.

Absorption Coefficient for Direct Transitions: ①a

$$\mu_{nn'}(\omega) = \frac{\alpha \hbar^2 |M_{nn'}|^2 N_{nn'}}{\eta m^2 \hbar\omega}$$

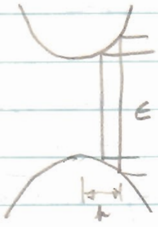
$$N_{nn'} = 4\pi \left(\frac{2\bar{m}^*}{\hbar^2}\right)^{3/2} (\hbar\omega - E_{nn'})^{1/2}$$

$$\bar{m}^* = \frac{m_c^* m_v^*}{m_c^* + m_v^*}$$

α = fine structure constant

η = refractive index

$M_{nn'}$ is m.e. derived by Brooks:



Recall the derivation of:

$$\int \frac{dS_k \, d\omega}{|\nabla_k \omega|} = \text{number of transitions}$$

Take $\hbar\omega = E_c(k) - E_v(k) = \frac{\hbar^2}{2}\left(\frac{1}{m_c^*} + \frac{1}{m_v^*}\right)k^2 + E_{nn'}(0)$

$$\nabla_k \omega = \frac{\hbar}{2}\left(\frac{1}{m_c^*} + \frac{1}{m_v^*}\right) 2k = \left(\frac{1}{m_c^*} + \frac{1}{m_v^*}\right)\hbar k$$

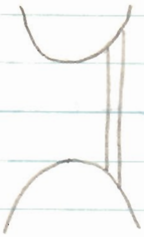
Thus:

$$\int \frac{d\omega \; 4\pi \left(\omega - \frac{E_{nn'}}{\hbar}\right)^{1/2}}{\hbar\left(\frac{1}{m_c^*} + \frac{1}{m_v^*}\right)\left\{\frac{\hbar}{2}\left(\frac{1}{m_c^*} + \frac{1}{m_v^*}\right)\right\}^{1/2}}$$

Although what we have done here aids in band edge broadening, but there are many other factors which contribute to this effect.

LECTURE XVIX   3-21-61

Reference: Direct Transitions: Burstein et al, PR113 (1959)



Assume transition allowed, therefore independent of k-vector. Transition probability is:

$$P = \frac{2\pi}{\hbar} |\langle 0|H'|n\rangle|^2 \rho(\omega_n)$$

$$= \frac{2\pi}{\hbar} \frac{e^2 E_0^2}{m^2} \frac{1}{4\omega^2} |\langle 0|\hat{e}\cdot p|n\rangle|^2 \rho(\omega_n)$$

where the density of state of the transition (vertical) is:

$$\rho(\omega) = \frac{1}{2\pi^2} \frac{(2m_v)^{3/2}}{\hbar^3} (h\nu - E_g)^{1/2}, \quad \frac{1}{m_r} = \frac{1}{m_c} + \frac{1}{m_v}$$

Energy Density $= \frac{K_0 E_0^2}{8\pi}$

Definition: absorption coefficient:

$$dI = -I\mu\, dx, \quad \mu = -\frac{dI}{I}$$

where: $dI = P(\hbar\omega)$; $I = \frac{K_0 E_0^2}{8\pi} \frac{c}{n}$

$$\therefore \mu = \frac{\hbar\omega\, 8\pi n}{K_0 E_0^2 c} \frac{2\pi}{\hbar} \frac{e^2 E_0^2}{m^2} \frac{1}{4\omega^2} |\langle\ |\ \rangle|^2 \frac{1}{2\pi^2} \frac{(2m_r)^{3/2}}{\hbar^3} \cdot (h\nu - E_g)^{1/2}$$

$$= \frac{8\pi^2 e^2 (2m_r)^{3/2} |\langle 0|\hat{e}\cdot p|n\rangle|^2 (h\nu - E_G)^{1/2}}{n c m^2 h^2 (\hbar\omega)}$$

Dependence of μ mainly on density of states term $(h\nu - E_G)^{1/2}$. Reference: Bardeen, Blatt, Hall
Dexter
Fan, Shepherd, Spitzer
Fan, Repts. on Prog. in Phys, vol 19

A more general way of writing the vertical transition matrix element is:

$$\langle u_0 + \sum_n{}' \alpha_n k\, u_n \,|\, \hat{e}\cdot p \,|\, u_1 + \sum_n{}' \beta_n k\, u_n \rangle$$

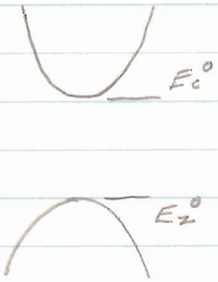
which gives term in k^2. Thus, we have:

$$\mu_{nn'}(\omega) \propto \frac{(h\nu - E_g)^{3/2}}{h\nu}$$

so that μ has 3/2 dependence on $h\nu - E_g$ rather than 1/2, if transition not allowed at $k=0$. However, dependence hard to see experimentally because of exciton smearing.

Quantum Theory of Cyclotron Resonance

Review of AP 295 results for solid in magnetic field: We use Burstein's notation.



For $H = 0$:

$$E_c(k) = E_c^0 + \frac{\hbar^2}{2m_c^*} k^2$$

$$E_v(k) = E_v^0 - \frac{\hbar^2}{2m_v^*} k^2$$

$$E_G^0 = E_c^0 - E_v^0$$

with $N_c(E) = \dfrac{\Omega}{4\pi^3} \displaystyle\int \dfrac{dS}{|\nabla_k E|} = \dfrac{\Omega}{\pi^2} \dfrac{(2m_c^*)^{3/2}}{\hbar^3} \left(E_c(k) - E^0 \right)^{1/2}$

and a similar expression for valence bands.

When H is applied, we can use m^* approximation (Luttinger & Kohn). We take H in z direction and gauge such that: $A_x = A_z = 0$; $A_y = -HX$. Then:

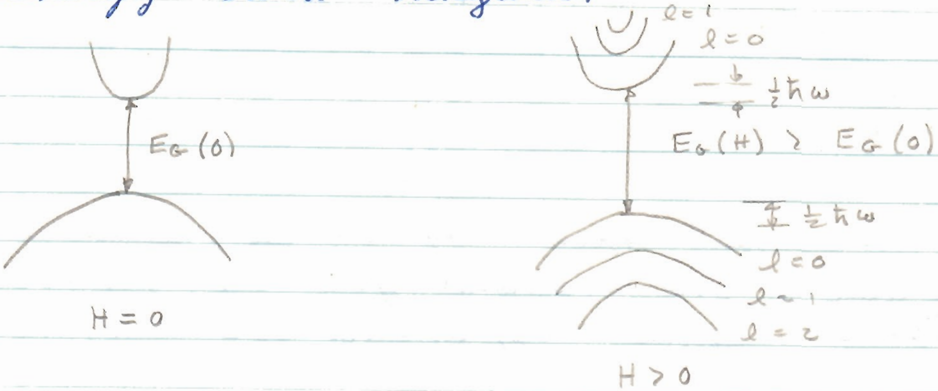
$$E_c(k_z, l_c) = E_c^0 + \hbar\omega_c\left(l_c + \tfrac{1}{2}\right) + \frac{\hbar^2}{2m_c^*} k_z^2$$

$$\omega_c = \frac{eH}{m_c^* c} \;; \qquad l > 0.$$

For valence band:

$$E_v(k_z, l_v) = E_v^0 - \hbar\omega_v \left(l_v + \tfrac{1}{2}\right) - \frac{\hbar^2}{2m_v^*} k_z^2$$

Energy Band Diagram:



The appropriate wave functions are:

$$\psi_c(r) = F_c(r)\, b_c(0, r)$$

$b_c(0, r)$ = KL functions

$$F_c(r) = (L_y L_z)^{-1/2} \exp\{i k_y y + i k_z z\}\, \varphi_l\left(x - \frac{\hbar c k_y}{eH}\right)$$

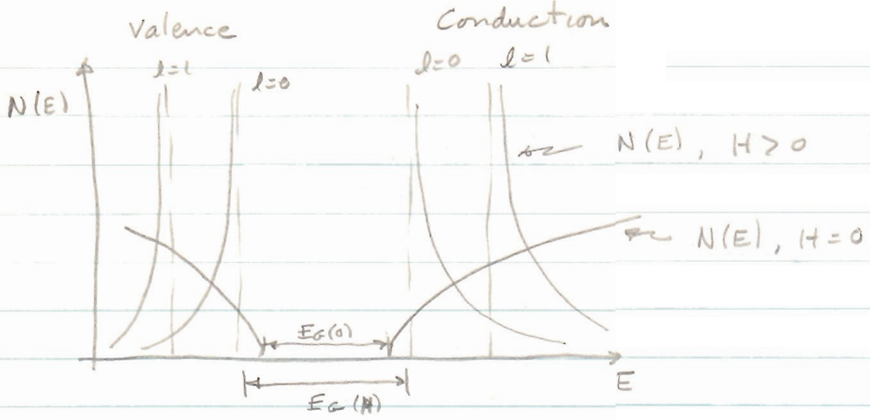
and similar for valence band. The density of states is:

$$\underset{\text{(no spin)}}{N_{cl}(E)\, dE} = \frac{L_y L_z}{4\pi^2} \frac{dk_z}{dE}\, dE \int_0^{\frac{eH}{\hbar c} L_x} dk_y$$

$$= \frac{\Omega}{4\pi^2} \left(\frac{eH}{\hbar c}\right) \underbrace{\frac{\sqrt{2m_c^*}}{\hbar} \frac{1}{\left[E_c - E_c^0 - (l_c + \frac{1}{2})\hbar\omega_c\right]^{1/2}}}_{\frac{dk_z}{dE}}$$

$$= \frac{\Omega}{4\pi^2} \left(\frac{eH}{\hbar c}\right) \frac{\sqrt{2m_c^*}}{\hbar} \frac{1}{\left[E_c - E_{cl}\right]^{1/2}}$$

$$E_{cl} = E_c^0 + \left(l_c + \tfrac{1}{2}\right)\hbar\omega_c$$



We have not included spin. If we do, assume subband divides, one subband for up, other for down. Thus same expression for N(E) holds.

Absorption:

Perturbing term in Hamiltonian is:

$$H' = \frac{eE_0}{m}\left(p + \frac{e}{c}A\right)\frac{1}{2i\omega}\cdot\hat{e}\left(e^{i\omega t} - e^{-i\omega t}\right)$$

and the matrix element becomes:

$$M \propto \langle n|\left(p + \frac{e}{c}A\right)\cdot\hat{e}\,|n'\rangle$$

where n, n' label two subbands in valence or conduction bands. M describes magneto-absorption transitions between valence subband and conduction band, and Cyclotron resonance transition between sub-band levels.

Selection Rules: $\Delta M = -1, 0, +1$ and $\Delta l = 0$.

LECTURE XX 3-23-61

Recall: $M = \langle n | (p + \frac{e}{c}A) \cdot \hat{e} | n' \rangle$

$$= \int F_n^*(r)\, b_n^*(0,r)\, (p + \frac{e}{c}A) \cdot \epsilon\, F_{n'}(r)\, b_{n'}(0,r)\, d^3r$$

$$= \int F_n^*\, b_n^*\, F_{n'} \left[(p + \frac{e}{c}A) \cdot \epsilon \right] b_{n'}\, d^3r + \int F_n^*\, b_n^*\, b_{n'}\, (p + \frac{e}{c}A) \cdot \epsilon$$

$$F_{n'}\, d^3r$$

Now F_n are slowly varying envelope functions and the b_n are cell-periodic functions, thus we can split up the M into integrals over crystal and cell.

$$M = \underbrace{\int_{xtal} F_n^* F_{n'}\, d^3r \int_{cell} b_n^* \left[(p + \frac{e}{c}\underset{\text{should not be here}}{\underbrace{A}}) \cdot \epsilon \right] b_{n'}\, d^3r}_{①} + \underbrace{\int_{xtal} F_n^* \left[(p + \frac{e}{c}A) \cdot \epsilon \right] F_{n'}\, d^3r}_{②}$$

$$\underbrace{\cdot \int_{cell} b_n^*\, b_{n'}\, d^3r}_{②}$$

$\xrightarrow{\quad}$ interband, given selection rules $\Delta l = 0$, $\Delta k = 0$ (vertical)

$$① \quad \underbrace{\int_{xtal} F_n^* F_{n'}\, d^3r}_{②} \int_{cell} \underbrace{b_n^*\, p\, b_{n'}\, d^3r}_{} \longrightarrow$$

$$+ \int_{xtal} F_n^* F_{n'}\, d^3r \int_{cell} b_n^* \left(\frac{e}{c} A \cdot \epsilon\right) b_{n'}\, d^3r$$

must be finite from symmetry, could be 0 if b_n ~ s function. Best method to test allowability is to use group theory.

② Cyclotron Resonance Terms: No interband transitions:

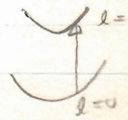
$$\int F_n^* (p + \frac{e}{c}A) \cdot \epsilon\, F_{n'}\, d^3r$$

where $F_n(r) = (L_y L_z)^{-1/2}\, e^{i(k_y y + k_z z)}\, \varphi_l \left(x - \frac{\hbar c k_y}{eH} \right)$

If $A \cdot \epsilon = 0$ Then m.e. finite if $\int F_n^*\, p\, F_{n'}\, d^3r \neq 0$

$H \perp E$

if $\int \varphi_l\, p\, \varphi_{l'} \neq 0$, $\Delta l = \pm 1$



If $n = n'$, $l = l'$, no energy absorbed.

We will consider that M is finite:
Consequences: (1) Energy gap widens
(2) Get intra-band transition between split band levels

$$E_G = E_c - E_v = E_c^0 - E_v^0 + \frac{1}{2}(\hbar\omega_c + \hbar\omega_v)$$

$$- \frac{1}{2}(|g_v| + |g_c|)\beta H$$

Assume $\Delta l = 0$
Recall:

$$\mu_l^{cv}(\omega) = \frac{2\alpha h^2}{\eta m^2}\left(\frac{eH}{\hbar c}\right)\left(\frac{2m}{h^2}\right)^{1/2} M^2 \frac{(\hbar\omega - E_l^{cv})^{-1/2}}{\hbar\omega}$$

$$E_l^{cv} = E_c^0 - E_v^0 + (l+\tfrac{1}{2})(\hbar\omega_c + \hbar\omega_v) + g_c\beta H m$$

$$- g_v\beta H m$$, m = magneto quantum number

This is absorbtion coefficient between sublevels in different bands. To get total μ must sum on l.

Can see condition for observation of cyclotron resonance is $\Delta E < \hbar\omega \approx$ separation
line broadening due to thermal action
between split levels

$\frac{\hbar}{\tau} < \hbar\omega$, $\omega\tau > 1$ as before.

Plot ω, fixed peak, versus H and the slope will be:

$$(l+\tfrac{1}{2})\hbar\frac{e}{c}\left(\frac{1}{m_c^*} + \frac{1}{m_v^*}\right) + (g_c - g_v)\beta m$$

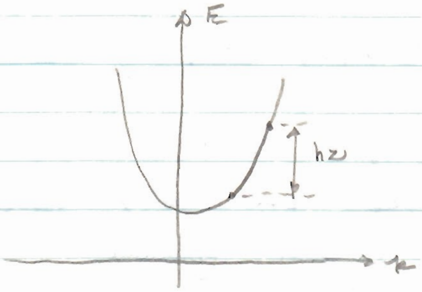
with intercept $E_c^0 - E_v^0$

This gives very accurate determination of energy gap, but not too good for masses although if last term small some determination can be made.

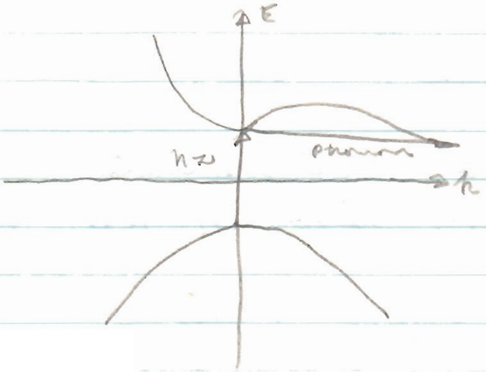
Indirect Transitions:

Selection rule $\Delta k = 0$ assumes λ of radiation is much greater than λ of electron.

How does one get damping in QM? Must introduce indirect transitions. Consider absorption in Ge and Si: must be two-step process. If electron in conduction band absorbs photon, energy is increased, but so is k-vector, thus violating $\Delta k = 0$. Get around this by making two step process which includes the action of a phonon.



Rise in E caused by $h\nu$, change in k or momentum is supplied by phonon

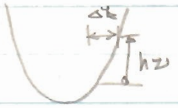


Another process is transition when $h\nu <$ band gap but can be assisted by phonon as shown.

References: H. J. G. Meyer: JCPS 8, 264 (1959)
PR 112, 298
Rosenberg & Lax: RR 112, 843 (1958)

LECTURE XXI 3-25-61

Indirect Transition: Free Carrier Absorption



$\Delta k = \sigma$ where σ is the wave number of the phonon involved in the process.

Phonon selection Rule: $(k' - k) = \sigma + (K)$
However, here K not needed because Δk will be small during this discussion.

Recall for direct transition:

$$\text{Probability} \propto \frac{2\pi}{\hbar} |\langle f | H | i \rangle|^2 \, \delta(E_f - E_i)$$

where $E_i = E_0(k) + h\nu$; $E_f = E_n(k)$

Only part of H that is used in $A \cdot p$ part. Now, when $h\nu$ is too small, we have for indirect transitions probabilities:

$$W_{(f|i)} = \frac{2\pi}{\hbar} \left| \sum_{\mu} \frac{\langle f | H | \mu \rangle \langle \mu | H | i \rangle}{E_i - E_\mu} \right|^2 \delta(E_f - E_i)$$

where μ is the so-called intermediate state. In our case here we take H as:

$$H = \underbrace{H_{xtal} + H_{EM\ field} + H_{phonon}}_{\text{usual part of } H} + \underbrace{H_{el}}_{\text{electron-}\cancel{\text{lattice}}\ \text{light}} + \underbrace{H_{ep}}_{\text{electron phonon}}$$

These taken as perturbation

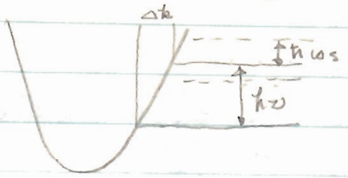
We are interested in cases where H_{el} and H_{ep} appear together in $W_{(f|i)}$: $\langle | H_{el} | \rangle \langle | H_{ep} | \rangle$ and $\langle | H_{ep} | \rangle \langle | H_{el} | \rangle$. $H_{el} \rightarrow \nu$; $H_{ep} \rightarrow \underset{\text{from selection rules}}{\sigma}$

Now: $E_i = E_0(k) + h\nu = E_f = E_0(k') \pm \underbrace{\hbar\omega_s}_{\text{in phonon}}$

Then: $E_f - E_i = 0 = E_0(k') - E_0(k) - h\nu \pm \hbar\omega_s$

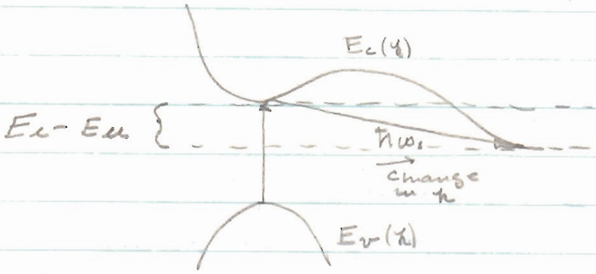
or: $\Delta E = h\nu \mp \hbar\omega_s$

Previous diagram not correct.



Also, polarization of phonons cause several more kinds of transitions for same $h\nu$. However, this is not to say these are intermediate states.

Intermediate state: $E_u = E_0(k)$ (energy need not be conserved in this state); then $E_i - E_u = h\nu$.



For this case of interband direct and intra-band absorption:

$E_i = E_v(k) + h\nu$
$E_f = E_c(k') \pm \hbar\omega_s$
$E_c(k') - E_v(k) = h\nu \mp \hbar\omega_s$
$E_u = E_c(k)$

Then: $E_i - E_u = E_v(k) - E_c(k) + h\nu$

NB: electron cannot change E because of selection rules on k, thus why $E_i = E_f$ and first matrix element is diagonal in p.

$E_i - E_u = h\nu$ is always true when we have photon and phonon transition keep E_u in the same band.

Now look at process for which $\langle | H_{ep} | \rangle \langle | H_{er} | \rangle$ or the phonon process occurs first.

$E_i = E_0(k) + h\nu$
$E_F = E_0(k') \pm \hbar\omega_s$
$E_u = E_0(k') + h\nu \pm \hbar\omega_s$
and $E_i - E_u = E_f - E_u = h\nu$, the same as before.

We are not interested in simultaneous occurrence of direct and indirect transitions, since it is forbidence of direct transition that lead to indirect transitions.

the total absorption will be equal to:

$$(n_i - n_f) \cdot W_{<f|i>}$$

where n_i is number of electrons in initial state, n_f in final state. Now: $\frac{n_f}{n_i} = e^{-\frac{h\nu \pm \hbar\omega_s}{kT}}$

Then total absorption $= W_{<f|i>} n_i (1 - e^{-z_\pm})$, $z_\pm = e^{\frac{-h\nu \mp \hbar\omega_s}{kT}}$
The emission here is stimulated by the actual absorption process.

Now, there is only one E_u that satisfies the selection rules, thus:

$$\frac{|\langle f| H_{er} |u\rangle|^2 \, |\langle u| H_{ep} |i\rangle|^2}{(h\nu)^2}$$

Properties of M. E: $\langle | H_{er} | \rangle \sim \frac{1}{\nu^2}$ since this is of the form

or more completely: $|\langle | H_{el} | \rangle|^2 \sim \frac{1}{\nu^2}\left[\hat{e} \cdot \underset{\sim}{\alpha} \cdot (k - k_0)\right]^2 \Big\{ A \cdot p$

The complete expression is:

$$\frac{|\langle H_{er}\rangle|^2 \, |\langle H_{ep}\rangle|^2}{(h\nu)^2} \sim \frac{\frac{1}{\nu^2}\left[\hat{e} \cdot \underset{\sim}{\alpha} \cdot (k - k_0)\right]^2}{\nu^2} \frac{Q_s^2}{\omega_s} \{ n_s, n_s + 1 \}$$

LECTURE XXII 3-27-61

Recall: $$W_{<f|i>} = \frac{2\pi}{\hbar} \left| \sum_u \frac{\langle f| H_{ep} |u\rangle \langle u| H_{ei} |i\rangle}{E_i - E_u} \right|^2 \delta(E_f - E_i)$$

which we found could be written:

$$W_{<f|i>} = \frac{2\pi}{\hbar} \left| \frac{\langle f| H_{ep} |u\rangle \langle u| H_{ei} |i\rangle}{h\nu} \right|^2 \delta(E_f - E_i)$$

with:

$$E_0(k') - E_0(k) = h\nu \pm \hbar\omega_s(\sigma)$$
$$k' - k = \sigma$$

and $$W_{<f|i>} = \frac{2\pi}{\hbar} \left(\frac{1}{h\nu}\right)^2 |\langle u| H_{er} |i\rangle|^2 \, |\langle f| H_{ep} |u\rangle|^2 \, \delta(E_f - E_i)$$

We now calculate the absorption.

$$\sum_{k} h\nu \, W_{\langle f|u\rangle} (k \to k') \, f_0(k) \left[1 - f_0(k')\right]$$

$$+ \sum_{k'} h\nu \, W_{\langle f|u\rangle} (k' \to k) \, f_0(k') \left[1 - f_0(k)\right]$$

which goes to:

$$\sum_{k} h\nu \, W_{\langle f|u\rangle} \, f_0(E) \left[1 - f_0(E_0 + h\nu)\right] + \sum_{k'} h\nu \, W_{\langle f|u\rangle} \, f_0(E_0 + h\nu) \left[1 - f_0(E)\right]$$

which must be multiplied by the state density. In Fermi statistics, we have the identity:

$$\frac{f_0(E_0)}{1 - f_0(E_0)} \Big/ \frac{f_0(E_0 + h\nu)}{1 - f_0(E_0 + h\nu)} = e^{h\nu/kT}$$

which allows the expression to be written:

$$\sum_{k} h\nu \, W_{\langle f|u\rangle} \, f_0(E_0) \left[1 - f_0(E_0 + h\nu)\right] \left[1 - e^{-\frac{h\nu}{kT}}\right]$$

From last lecture:

$$|\langle u|H_{eL}|u\rangle|^2 = \left[\hat{e} \cdot \underset{\sim}{\alpha} \cdot \underline{k} - \underline{k_0}\right]^2 \frac{e^2}{m^2} \frac{1}{4\pi^2 \nu^2}$$

$\underset{\sim}{\alpha}$ comes from energy being written as:
$E_0(k) - E_0(0) = \frac{\hbar^2}{2m} (k - k_0) \cdot \underset{\sim}{\alpha} \cdot (k - k_0)$
which is tensor equation of ellipsoid in k space. $\hat{e}$ is the polarization vector of the EM field. A similar expression arises for the phonon ME:

$|\langle f|H_{ep}|u\rangle|^2 \sim \frac{Q_s^2}{\omega_s} \, n_s, n_{s+1}$, Q_s is the strength of the phonon reaction. n_s, n_{s+1} are phonon quantum numbers in ladder stepping scheme.
We get for absorption:

$$\mu(\nu) = \frac{n}{192\pi^4} \det \alpha \, \frac{e^2 \hbar \Omega}{m^2 M_C \epsilon^{1/2}} \left(\frac{\hbar^2}{2\pi m k T}\right)^{3/2} \frac{1}{\nu^3} \int dk' \int dk$$

$$\cdot \, e^{-\frac{E_0(k)}{kT}} \left\{ \sum_{s=1}^{4} \frac{Q_s^2}{\omega_s} \left[n_s \, \delta\left\{E_0(k') - (E_0(k) + h\nu + \hbar\omega_s)\right\} \right.\right.$$

$$\left.\left. + (n_s + 1) \, \delta\left\{E_0(k') - (E_0(k) + h\nu - \hbar\omega_s)\right\} \right] \right.$$

Sum on s is over two polarizations of two acoustic and optical branch phonons. M is mass of atoms, m of electrons, ϵ is dielectric constant, c is the velocity of light, Ω is the cell volume. Q_s can be measured by DC resistance.

Consider case of acoustical phonons and $h\nu \ll kT$ or the long wavelength case. At $T = 300^\circ$, $kT = \frac{1}{40}$ ev and $\lambda(\mu) = \frac{1.24}{h\nu(\text{ev})} \sim 50\mu$. Then in this case:

$$\mu(\nu) \sim \nu^{-2}\, T^{3/2}$$

Case of $h\nu > 3kT$ (Fan) : $\mu(\nu) \sim -\nu^{-3/2}\, T$

$$\text{Get}\quad \underset{\substack{\uparrow\\ \text{light}\\ \text{m.e.}}}{\frac{1}{\nu}}\quad \nu\ \underset{\substack{\uparrow\\ \text{phonons}}}{T}\quad \underset{\substack{\uparrow\\ \text{density}\\ \text{of states}}}{\nu^{1/2}}\quad \underset{\substack{\uparrow\\ \text{energy}\\ \text{denominator}}}{\frac{1}{\nu^{2}}}\quad — \quad \nu^{-3/2}\, T$$

In these two extremes:

$$\mu^{\sigma}_{net} = n\, 4.35 \cdot 10^{-23}\, \lambda^{*2}\, T^{3/2} \quad \text{cm}^{-1}$$

$$\mu^{\sigma}_{net} = n\, 1.16 \cdot 10^{-21}\, \lambda^{+3/2}\, T$$

where λ^* is the vacuum wavelength.

For the optical modes, $\hbar\omega_s \sim kT$. Treatment of this situation is still incomplete. Acoustical modes contribute only 1/3 to 1/5 of the absorption. Trouble may be in the deformation potential constants Q_s. See Rosenberg and Lax in PR. Find λ^{*2} variation holds even less than 50μ. This is present state of free carrier absorption.

LECTURE XXIII 3-30-61

Paul :- Optical Properties:
Degenerate Band Structure.

In most semiconductors, most valence bands cause difficulty. Including S.O. have 4 fold at $k=0$ and lower band 2 fold degenerate.

References: Luttinger & Kohn, PR97, 869 (1955)
Luttinger, PR102, 1030 (1956)
Burstein, PR113, 15
Lax, et al, PR114, 90

In Luttinger's article, it is shown that levels split into 4 sub-bands. In Burstein's notation:

$$\epsilon_1^+(n), \quad \epsilon_1^-(n), \quad \epsilon_2^+(n), \quad \epsilon_2^-(n)$$

and the wave functions are products of Bloch functions and modulating functions:

$$\psi_1^+ = a_1 G_{l-2}\varphi_{3/2}^{3/2} + a_2 G_l \varphi_{-1/2}^{3/2} \qquad l \geq 0$$

If we drop assumption of $k_H = 0$, no band warping, wave functions become linear combination of 4 Bloch functions.

Transitions: from v_1, v_2, v_3 to Γ_2' are allowed if no field, transitions vertical, $\Delta l = 0$. In field, $\epsilon_3^+, \epsilon_3^-$ to Γ_2' are same as simple case. More complicated for v_1, v_2. All this is reviewed in Lax, et al. and Burstein.
Now consider inter valence band transitions.
Cyclotron Resonance: B function of initial and final state same.
I.M.O.: B function different.

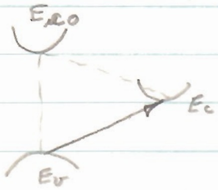
Can have cyclotron resonance between two valence levels.

Cyclotron resonance
between valence bands. Spread in
frequency for transitions between
sub-bands of low values of m^*.

Could also get information from IMO transitions. Allowable in second order, as one moves away from $k=0$. Above remarks apply to Germanium. For Silicon, absorption background blots out direct transition lines.

Magnetic Field Effect on Indirect Transitions:

no field:
$$W_{\langle i|f\rangle} = \frac{2\pi}{\hbar}\left|\sum_{n'}\frac{\overset{\text{phonon}}{(n'k|M_1|nk)}\overset{A\cdot p}{\langle n''k'|M_2|n'k\rangle}}{E_0 - E_I}\right|^2$$
$$\cdot\,\rho_f(E)$$



$$E_0 = E_v \pm \hbar\omega + h\nu$$
$$E_F = E_c$$
$$E_I = E_{c0} \pm \hbar\omega$$

Then: $E_0 - E_I = E_F - E_I = E_c - E_{c0} \mp \hbar\omega$

Here we have taken phonon transition before photon transition as opposite to Brooks, but makes no difference in answer.

$$E_0 = E_v + h\nu$$
$$E_F = E_c \pm \hbar\omega$$

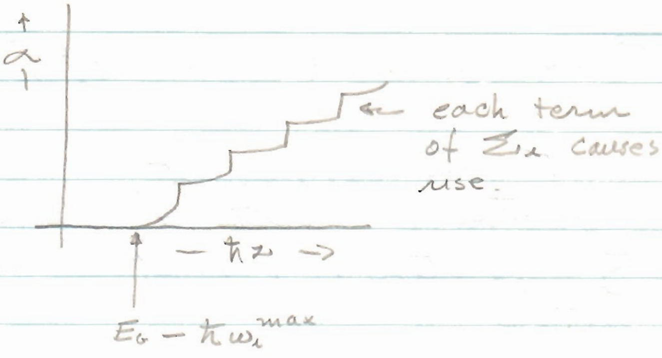
Result:

$$\alpha_{\langle n''k'|nk\rangle} = \sum_{n'}\sum_{i}\left\{\frac{A_{n'i}\left(\hbar\nu - E_G + \hbar\omega_i\right)^2}{\left(e^{\hbar\omega_i/kT}-1\right)\left(E_{n'} - E_c - \hbar\omega_i\right)^2}\right.$$

$$\left. + \frac{A_{n'i}\left(\hbar\nu - E_G - \hbar\omega_i\right)^2}{\left(1-e^{-\hbar\omega_i/kT}\right)\left(E_{n'} - E_c + \hbar\omega_i\right)^2}\right\}$$ for allowed transitions into n' only.

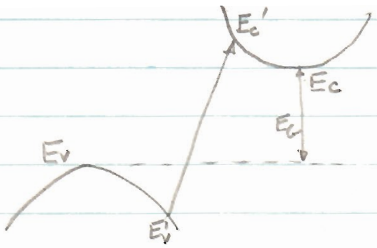
n' in intermediate state.

For direct transition, we had 1/2 and 3/2 dependence. Here we have squared dependence.



If we could locate each of the rise one could determine each of the ω_i.

LECTURE XXIV 4-1-61



Conservation law:

$$h\nu = E_c' - E_c + E_G + E_v - E_v' \pm \hbar\omega$$

$$E_c' - E_c = \hbar\nu - E_G - E_v + E_v' \pm \hbar\omega$$

$$\text{No. of transitions} = a\,(E_c' - E_c)^{1/2}\,dE$$

$$N_c(E) = a\,(h\nu - E_G - E_v + E_v' \pm \hbar\omega)^{1/2}\,dE$$

$$N(\nu)\,d\nu = a a'\,d\nu \int_0^{h\nu - E_G \mp \hbar\omega} (h\nu - E_G - E_v + E_v' \mp \hbar\omega)^{1/2} \cdot (E_v - E_v')^{1/2}\, d(E_v - E_v')$$

$$\propto (h\nu - E_G \pm \hbar\omega)^2$$

phonons vary slowly under the integral. Also assume that intermediate states are allowed. If not $(\ )^2 \rightarrow (\ )^3$. Interaction of phonons with impurities is not well understood.

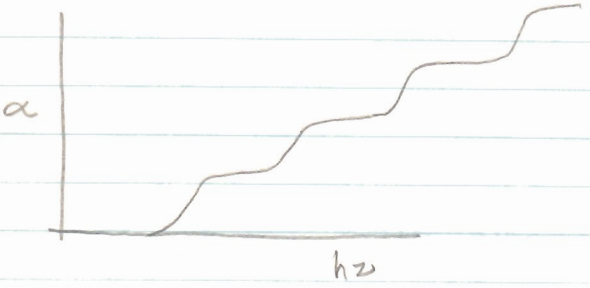
What about magnetic Field on Indirect Transitions?

Recall for absorption Coefficient:

Direct without H: $(h\nu - E_G)^{1/2}$ → Indirect $(h\nu - E_G)^2$

Direct with H: $(h\nu - E_\ell^{cv})^{-1/2}$ → Indirect $(h\nu - E_\ell^{cv})^0$

When one goes from Direct to indirect, multiply by density factor. With H, have one-dimensional density factor. Result is that you get finite steps:
Reference: Lax, et al, Roch. Conf., Paper L2



Only been observed in Ge.

Other Optical Properties:
Impurity absorption: H_2-like

$$E = E_H \frac{m^*}{m n^2 K^2}$$

For .01 ev, 120 microns
.05 ev, 24 microns

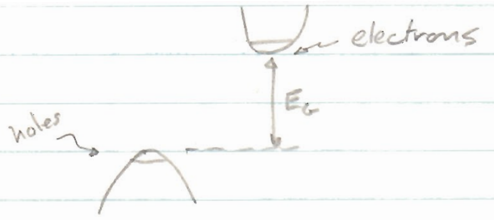
Observations must be made at He Temp. to keep impurities unionized. For deep lying impurities, have experimental difficulties. See Kohn, SSP.

Photoconduction:
Concerned with carrier lifetime so as to calculate contribution of generated electrons. If number of excitations is low, current ∝ number of excitations. Provides means to check absorption coefficients which are small, and is at present only means to get at deep lying levels.

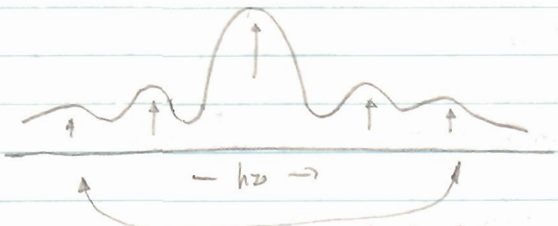
Radiative Recombination:

Observed by creating excess of carriers in conduction band, usually thru radiation or carrier injection. When excitation removed, electrons fall from conduction to valence band. Three possibilities: phonon creation, photon emission, increase in energy of an electron. Another is falling temporarily into recombination center, creating phonon showers.

When radiative recombination takes place emission of one photon is released. Suppose thermal equilibrium of carriers. When recombination takes place, same selection hold as for absorption.



$$h\nu \pm \hbar\omega_l = E_g + \Delta E$$



should say that this corresponds to ± ħω phonon.

LECTURE XXV 4-11-61

Effective - Mass Approximation:

Reference: W. Kohn SSP 5, 257-320 (1957)

Can be introduced through Wannier function with resulting hydrogenic levels for an impurity atom. Recall from Ehrenreich - 295. Use bulk dielectric constant because dielectric constant will act at large distance of donor electron from ionized impurity. Use for potential $\frac{e^2}{\kappa r}$ which is slowly varying. κ is not a tensor in a cubic crystal, since it is diagonal.

Reference: W. Kohn, PR105, 509 (1957)

This article proves validity of using dielectric constant. Actually, rigourously holds only for infinitely weak forces. The proper Schroedinger equation is:

$$\left[H_0 + V(r) + U(r) \right] \Psi = E \Psi$$

where $U(r) \to -\frac{e^2}{\kappa r}$ for large r. Assume for Ψ, since it is near a band edge (shallow impurity)

$$\Psi = \sum_{nk} A_{nk}\, b_n(k, r)$$

We get then:

$$\left[E_n(k) - E \right] A_{nk} + \sum_{n'k'} \langle nk | U | n'k' \rangle A_{n'k'} = 0$$

Now $U(r)$ is slowly varying:

$$\langle nk | U | n'k' \rangle = \int b_n^*(k, r)\, U(r)\, b_{n'}(k', r)\, d^3r$$

$$= \int e^{i(k-k')\cdot r} u_n^*(k, r)\, u_n(k', r)\, U(r)\, d^3r$$

since most of the contribution comes from $n = n'$. Now, if k and k' are small, $u_n^* u_n$ is small and $\simeq 1$ over the unit cell:

$$\langle nk | U | nk' \rangle \simeq \int e^{i(k'-k)\cdot r}\, U(r)\, d^3r$$

or the Fourier transform of $U(r)$. We have first integrated the cell periodic part and summed over all cells which we replase by an integral. Make $n \to 0$, we then have:

$$\left[E_0(k) - E \right] A_{0k} + \sum_{k'} \langle 0k | U | 0k' \rangle A_{0k'}$$

$$+ \sum_{\substack{n' \neq 0 \\ k'}} \langle 0k | U | n'k' \rangle A_{n'k'} = 0$$

The effective mass approximation amounts to neglecting the interband term.
A_{0k} vanishes rapidly as one moves away from band edge, justifies making $\sum_{k}^{0}$.

$$\left[E_0(k) - E\right] A_{0k} + \sum_{k'} \langle 0k|U|0k'\rangle A_{0k'} = 0$$

with $\langle 0k|U|0k'\rangle = \frac{1}{\Omega_0}\int e^{i(k'-k)\cdot r}\, U(r)\, d^3r$
This is Fourier transformed Schroedinger equation. Compare with:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \quad , \quad \psi = \sum_k a(k)\, e^{ik\cdot r}$$

$$\frac{\hbar^2}{2m} k^2 a(k) + \sum_{k'} V(k,k')\, a(k') = E\, a(k) \quad \text{F-transform}$$

We see $E_0(k) \to E_0(\frac{1}{i}\nabla)$

If we define $F(r) = \sum_k A_{0k}\, e^{ik\cdot r}$ we obtain Ehrenriechi result:

$$\left[E_0(\tfrac{1}{i}\nabla) - E\right] F(r) + U(r)\, F(r) = 0$$

Now $\psi = \sum_k A_{0k}\, b_0(k,r) = \sum_k A_{0k}\, u_0(\frac{1}{i}\nabla, r)\, e^{ik\cdot r}$

$$= u_0(\tfrac{1}{i}\nabla, r) \sum_k A_{0k}\, e^{ik\cdot r}$$

or $\boxed{\psi = u_0(\tfrac{1}{i}\nabla, r)\, F(r)}$

This derivation is for non-degenerate band edge at $k=0$. However, usually have multiple minima, say, one at $k = k_j$. Make change:

$$F(r) = e^{ik_j\cdot r}\, G(r)$$

Then Wannier equation becomes:

$$\left[E_0(\tfrac{1}{i}\nabla + k_j) - E\right] G(r) + U(r)\, G(r) = 0$$

$$E_0(k) = E_0(k_j) + \frac{\hbar^2}{2m}(k-k_j)\cdot\underset{\sim}{\alpha}\cdot(k-k_j)$$

$$= E_0(k_j) + \frac{\hbar^2}{2m}\underbrace{\underset{\sim}{\alpha} : \nabla\nabla}_{\alpha_{ij}\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}}$$

Then: $\Psi = e^{ik_j\cdot r}\, u_0\left(\frac{1}{i}\nabla + k_j, r\right) G(r)$

Now if more than one k_j exists, have degeneracy and linear combination form solution:

$$\Psi = \sum_j \alpha_j e^{ik_j\cdot r}\, u_{0j}\left(\frac{1}{i}\nabla, r\right) G_j(r)$$

There are as many terms as minima. The α_j's can be found by group theory. There will be coupling between minima which lift degeneracies, so not just any linear combination will do. Can make test to find proper combination to get proper irreducible representation:

$$\varphi_\lambda = \sum_R \chi_\lambda(R)\, R\, \varphi$$

LECTURE XXVI 4-13-61

Recall: $\sum_j e^{ik_j\cdot r}\, u_j\left(\frac{1}{i}\nabla, r\right) G_j(r)$

where $u_j(k-k_j; r)$ = periodic part of Bloch function in the vicinity of $k = k_j$

and: $E_1\left(\frac{1}{i}\nabla - k_j\right) e^{ik_j\cdot r} G_j(r) = e^{ik_j\cdot r} E\left(\frac{1}{i}\nabla\right) G_j(r)$

$$F_j(r) = e^{ik_j\cdot r} G_j(r)$$

For ellipsoidal energy surfaces:

$$\left\{\alpha_2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \alpha_1\frac{\partial^2}{\partial z^2} + E - U(r)\right\} G_j(r) = 0$$

We use Rydberg units and make the following substitutions:

$$\xi = \frac{x}{b}, \; \eta = \frac{y}{b}, \; \zeta = \frac{z}{a} \; ; \qquad a_H = \frac{\hbar^2}{me^2}, \; E \rightarrow \frac{e^2}{2a_H}$$

$$U(r) = -\frac{2}{Kr} = -\frac{2}{K\left[b^2(\xi^2+\eta^2)+a^2\zeta^2\right]^{1/2}}$$

$$\rho = (\xi^2+\eta^2+\zeta^2)^{1/2}$$

and get:

$$\left\{ \frac{\alpha_2}{b^2}\left(\frac{\partial^2}{\partial\xi^2}+\frac{\partial^2}{\partial\eta^2}\right) + \frac{\alpha_1}{a^2}\frac{\partial^2}{\partial\zeta^2} + E + \frac{2}{K\left[b^2(\xi^2+\eta^2)+a^2\zeta^2\right]^{1/2}} \right\}$$

$$G(\xi,\eta,\zeta) = 0$$

Assume $G(\xi,\eta,\zeta) = G(\rho) = f(\rho)$

Use variational principle:

$$E = \frac{\int f(\rho)\, H\, f(\rho)\, d\xi\, d\eta\, d\zeta}{\int [f(\rho)]^2\, d\xi\, d\eta\, d\zeta}$$

Average over angles:

$$\left(\frac{1}{3}\frac{\alpha_1}{a^2} + \frac{2}{3}\frac{\alpha_2}{b^2}\right)\left(\frac{d^2f}{d\rho^2} + \frac{2}{\rho}\frac{df}{d\rho}\right) + Ef + \underbrace{\frac{2}{K}\left\langle \frac{1}{\left[b^2(\xi^2+\eta^2)+a^2\zeta^2\right]^{1/2}} \right\rangle_{AV}}_{\frac{2}{K}\frac{1}{\sqrt{b^2-a^2}}\sin^{-1}\sqrt{1-\frac{a^2}{b^2}}} f = 0$$

$$= \frac{2}{K}\frac{1}{\sqrt{b^2-a^2}}\cos^{-1}\frac{a}{b}, \qquad Z_{eff} = \frac{1}{\sqrt{b^2-a^2}}\cos^{-1}\frac{a}{b}$$

Thus we have a pseudo-hydrogenic case and can write the result by inspection.

Define $\gamma = \frac{a}{b}$: then $E = - \frac{Z_{eff}^2}{\kappa^2 n^2 \bar{\alpha}}$

or $E = - \frac{1}{\kappa} \frac{\gamma^2}{1-\gamma^2} (\cos^{-1}\gamma)^2 \frac{1}{\frac{1}{3}\alpha_1 + \frac{2}{3}\gamma^2 \alpha_2}$

Some Typical values of the parameters are:

$b_{Si} = 2.5 \cdot 10^{-8}$ $a_{Si} = 14.2 \cdot 10^{-8}$

$b_{Ge} = 64.5 \cdot 10^{-8}$ $a_{Ge} = 22.7 \cdot 10^{-8}$

.98 m	.19 m	−.032 ev	−.045	Si
1.58 m	.083 m	−.0092 ev	.011	Ge

make approximation $b^2 = \alpha_2$, $a^2 = \alpha_1$

$Z_{eff} = \frac{\cos^{-1}\sqrt{\frac{\alpha_1}{\alpha_2}}}{\sqrt{\alpha_2 - \alpha_1}}$ gives $E =$ 1.54 before
1.63 now
in units of $\frac{1}{\kappa^2 \alpha_2}$

Another Approach:
Take: $G(\xi, \eta, \zeta) = f(\rho) \cos\theta$, that is, p-functions

Changes: get $u^2 = \cos^2\theta$ in potential term numerator and centripetal force term.

Get, when $b^2 = \alpha_2$, $a^2 = \alpha_1$:

$$Z_{eff} = \left(\overset{P}{m=0}\right) = \frac{3}{2} \frac{\alpha_2}{\alpha_2 - \alpha_1} \frac{\cos^{-1}\sqrt{\frac{\alpha_1}{\alpha_2}}}{\sqrt{\alpha_2 - \alpha_1}} - \frac{3}{2} \frac{\sqrt{\alpha_1}}{\alpha_2 - \alpha_1}$$

$$Z_{eff}\left(\overset{P}{m=1}\right) = \frac{1}{2}\left[3\, Z_{eff}\left(\overset{S}{m=0}\right) - Z_{eff}\left(\overset{P}{m=0}\right)\right]$$

Reference: Luttinger & Kohn <u>PR 98</u>, 915 (1955)

Table of Values: Silicon:

	Zeff	E- This Method	E- Exact Variation Method
1s m=0	.541	1.54	1.63
2s m=0	.541	.385	.49
2p m=0	.645	.547	.63
2p m=±1	.489	.314	.33
3p m=0	.645	.243	.32

Reference: PR 98, 922 (1955). to get arrangement of energy levels and degeneracy.

For degenerate band edges, we must solve a secular equation (valence band):

$$\text{Det}\left| D_{jj'}^{\alpha\beta} k_\alpha k_\beta - \underbrace{\lambda \epsilon_j \delta_{jj'}}_{\substack{\text{split off}\\ \text{by S.O. coupling.}}} - E\,\delta_{jj'} \right| = 0$$

LECTURE XXVII 4-15-61

Determination of Band Structure (Paul)

1) ρ vs T:

$$\frac{1}{\rho} = \sigma = e n \mu_n(T) + e p \mu_p(T)$$

At high temperature, can neglect extrinsic contribution:

$$\frac{1}{\rho} = e\left(\mu_n(T) + \mu_p(T)\right) A(m)\, T^{3/2}\, e^{-E_G/2kT}$$

$$-\ln\rho - \ln\left[D\, T^{3/2}\left(\mu_n(T) + \mu_p(T)\right)\right] = -\frac{1}{2kT} E_g$$

Slope of $\ln\rho$ vs $\frac{1}{T}$ gives E_g from slope. E_g is temperature dependent as mobilities are.

Galvano-Magnetic Properties: All these effects are listed by Blatt in SSP. These effects give direction of minima in k-space, and give some information concerning constant energy surfaces.

Hall Effect: All anisotropy is removed in cubic crystal. Tensors become scalars.

Hall potential balances Lorentz force for those carriers of average velocity. Magnetoresistance (transverse) arises from those electrons with non-average velocity. If no MR, energy surfaces are spherical.

Classical treatment of transport phenomena uses Boltzmann equation. Seitz has shown that the transport equations can be written:

$$J = \sigma E + \alpha E \times H + \beta E H^2 + \gamma H (E \cdot H) + \delta T E$$

$$T = \begin{pmatrix} H_1^2 & 0 & 0 \\ 0 & H_2^2 & 0 \\ 0 & 0 & H_3^2 \end{pmatrix}$$

or: $$E = \rho J + R_H (J \times H) + \rho \left(b H^2 J + (c H (J \cdot H)) + d T J\right)$$

These coefficients can be related to the E vs k curve and τ vs k curve.

The Hall constant is given by:

$$R_H = \frac{3\pi^{1/2}}{4} (kT)^{5/2} \frac{F_2}{F_1} \frac{3K(K+2)}{(2K+1)^2} \frac{1}{nec} , \quad K = \frac{m_l}{m_t}$$

$$b = (R_H \sigma)^2 \left\{ \frac{F_1 F_3}{F_2^2} \cdot M_1(K) - 1 \right\}$$

$$c = (R_H \sigma)^2 \left\{ 1 - \frac{F_1 F_3}{F_2^2} M_2(K) \right\}$$

$$d = (R_H \sigma)^2 \left\{ \frac{F_1 F_3}{F_2^2} M_3(K) \right\}$$

and $$F_\alpha = \int_0^\infty \tau^\alpha \epsilon^{3/2} e^{-\epsilon/kT} \, d\epsilon$$

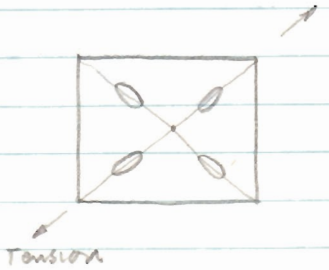
M's are orientation functions of spheroid:

Direction of minima	Condition
0	$b + c = 0$, $d = 0$
111	$b + c = 0$, $d > 0$
100	$b + c = -d$, $d < 0$
110	$b + c = d$, $d > 0$

This concludes magneto-resistance. Magneto-conductance does away with need to know $R_H \sigma$.

Magneto-elasticity.

In the rank 9 tensor for cubic crystal we have C_{11}, C_{12}, C_{44}; π_{11}, π_{12}, π_{44}. Consider two dimensional crystal:



Carriers will spill over into minima of lowest energy. Thus resistivity becomes anisotropic

References: Keyes, SSP 11
Smith, PR 94, 42 (1954)
Herring, BSTJ 34, 237 (1955)
Brooks, Adv. in Electronics

Hot Electrons: Transport in high fields, electrons go into higher region of conduction bands, disobey Boltzmann equation.

References: J. B. Gunn, Prog. in S.C 2
Hoenig: JPCS 8

Semiconductor Alloys:

Experiments can be made in Ge-Si alloys in determining band structure by extrapolation. Pressure: also band structure determination by extrapolation to atmospheric pressure.

Impurities: ionization determined by $\ln \rho$ vs $\frac{1}{T}$ or photoconductive edge or absorbtion edge. Most accurate is to find photon that takes one from ground state into excited state from far infra-red absorption and then could use theory outlined by Brooks to determine ionization energy.

LECTURE XXVIII 4-18-61

Spin-Resonance Phenomena:

Resonance frequency depends on hyperfine interactions with all magnetic moments in crystal. In silicon, interaction with donor nucleus and silicon 29 isotope. Splitting is:

$$\underbrace{g\beta HM}_{\substack{\text{electron}\\ \text{spin}}} + \underbrace{aMm}_{\substack{\text{electron}\\ \text{-nuclear}\\ \text{interaction}}} - \underbrace{\gamma\beta_N Hm}_{\substack{\text{nuclear}\\ \text{spin}}}$$

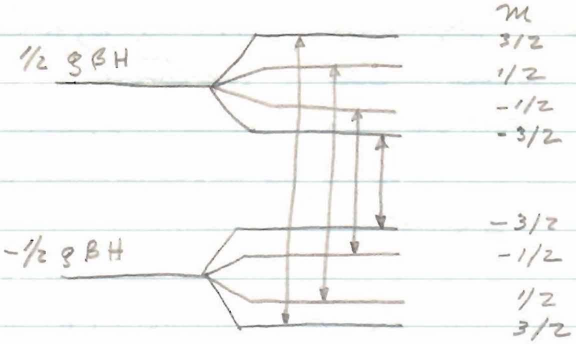
where M is electron spin quantum number, and m is nuclear spin quantum number. Above is for whole electron-nuclear problem.

$$a = \frac{16\pi}{3}\beta\frac{\mu_0}{I_0}\cdot|\psi(0)|^2$$

Upon introducing EM field, have transition which obey selection rules $\Delta M = \pm 1$, $\Delta m = 0$

$$h\nu_e = g\beta H + \frac{16\pi}{3}\frac{\mu_0}{I_0}\beta|\psi(0)|^2 m$$

As : $I_0 = 3/2$

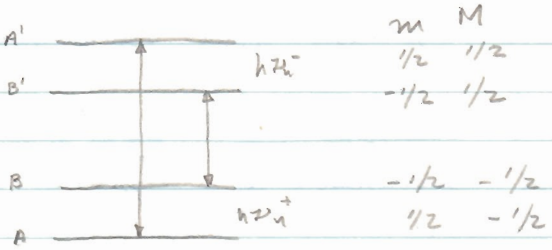


For P-doped Si: get two lines.

	I_0	
P	1/2	2
As	3/2	4
Sb	5/2 7/2	6 8

From experimental observation of hyperfine splitting can obtain value of $|\psi(0)|^2$.
Still must include Si^{29} interaction, leads to fuzzing of lines and determines line breadths

Endor Technique: Double Resonance:
Used to find $|\psi(0)|^2$ and band minima in Si, Use Phosphorus as impurity.



With these transitions we get:

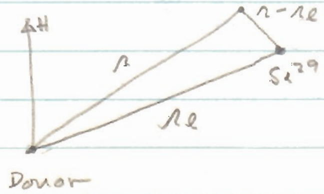
$$h\nu_n^{\pm} = 2\mu_p \left(H \pm \frac{8\pi}{3} \beta |\psi(0)|^2 \right)$$

in radio freq. range.

First saturate A-A' by microwave radiation. Then apply RF to effect A-B or B'-A' which changes population of A' or B, thus effecting microwave absorption.

Now take into account Si^{29} interaction. In above equation we have the changes:

$$h\nu_l^{\pm} = \left| -\frac{\mu_{Si}}{I_{Si}} H \pm \frac{8\pi}{3} \frac{\mu_{Si}}{I_{Si}} \beta |\psi(r_l)|^2 \mp \beta \frac{\mu_{Si}}{I_{Si}} \left(\frac{3\cos^2\alpha - 1}{(r - r_l)^3} \right) (1 - 3\cos^2\theta) \right|$$



How does one know which lattice site one is dealing with?

Experimentally, we get resonance points for each lattice site of Si^{29}. Also depends on angular variation, which we can use to obtain lattice site positions. How do we use these? Recall:

$$\psi(r) = \frac{1}{\sqrt{6}} \sum_{j=1}^{6} F_j(r)\, u_j(r)\, e^{i k_j r}$$

and: $$h\nu_e^{\pm} = \left| -\frac{\mu_{Si}}{I_{Si}} H \pm \frac{a_e}{2} \mp \frac{b_e}{2}\left(1-3\cos^2\theta\right)\right|$$

LECTURE XXIX 4-20-61

Reference on Endor Technique: Feher, PR 114, 1219-1256 (1959)

Comparison of Ground States of Impurities measured optically and thermally: Invariably experimental values of ionization are higher than theoretical and vary with type of impurity. Also discrepancy between optical and thermal that seems unresolved.

There is usually good agreement between excited states of different impurity types but not between ground states.

See Kohn's article for degree of experimental check of effective mass theory. Excited state orbits are large, thus checking with theory.

Wave function at donor nucleus $\psi(0)$:
need to determine $F_j(r)$ in:

$$\psi(r) = \frac{1}{\sqrt{6}} \sum_{j=1}^{6} F_j(r)\, u_j(r)\, e^{i k_j \cdot r}$$

Kohn gives: $$F = \frac{1}{(\pi a^2 b)^{1/2}}\, e^{-\sqrt{(x^2+y^2)/a^2 + \frac{z^2}{b^2}}}$$

$$a = 25 \cdot 10^{-8}, \quad b = 14.2 \cdot 10^{-8}$$

From this we can get $|\psi(0)|^2$:

Effective Mass: $|\psi(0)|^2 = .042 \cdot 10^{24}$ cm^{-3}

Endor: Hyperfine Splitting: $.44 \cdot 10^{24}$ cm^{-3}

Off by a factor of 10, so adjustment needed in theory. Kohn's explanation relates discepancy in $\psi(0)$ to difference in ground state energy. Consider effective mass equation in the following form:

$$\left\{ -\frac{\hbar^2}{2m^*}\nabla^2 - \frac{e^2}{\kappa r} \right\} F(r) = E_{obs} F(r)$$

Adjust m^* to give E_{obs}, that is, obtain an isotropic effective mass from experimental ionization energy: $E_{obs} = -\frac{m^*}{\kappa^2}$

However, now $F(r)$ no longer vanishes at origin, and is now singular. Define effective radius: $r_{eff} = \frac{\kappa}{\sqrt{m^*}} a_H \sim \frac{1}{20} a_H$

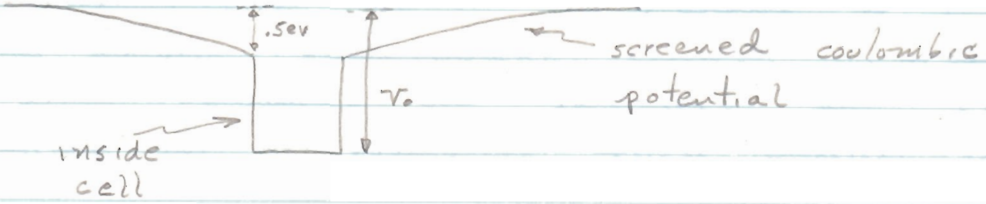
This means that at boundary of cell, wave function is like that near nucleus of hydrogen atom.

All we can do now with effective mass is to limit its application outside boundary of first unit cell of impurity. If we take ratio of $F(r)$'s at boundary found with effective mass and with isotropic adjusted effective mass, get very nearly factor of 10 or discrepancy shown above.

Justification for this approach: Brooks and Fletcher: divide crystal into outside impurity cell where m^* applies and inside impurity cell where solution of Schroedinger equation must be had. If we assume impurity acts as hole in dielectric, can use this to get potential. Must solve and then match to exterior m^* boundary conditions.

set $v(r) = \frac{e^2}{r} f(r)$. This problem is treated in detail by a variation technique. Find that wave function is same as Kohn's isotropized m^*.

Potential inside cell:



Find: that depth of potential well matches somewhat with ionization energy:

	Si		Ge	
P	-5ev	(-6.3)	-6	(-6.9)
As	-5.3	(-5.9)	-6.5	(-6.5)
Sb	-4	(-3.9)	-5.0	(-4.5)

needed to get observed E_{obs}

get from model of pt. charge in hole in dielectric

It has been suggested that further agreement can be obtained by including piezo-electric effect local to impurity.

Deep levels or Deep lying impurity. Ground state lies down in potential well. Level will be in middle of band, thus needing conduction and valence band wave functions in its make-up.

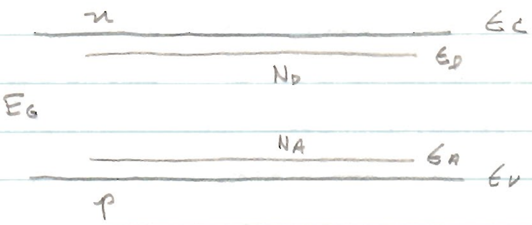
LECTURE XXX 4-22-61

Effects of strain: splitting of Hydrogenic levels of impurities. Also affects impurity banding. Envelope functions are extremely distorted in direction of strain causing changes in resistivity of the order of 10^3 because of overlap:

References: Fritzsche: PR115, 336
PR119, 1238, 1899
PR120, 1120

Statistics

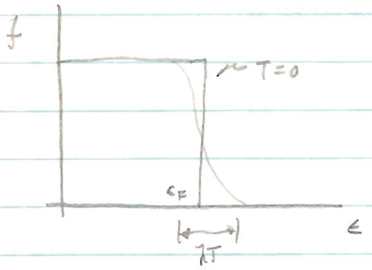
Applications to Bands and Impurities. Usually only seen for bands and not for degenerate impurities levels. What we do now should follow Brooks treatment:



The usual expression for the Fermi function is well-known:

$$f(\epsilon) = \frac{1}{1 + e^{(\epsilon - \epsilon_F)/kT}}$$

Recall in Metals:



In semiconductors:
Impurities: although we have spin degeneracy, because of coulomb repulsion we have only one electron per level.

Ground states in deep levels may be degenerate. Now the Fermi statistics for the levels is:

$$f = \frac{1}{1 + \exp\{(E_D + \epsilon_f)/kT\}}$$

$$E_D = -kT \ln \left[\sum_{l} g_l \, e^{-\epsilon_l/kT} \right.$$

For spin degeneracy, $g_\ell = 2$ and get:

$$f \rightarrow \frac{1}{1 + \frac{1}{2}\exp\left\{(\epsilon_D - \epsilon_F)/kT\right\}}$$

Let: n_a = no. of holes in ϵ_A
n_D = no. of electrons in ϵ_D

$$\therefore \quad n - p + n_D - n_A = N_D - N_A$$

as required for electrical neutrality.
Thus:

$$n = \int_{\epsilon_c}^{\infty} f(\epsilon - \epsilon_f)\, n_c(\epsilon)\, d\epsilon = \int_{\epsilon_c}^{\infty} \frac{n_c(\epsilon)\, d\epsilon}{1 + e^{(\epsilon - \epsilon_F)/kT}}$$

If $\epsilon - \epsilon_F \gg kT$ then $f \rightarrow e^{(\epsilon_F - \epsilon)/kT}$ (MB)
a MB usually means that too few electrons and too many states to compete on basis of Pauli exclusion principle. In semiconductors usually above holds except in bands of high mass that become filled quickly.
FD condition is called degenerate.
MB condition is called non-degenerate.

Consider $\frac{\epsilon - \epsilon_F}{kT} > 1$ by not very much

$$\frac{1}{1 + e^{\frac{\epsilon - \epsilon_F}{kT}}} = e^{\epsilon_F - \epsilon/kT} - e^{2\left(\frac{\epsilon_F - \epsilon}{kT}\right)}$$

$$n = e^{\epsilon_F - \epsilon_c/kT}\left\{\int_{\epsilon_c}^{\infty} C e^{-\left(\frac{\epsilon - \epsilon_c}{kT}\right)} d\epsilon\right\} - e^{2\frac{(\epsilon_F - \epsilon_c)}{kT}} \int_{\epsilon_c}^{\infty} C e^{-2\frac{(\epsilon - \epsilon_c)}{kT}} d\epsilon$$

$$n = 2A\, e^{\frac{\epsilon_F - \epsilon_c}{kT}} - 2^{1/2} A\, e^{2\left(\frac{\epsilon_F - \epsilon_c}{kT}\right)}$$

where: $2A = \int_{\epsilon_c}^{\infty} C e^{-\left(\frac{\epsilon - \epsilon_c}{kT}\right)} (\epsilon - \epsilon_c)^{1/2}\, d\epsilon = C' T^{3/2}$

Now the condition for MB statistics is:

$$e^{\left(\frac{\epsilon_F-\epsilon_c}{kT}\right)} \ll \sqrt{8} \quad ; \quad \frac{\epsilon_F-\epsilon_c}{kT} \ll 1$$

$$\frac{n}{T^{3/2}} \ll \sqrt{8}\, C'$$

These are the degeneracy numbers and degeneracy temperature. We shall use the non-degenerate MB statistics:

$$n = \int_{\epsilon_c}^{\infty} n_c(\epsilon)\, e^{(\epsilon_F-\epsilon)/kT}\, d\epsilon$$

$$n_c(\epsilon) = 4\pi\left(\frac{2m_e}{h^2}\right)^{3/2}(\epsilon-\epsilon_c)^{1/2}$$

$$n = 2\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{(\epsilon_F-\epsilon_c)/kT} = 2A_e\, e^{(\epsilon_F-\epsilon_c)/kT}$$

For multiple minima, <u>show that</u> (for exercise):

$$n = 2s\left(\frac{2\pi m_1^{1/3} m_2^{2/3} kT}{h^2}\right)^{3/2} e^{(\epsilon_F-\epsilon_c)/kT}$$

Valence Band: probability of occupation by hole:

$$1-f(\epsilon) = \frac{1}{1+e^{(\epsilon_F-\epsilon)/kT}}$$

Using MB statistics:

$$p = 2A_p\, e^{(\epsilon_v-\epsilon_F)/kT} \quad ; \quad A_p = \left(\frac{2\pi m_p kT}{h^2}\right)^{3/2}$$

For degenerate valence band maximum, get two terms: $p = 2(A_p' + A_p'')\, e^{(\epsilon_v-\epsilon_F)/kT}$
Use average effective mass for warped bands.

LECTURE XXXI 4-25-61

From previous results:

$$n_d = \frac{N_d}{1+\frac{1}{g_D} e^{\epsilon_D - \epsilon_F/kT}}$$; g = degree of degeneracy which is sometimes hard to determine

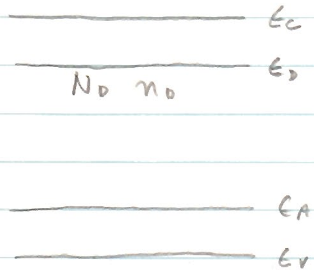
$$n_a = \frac{N_A}{1+\frac{1}{g_A} e^{\epsilon_F - \epsilon_A/kT}}$$

g = 2 is usually found in the literature denoting spin degeneracy.

Neutrality Condition:

$$n_0 = N_D - N_a = 2A_e\, e^{\frac{\epsilon_F - \epsilon_c}{kT}} - 2A_p\, e^{\frac{\epsilon_v - \epsilon_F}{kT}} + \frac{N_D}{1+\frac{1}{g_D} e^{\frac{\epsilon_D - \epsilon_F}{kT}}} - \frac{N_A}{1+\frac{1}{g_A} e^{\frac{\epsilon_F - \epsilon_A}{kT}}}$$

Consider donor and acceptor level problem at low temperatures:



Consider $n_D > n_A$ and Fermi level between ϵ_c and ϵ_D so that ϵ_A are filled with electrons with no holes generated in valence band. Ignore intrinsic conduction.

Thus: $$n_0 = 2A_e e^{\frac{\epsilon_F - \epsilon_c}{kT}} + \frac{N_D}{1+\frac{1}{g_D} e^{\frac{\epsilon_D - \epsilon_F}{kT}}}$$

$$x = A_e\, e^{\frac{\epsilon_F - \epsilon_c}{kT}}$$; $$y = A_e\, e^{\epsilon_D - \epsilon_c/kT}$$

$$n_0 = 2x + \frac{N_D}{1+\frac{1}{g}\frac{y}{x}}$$

Therefore: $$x = \frac{-\left(\frac{2y}{g} + N_D - n_0\right)}{4} + \left\{\left(\frac{\frac{2y}{g} + N_D - n_0}{4}\right)^2 + \frac{n_0 y}{2g}\right\}^{1/2}$$

from $2x = n$.

Case I: $N_A = 0$; $N_D = n_0$; $|\epsilon_D - \epsilon_c| << kT$
so $y >> N_D$

$$x = \frac{n_0}{2} \quad \text{so} \quad 2x = n_0$$

Then: $$\left(\frac{2y}{g}\right)^2 >> \frac{16 n_0 y}{2g} \quad \text{or} \quad y >> 2 n_0 g$$

or $$e^{\frac{\epsilon_D - \epsilon_c}{kT}} >> \frac{2 n_0 g}{A_e} = \frac{n_0}{A_e}$$

This approximation of having all donors ionized is justified (be) at room temperature for doping levels up to $10^{16}/cm^3$. We can also find Fermi level:

$$n_0 = 2 A_e e^{\frac{\epsilon_F - \epsilon_c}{kT}}$$

$$\epsilon_F - \epsilon_c = kT \ln \frac{n_0}{2 A_e}$$

$$\epsilon_F - \epsilon_c = kT \ln C T^{-3/2}$$

Case II: $N_D > n_0$, $y << N_D, n_0, N_D - n_0$ or low T
or high $|\epsilon_D - \epsilon_c|$

Then: $$2x = \frac{2 n_0 A_e e^{\frac{\epsilon_D - \epsilon_c}{kT}}}{g (N_D - n_0)}$$

Almost always holds for some low temperature, or when:

$$\frac{n_0 y}{2g} << \frac{(N_D - n_0)^2}{16} \longrightarrow e^{\frac{\epsilon_D - \epsilon_c}{kT}} << \frac{g (N_D - n_0)^2}{8 A_e}$$

We can also find the fermi level:

$$\epsilon_F - \epsilon_c = kT \left\{ \frac{\epsilon_D - \epsilon_c}{kT} + \ln \frac{n_0}{g(N_D - n_0)} \right\}$$

As $T \to 0$, $\epsilon_F \to \epsilon_D$

Usually see in literature the assumption of no acceptors which gives factor of two to put ϵ_F in middle of $|\epsilon_D - \epsilon_c|$. In this, gives for plot of:

$\ln(n T^{3/2})$ vs $\frac{1}{T}$ gives slope of $\frac{(\epsilon_D - \epsilon_c)_0}{k}$

or $\epsilon_d - \epsilon_c = (\epsilon_d - \epsilon_c)_0 + \beta T$

Intercept at $\frac{1}{T} = 0$ is $\frac{\beta}{k} + \ln \frac{2 n_0 A_e}{g(N_D - n_0)}$

However, must watch out for factor of 2. However, can determine N_D, N_A etc in other ways so would have this knowledge in advance.

If we consider intrinsic excitation:

$$n = 2 A_e\, e^{\frac{\epsilon_F - \epsilon_c}{kT}} \quad ; \quad p = 2 A_p\, e^{\frac{\epsilon_v - \epsilon_c}{kT}}$$

$$\frac{\epsilon_F - \epsilon_c}{kT} = \frac{\epsilon_v - \epsilon_F}{kT} + \ln \frac{A_p}{A_e}$$

$$\epsilon_F = \frac{\epsilon_v + \epsilon_c}{2} + \frac{1}{2} kT \ln \frac{A_p}{A_e}$$

We see even for unbalance in carriers ϵ_F is about in middle of band by reason of order of kT. Note that in general, whether impurities present or not:

$np = 4 A_e A_p\, e^{\frac{\epsilon_v - \epsilon_c}{kT}}$ if we can use MB statistics

$n - p = n_0$ if impurities are ionized

LECTURE XXXII 4-27-61

Recall: $np = 4 A_e A_p e^{-E_g/kT} = n_i^2(T)$

$$\therefore \quad np = n_i^2(T)$$

$$n - p = n_0$$

$$n = \frac{n_0}{2} + \left[\left(\frac{n_0}{2}\right)^2 + n_i^2 \right]^{1/2}$$

$$p = -\frac{n_0}{2} + \left\{ \left(\frac{n_0}{2}\right)^2 + n_i^2 \right]^{1/2}$$

If $n_i << n_0$:

$$n = \frac{n_0}{2} + \left(\frac{n_0}{2}\right)\left(1 + \frac{1}{2}\frac{4n_i^2}{n_0^2}\right)$$

$$n = n_0 + \frac{n_i^2}{n_0} , \quad p = \frac{n_i^2}{n_0}$$

If $n_i >> n_0$: $n = n_i + \frac{n_0}{2}$; $p = n_i - \frac{n_0}{2}$

Mechanisms of Recombination:

Mostly approached through phenomenological channels. Suppose we know all states in crystal and the equilibrium statistics. Then inject carriers in a photoionization, injection, etc. sense. What is mechanism determining lifetimes of these carriers? This is the problem. We restrict to the cases where we maintain electrical neutrality, might not be case in low conductivity cases.

Recombination Processes:

(a) band to band transition ... radiative
(b) " ... non-radiative
(c) " .... Auger process
(d) by a recombination center ... radiative
(e) " ... non-radiative
(f) " ... Auger process

Auger process gives energy of recombination to conduction band electrons or valence band holes. Recombination centers can be ionized impurities, lattice imperfections, etc.

Some Definitions:

r_n = rate per unit volume of disappearance due to a given process.

R_n = net rate of recombination of electron = $r_n(n,p) - r_n(n_0,p_0)$

$n_0 p_0 = n_i^2$

$R_p = r_p(n,p) - r_p(n_0,p_0)$

Lifetime: $\tau_n = \frac{n-n_0}{R_n}$; $\tau_p = \frac{p-p_0}{R_p}$

Capture Lifetime: $\frac{n}{r_n(n,p)} \neq \frac{n-n_0}{r_n(n,p) - r_n(n_0,p_0)}$

There are many anomalies of these definitions in the literature, especially lifetime; can have equilibrium lifetime, decay lifetime. Do not confuse with scattering lifetime.

If electron and holes fall into recombination centers at different rates, we have no electrical neutrality. If this rate is unequal, these centers are called traps. Example of single carrier trap would be doubly ionized donor level. Important in photoconductivity.

Methods of determining lifetime:

(1) Injection - point contact
(2) " - broad contact
(3) photoionization.

Can measure change in conductivity, free carrier absorption, anything that connects with extra carriers which we can relate to lifetime.

(a) Radiative Recombination: observed in almost all semiconductors. Inverse of radiative absorption process in every way including indirect transitions. What sort of lifetime does this lead to?

We by-pass matrix element methods because have been handled before in optical transitions.

Rate of recombination = Bnp

Rate of excess recombination = $R = B(np - n_i^2)$

$$\tau_n = \frac{n - n_0}{R_n} \; ; \; \tau_p = \frac{p - p_0}{R_p}$$

$$\tau_n = \frac{1}{B(n_0 + p_0)} = \tau_p$$

Assuming: $$\tau_n = \frac{n - n_0}{B(np - n_i^2)} = \frac{n - n_0}{B\left\{(n_0 + \Delta n)(p_0 + \Delta n) - n_i^2\right\}}$$

$\Delta n \ll n_0, p_0$ and get above.

Consider the Planck law of black-body radiation:

$$n(E)\,dE = \frac{8\pi N^3}{h^3 c^3} \frac{E^2}{e^{E/kT} - 1}\,dE \quad \text{(one photon - one ep pair)}$$

$$n(E) = n_0(E)\,e^{-\mu x} = n_0(E)\,e^{-\mu \frac{c}{N} t}$$

$$\frac{dn}{dt} = -\frac{\mu c n_0}{N}$$

No. of pairs generated per unit time:

$$G = \int_0^\infty \frac{c}{N(E)} \mu(E)\, n(E)\, dE$$

However, in equilibrium; generation equals recombination: $G = B n_i^2 (T)$. If use theoretical $\mu(E)$, holds only near band edge. Thus should use experimental $\mu(E)$ because of $\int$

LECTURE XXXIII 4-29-61

Some useful physical parameters:

	E_G	n_i $\cdot 10^{-12}$	B $cm^3 sec^{-1}$	τ intrinsic n_i	τ $10^{17} cm^{-3}$ μsec
Si	1.08	.00015	.002	4.6 hours	2500
Ge	.66	.24	.034	.61 sec	150
InSb	.18	200	40	.62 μsec	.12
PbS	.41	7.1	48	15 μ sec	.21

(b) Band to Band Recombination that is non-radiative. Many-phonon shower is not probable and no experimental evidence exists to support it.

(c) $r = \beta_n n^2 p + \beta_p n p^2$ (Auger Process)

Energy and momentum must be conserved without use of phonons so starting particle must have high energy. See Franz, Hand. f. Phys. 17 for calculation of impact ionization which is inverse of this process.

$$R = \beta_n\left(n^2 p - n_0^2 p_0\right) + \beta_p\left(n p^2 - n_0 p_0^2\right)$$

Franz gets: $n_i^2 \beta_n = \frac{\nu!}{\sqrt{\pi}} \frac{me^4}{\hbar^3} G \left(\frac{kT}{E_t}\right)^{\nu - 1/2} e^{-E_t/kT}$

$E_t \cong 3/2\, E_G$

E_t = threshold energy. See also Rochester Conference.

$$\tau = \frac{n - n_0}{R_n} = \frac{1}{n_0^2 \beta_n + 2 n_i^2 (\beta_n + \beta_p)}$$

Small E_G and high temperature gives shorter lifetime. Could be identified by exponential — remember important at high temperatures and high carrier densities.

(d) Travel of electrons from conduction band to valence band via imperfection levels. Not much evidence that photon recombination is dominant in those materials which have recombination. Happens in Phosphors

(e) Phonon emitters; dominant process. Carrier captured in higher states and dribbles down emitting phonons, photons, and Auger electrons on the way.
References: PR 87, 835, 1952 Schockley - Read

Hall, PR 83, 228, 1951; 87, 387, 1952

See Fax on Giant Traps.

One Recombination Center Model:

Consider n, p, n_t, N_t:

c_n = rate of combination of an electron with r.c
c_p = " hole "
c_n' = " ejection " electron from r.c
c_p' = " hole "

Rate Equation:

$$\frac{dn}{dt} = -n c_n (N_t - n_t) + c_n' n_t$$

$$\frac{dp}{dt} = -p c_p n_t + c_p' (N_t - n_t)$$

$\frac{dn}{dt} = 0$, so that $\frac{c_n'}{c_n} = \frac{2A_n}{g} e^{\frac{E_t - E_c}{kT}}$

$\frac{dp}{dt} = 0$, so that $\frac{c_p'}{c_p} = \frac{2A_p}{g} e^{\frac{E_v - E_t}{kT}}$

these g's need not be the same. what follows assumes them equal.

Redefine: $E_t' = E_t - kT \ln g$

$$\frac{c_n'}{c_n} = 2A_n e^{\frac{E_t' - E_c}{kT}} = n_1 \; ; \quad \frac{c_p'}{c_p} = 2A_p e^{\frac{E_v - E_t'}{kT}} = p_1$$

$$\frac{dn}{dt} = c_n \left[-n(N_t - n_t) + n_1 n_t \right]$$

$$\frac{dp}{dt} = c_p \left[-p\, n_t + p_1 (N_t - n_t) \right]$$

$$\frac{dn}{dt} = \frac{dp}{dt} \qquad \text{(charge neutrality)}$$

$$n_t = N_t \frac{n c_n + p_1 c_p}{(n+n_1) c_n + (p+p_1) c_p}$$

$$\frac{dn}{dt} = \frac{c_p c_n N_t (n_i^2 - np)}{(n+n_1) c_n + (p+p_1) c_p} = \frac{dp}{dt}$$

$$n = n_0 + \delta n \qquad \delta n \ll n_0$$
$$\delta p \ll p_0$$

$$\frac{d}{dt}\delta n = \frac{-c_p c_n N_t (n_0 + p_0)\,\delta n}{(n_0+n_1) c_n + (p_0+p_1) c_p} = -\frac{\delta n}{\tau}$$

$$\tau = \left(\frac{n_0 + n_1}{n_0 + p_0}\right) \frac{1}{c_p N_t} + \left(\frac{p_0 + p_1}{n_0 + p_0}\right) \frac{1}{c_n N_t}$$

When $n_0 \gg p_0$, $p_1 \ll n_0$ $\qquad \tau_p^{ext} = \frac{1}{c_p N_t}$

$n_0 \gg n_1$

$n_1 \ll n_0$

LECTURE XXXIV 5-2-61

Statistical Mechanics of Energy Levels

The energy bands in the one electron model are essentially independent of the occupation.

For impurities in Ge we have 8 fold degenerate levels, but the impurity changes the potential seen by neighboring electrons.

Introduce the crystal partition function Z:

$$Z = \sum_r e^{-W_r/kT}$$

W_r = energy level of whole crystal

We assume that W_r can be written as a sum of the one-electron energy levels:

$$W_r = \sum_{s=0}^{\infty} n_s E_s \quad ; \quad n_s = 0, 1, 2, 3, \dots$$

Then:

$$Z = \sum_r e^{-W_r/kT} = \sum_{n_1, n_2, \cdots, n_s, \cdots} e^{-\sum_{s=0}^{\infty} \frac{n_s E_s}{kT}}$$

all subject to $\sum_{s=0}^{\infty} n_s = N$. We include this condition by a dummy variable

$$Z = \sum_{n_1, \cdots n_s} e^{-\sum_{s=0}^{\infty} \frac{n_s E_s}{kT}} x^{\sum_0^{\infty} n_s}$$

from which we pick out those terms that satisfy the constraint. We can write:

$$Z = \sum_{n_1, \cdots n_s} \prod_{s=0}^{\infty} e^{-\frac{n_s E_s}{kT}} x^{n_s} = \prod_{s=0}^{\infty} \left\{ \sum_{n_s} e^{-\frac{n_s E_s}{kT}} x^{n_s} \right\}$$

$$= F(x).$$

By using Cauchy's integral, we can pick out the coefficients of x^N.

That is : $\oint \frac{F(x)}{x^{N+1}} dx$

We can approximate the integral by considering only the range where it is large.

New definitions :

$$x = e^{\epsilon_F / kT}$$

and $\{ \ \} = Z(\epsilon_F, T) = F(\epsilon_F, T)$

We want the maximum value of $\dfrac{F(\epsilon_F, T)}{e^{(N+1)\epsilon_F/kT}}$

which is found by :

$$\frac{\partial}{\partial \epsilon_F}\left[\frac{F(\epsilon_F, T)}{e^{(N+1)\epsilon_F/kT}}\right] = 0$$

Consider the case for bands :

$$\sum_{n_s} e^{-\frac{n_s \epsilon_s}{kT} + \frac{n_s \epsilon_F}{kT}}$$

$n_s = 0$

$n_s = 1$: can go in two ways due to spin

$n_s = 2$: two electrons allowed in this state

This gives : $1 + 2e^{\frac{\epsilon_F - \epsilon_s}{kT}} + e^{2\left[\frac{\epsilon_F - \epsilon_s}{kT}\right]}$

$$= \left[1 + e^{\frac{\epsilon_F - \epsilon_s}{kT}}\right]^2$$

Now : $\ln F(\epsilon_F, T) = \sum_s 2 \ln\left(1 + e^{\frac{\epsilon_F - \epsilon_s}{kT}}\right)$

and $\frac{\partial}{\partial \epsilon_F}\left\{ \ln F(\epsilon_F, T) - (N+1)\frac{\epsilon_F}{kT} \right\} = 0$

Now : $A = -kT \ln Z$ (Helmholtz Free Energy)

or $A = -2kT \sum_s \ln\left(1 + e^{\frac{\epsilon_F - \epsilon_s}{kT}}\right) + (N+1)\epsilon_F$

since $\frac{\partial A}{\partial \epsilon_F} = 0$: $\quad -2 \sum_s \frac{e^{\frac{\epsilon_F - \epsilon_s}{kT}}}{1 + e^{\frac{\epsilon_F - \epsilon_s}{kT}}} + N = 0$

since $N \approx N+1$

Then: $\quad \sum_s \frac{2}{1 + e^{\frac{\epsilon_s - \epsilon_F}{kT}}} = N$

Now what about discrete levels? Consider only spin degeneracy: In previous results, $n_s = 2$ cannot occur since of coulomb repulsion. We then get for the free energy:

$$A = -2kT \sum_s \ln\left(1 + e^{\frac{\epsilon_F - \epsilon_s}{kT}}\right) + (N+1)\epsilon_F - kT N_D \ln\left(1 + 2e^{\frac{\epsilon_F - \epsilon_D}{kT}}\right)$$

From $\frac{\partial A}{\partial \epsilon_F} = 0$:

$$\underbrace{\sum_s \frac{2}{1 + e^{\frac{\epsilon_s - \epsilon_F}{kT}}}}_{\text{electron in band}} + \underbrace{N_D \frac{1}{1 + \frac{1}{2} e^{\frac{\epsilon_D - \epsilon_F}{kT}}}}_{\text{electron in impurity level}} = N$$

We can write in general for g-degenerate level a $\frac{1}{g}$ instead of $\frac{1}{2}$ in the fermi term above for impurity levels.

Consider the limit of Boltzmann statistics:

$$e^{\epsilon_F/kT} \left\{ 2 \sum_s e^{-\frac{\epsilon_s}{kT}} + g N_D e^{-\epsilon_D/kT} \right\} = N$$

Reference: Teitler and Wallis, JPCS 16, 71 (1960).

Consider now multiple impurity levels, for example, Au. In bond picture, impurity tries to form tetrahedral bonds with the host. Au gives single donor or single, double, triple acceptor.

Recall that in diamond lattice, have essentially 4 valence bands: V_1, V_2 } two highest, degenerate at $k=0$

V_3 S-O split

V_4 deep s-band.

Again consider different values of n_s. For $n_s = 1$, there are 4 ways to go into the Au. For the case $n_s = 2$, consider only lowest states so two electrons go into two lowest states. Number of ways to arrange two electrons among four possibilities is $\frac{4!}{2!\,2!}$: Addition of 1 electron causes new energy ϵ_1, two electrons give ϵ_2 which is added to the system relative to the conduction band. Thus:

$$1 + 4e^{\frac{\epsilon_F - \epsilon_1}{kT}} + 6e^{\frac{2\epsilon_F - \epsilon_1 - \epsilon_2}{kT}} + 4e^{\frac{3\epsilon_F - \epsilon_1 - \epsilon_2 - \epsilon_3}{kT}}$$

$$+ \ e^{\frac{4\epsilon_F - \epsilon_1 - \epsilon_2 - \epsilon_3 - \epsilon_4}{kT}}$$

and we get an additional term in the free energy: $-kT\, N_G \ln(\text{mess})$

Carrying through the analysis as before can get Fermi term for this complicated structure.

LECTURE XXXV 5-4-61

Impurity Level Statistics (Paul):

Excited States:

Recall necessity to find maximum value of:

$$\frac{F(\epsilon_F, T)}{e^{(N+1)\epsilon_F/kT}} \quad ; \quad F(\epsilon_F, T) = \prod_{s=0}^{\infty} \left\{ \sum_{n_s} e^{n_s(\epsilon_F - \epsilon_s)/kT} \right\}$$

Band states give: $\displaystyle\prod_{s,\,\text{band}} \left(1 + e^{\frac{\epsilon_F - \epsilon_s}{kT}}\right)^2$

$n_s = 0 \quad : \quad 1$

$n_s = 1 \quad : \quad 2e^{(\epsilon_F - \epsilon_s)/kT}$

Site is denoted by s for impurity levels; also gives degeneracy, which is reason for 2 above.

Consider impurity states: model; site has ground state with energy ϵ_1; degeneracy g_1; an excited state energy ϵ_2, degeneracy g_2, etc., for 1 electron inserted into impurity.

Two electrons (ϵ_{21}, g_{21}), (ϵ_{22}, g_{22}), ...

Thus; for impurity contribution:

$$\prod_{s,\,\text{impurities}}^{N_D} \Big(1 + g_1 e^{(\epsilon_F - \epsilon_1)/kT} + g_2 e^{(\epsilon_F - \epsilon_2)/kT} + \cdots$$

$$+ g_\ell e^{(\epsilon_F - \epsilon_\ell)/kT} + \cdots$$

$$+ g_{21} e^{2\left(\frac{\epsilon_F - \epsilon_{21}}{kT}\right)} + \cdots$$

We throw away $n_s = 1$ terms as their exponents are so high they are negligible. Now consider maximization. Take:

$$\frac{\partial}{\partial \epsilon_F}\left[kT \ln\left[\frac{F(\epsilon_F, T)}{e^{(N+1)\epsilon_F/kT}} \right]\right] = 0$$

get:
$$N = \sum_{s,\,\text{band}} \frac{2 e^{\frac{\epsilon_F - \epsilon_s}{kT}}}{1 + e^{\frac{\epsilon_F - \epsilon_s}{kT}}}$$

$$+ N_D \frac{\sum_{\ell=1}^{\infty} g_\ell e^{(\epsilon_F - \epsilon_\ell)/kT}}{1 + \sum_{\ell=1}^{\infty} g_\ell e^{\frac{\epsilon_F - \epsilon_\ell}{kT}}}$$ assuming all impurities the same (donors)

$$N = \sum_{s,\,\text{band}} \frac{2}{1 + e^{\frac{\epsilon_s - \epsilon_F}{kT}}} + N_D \frac{1}{1 + \frac{1}{\sum_{\ell=1}^{\infty} g_\ell e^{\frac{\epsilon_F - \epsilon_\ell}{kT}}}} \qquad (29.10)$$

which is for impurities that have excited states occupied by one electron.

Changing the form slightly:

$$\text{Impurities} = \frac{1}{1 + \dfrac{1}{g_1 e^{\frac{\epsilon_F - \epsilon_1}{kT}}\left(1 + \frac{g_2}{g_1} e^{\frac{\epsilon_1 - \epsilon_2}{kT}} + \cdots\right)}}$$

$$= \frac{1}{1 + \left(\frac{1}{g_1}\right) e^{\frac{\epsilon_1 - \epsilon_F}{kT}} \left(\dfrac{1}{1 + \frac{g_2}{g_1} e^{\frac{\epsilon_1 - \epsilon_2}{kT}} + \cdots}\right)}$$

Note that excited state terms are neglectable only if $\epsilon_2 >> \epsilon_1$ and at low temp. However, no one seems to know if these conditions are met in reality. Usually everybody neglects extra terms

Acceptor States:

Using K-L model, have 4-fold degenerate ground acceptor state, can see from above results that we get:

$$\frac{1}{1 + \frac{1}{4} e^{\frac{\epsilon_F - \epsilon_A}{kT}}}$$

$$\prod_{\text{imp.}} \left\{ \sum_{n_s} e^{n_s \frac{(\epsilon_F - \epsilon_s)}{kT}} \right\} = \prod \left\{ 1 + 4 e^{\frac{\epsilon_F - \epsilon_A}{kT}} \right\}$$

neglecting $n_s > 1$. Taking:

$$\frac{\partial}{\partial \epsilon_F} \left\{ kT \ln \frac{F(\epsilon_F, T)}{e^{(N+1)\epsilon_F/kT}} \right\} = 0$$

$$\frac{4 e^{(\epsilon_F - \epsilon_A)/kT}}{1 + 4 e^{(\epsilon_F - \epsilon_A)/kT}} = \frac{1}{1 + \frac{1}{4} e^{\frac{-\epsilon_A + \epsilon_F}{kT}}}$$

where we have inverted signs on the argument we are working with holes.

Consider Acceptor with 4 states, 3 in the valence band and one in the gap:

$$\prod_{\text{imp.}} \left\{ \sum_{n_s} e^{n_s \frac{(\epsilon_F - \epsilon_s)}{kT}} \right\}$$

$n_s = 0 \quad : \quad 1$

$n_s = 1 \quad : \quad 4e^{\frac{\epsilon_F - \epsilon_1}{kT}}$

$n_s = 2 \quad : \quad 6\, e^{2\left(\frac{\epsilon_F - \epsilon_1}{kT}\right)}$

$n_s = 3 \quad : \quad 4\, e^{3\left(\frac{\epsilon_F - \epsilon_1}{kT}\right)}$

$n_s = 4 \quad : \quad e^{4\left(\frac{\epsilon_F - \epsilon_1}{kT}\right) - \frac{\epsilon_2}{kT}}$

} consider bonding energy same for each electron

; ϵ_2 is the difference in energy between host be atom and impurity.

Summing, we get:

$$\left(1 + e^{\frac{\epsilon_F - \epsilon_1}{kT}}\right)^4 + e^{4\left(\frac{\epsilon_F - \epsilon_1}{kT}\right)}\left(e^{-\frac{\epsilon_2}{kT}} - 1\right)$$

Then the fermi level for impurities is:

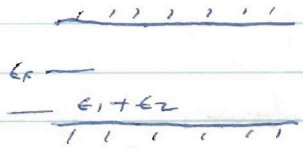
$$\frac{4\left(1 + e^{\frac{\epsilon_F - \epsilon_1}{kT}}\right)^3 e^{\frac{\epsilon_F - \epsilon_1}{kT}} + 4e^{4\left(\frac{\epsilon_F - \epsilon_1}{kT}\right)}\left(e^{-\frac{\epsilon_2}{kT}} - 1\right)}{\left(1 + e^{\frac{\epsilon_F - \epsilon_1}{kT}}\right)^4 + e^{4\left(\frac{\epsilon_F - \epsilon_1}{kT}\right)}\left(e^{\frac{\epsilon_2}{kT}} - 1\right)}$$

We must now argue that ϵ_1 is deep in the valence band and ϵ_F is in the forbidden gap, thus making $|\epsilon_F - \epsilon_1|$ large:

$$\frac{12\, e^{3\left(\frac{\epsilon_F - \epsilon_1}{kT}\right)} + 4\, e^{4\left(\frac{\epsilon_F - \epsilon_1}{kT}\right)} e^{-\epsilon_2/kT}}{4\, e^{3\left(\frac{\epsilon_F - \epsilon_1}{kT}\right)} + e^{4\left(\frac{\epsilon_F - \epsilon_1}{kT}\right)} e^{-\epsilon_2/kT}}$$

$$= \frac{12 + 4\, e^{\frac{\epsilon_F - \epsilon_1 - \epsilon_2}{kT}}}{4 + e^{\frac{\epsilon_F - \epsilon_1 - \epsilon_2}{kT}}}$$

; this is probability of electron filling.



Probability of hole filling = 4 − above:

$$= \frac{1}{1 + \frac{1}{4} e^{\frac{\epsilon_F - (\epsilon_1 + \epsilon_2)}{kT}}}$$

we relable $\epsilon_1 + \epsilon_2 = \epsilon_A$ as we have to consider reference.

We do not see this in literature for hydrogenic levels.

LECTURE XXXVI 5-6-61

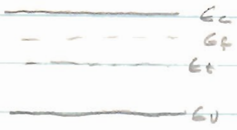
Recombination Lifetimes:

$$\tau = \frac{n_0 + n_1}{n_0 + p_0}\frac{1}{C_p N_t} + \frac{(p_0 + p_1)}{(n_0 + p_0)}\frac{1}{C_n N_t}$$

ϵ_t' fixed:

$$n_0 = 2A_n e^{\frac{\epsilon_F - \epsilon_c}{kT}}$$
$$n_1 = 2A_n e^{\frac{\epsilon_t' - \epsilon_c}{kT}}$$
$$p_0 = 2A_p e^{\frac{\epsilon_v - \epsilon_f}{kT}}$$
$$p_1 = 2A_p e^{\frac{\epsilon_v - \epsilon_t'}{kT}}$$

For a very n-type sample:



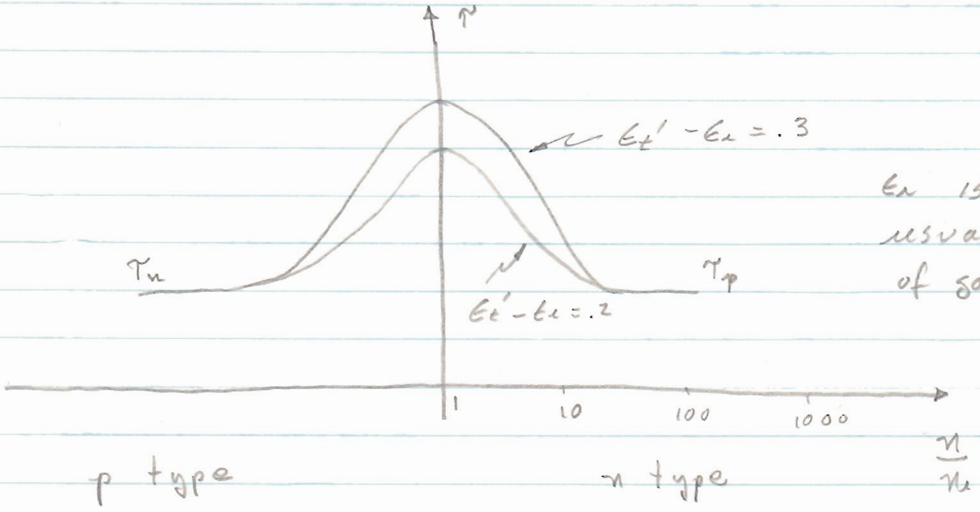
$n_0 >> p_0$, $n_0 >> n_1$, $n_0 >> p_1$

get: $\tau_p^{ext} \rightarrow \frac{1}{C_p N_t}$

so that lifetime is that of recombination of minority carriers. Similarly:

$$\tau_n^{ext} = \frac{1}{C_n N_t}$$

so that: $\tau = \tau_n^{ext}\frac{p_0 + p_1}{n_0 + p_0} + \tau_p^{ext}\frac{p_0 + p_1}{n_0 + p_0}$



ϵ_i is intrinsic level, usually at middle of gap.

In above, we assume N_t and ϵ_t and C_n, C_p fixed throughout varying concentration. Maximums at intrinsic and $\epsilon_t' = \epsilon_i$.

We can write the lifetime as:

$$\tau = \frac{\tau_n^{ext} p_0 + \tau_p^{ext} n_0}{n_0 + p_0} + \frac{\tau_n p_1 + \tau_p n_1}{n_0 + p_0}$$

If $\tau_n^{ext} = \tau_p^{ext}$ and with above expressions:

$$\tau = \tau_n^{ext} + \tau_n^{ext} \left\{ \frac{\cosh \frac{1}{kT}(E_t' - E_c + E_g/2)}{\cosh \frac{1}{kT}(E_t - E_c + E_g/2)} \right\}$$

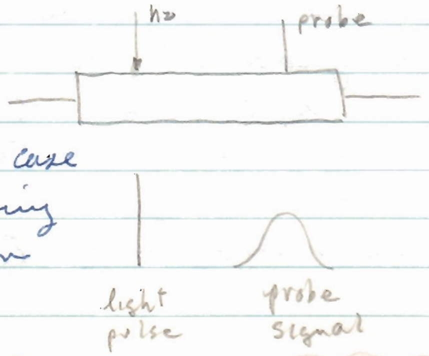
Can now plot above graph using this equation and show maximums appear at intrinsic levels.

Usually lifetimes can go either way with temperature so no general results can be given.

Difficulties with above model:
1) level of disturbance
2) multiple recombination levels
3) different statistics than MB.

Models using two recombination levels sometimes give better fit to experiment. This phenomenological theory is hard to verify experimentally. Auger effect has not been observed so far.

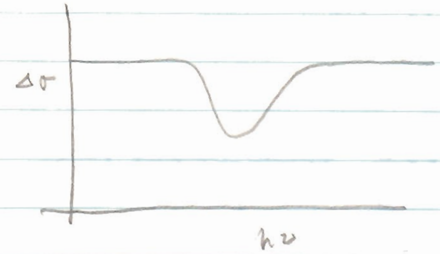
Trapping: Trap: higher capture cross section much greater for one carrier than other. Recall Haynes mobility experiment:



usual case involving diffusion

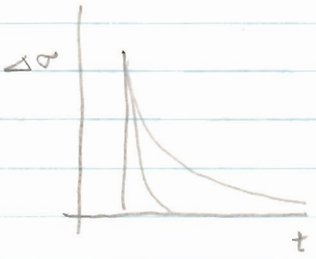
We sometimes see the following due to trapping: Background light will kick carriers out of trap and will suppress tail.

Quenching: shine monochromatic light with white background:



Explanation is that hole recombines in center so electron corresponding to hole must stay in conduction band. However when monochromatic light has hν to excite hole and cause removal of conduction band electron.

Lifetimes and Trapping can be studied thru decay times:



Trapping is important in wide gap materials. Can be studied phenomenologically and by identifying traps thru spin resonance.

Transport Phenomena and Theory

We begin by considering a distribution function $f(p,r,t)$, which can change to $f'(p,r,t)$ under application of electric and magnetic fields. Assume f_0 is given by FD statistics and upon application of field get only first order change. We will get the Boltzmann equation:

$$\vec{v}\cdot\nabla_r f-\left(e\vec{E}+\frac{e}{c}\vec{v}\times\vec{H}\right)\cdot\nabla_p f=\left(\frac{\partial f}{\partial t}\right)_c$$

It will turn out that f is independent of r unless there is thermal gradient in material so first term on RHS is left out. Major assumption is that RHS can be written

$$\left(\frac{\partial f}{\partial t}\right)_c=-\frac{f_1}{\tau}\quad ;\ \tau \text{ is relaxation time}$$

LECTURE XXXVII 5-9-61

References on Transport theory:

(Electric) Kohn & Luttinger, PR 108, 590 (1957)
PR 109, 1892 (1958)
(Magnetic) Argyres PR 117, 315 (1960)
Lifshitz JPCS 4, 11 (1958)
Adams & Goldstein JPCS 10, 254 (1959)

Case of No Periodicity and Electric Field Only:

$H_T = H_0 + H' + H_F$; $H_0 = \frac{p^2}{2m}$, $H' = \lambda V$, λ = perturbation parameter

or $H' = \lambda V = \sum_{i}^{N} \varphi(r - r_i)$, i denotes impurity.

$H_F = -e E_\alpha x_\alpha = -e E_\alpha^0 x_\alpha e^{st}$

e^{st} is needed in order to turn on the potential at $t=0$.

Recall density matrix:

$\langle m | \rho_T | n \rangle = \frac{1}{\nu} \sum_{i=1}^{\nu} a_m^i(t)\, a_n^{i*}(t)$; i denotes electron, ν of them

the a's come from: $\Psi_i(r,t) = \sum_m a_m^i(t)\, \psi_n(r)$

Now, in usual manner: $\overline{A(t)} = \mathrm{Tr}\left[\rho_T(t) A\right]$ with $\rho_T = \rho + \rho_F$ and:

$$i\hbar \dot{\rho}_F = [H_F, \rho] + [H_0 + H', \rho_F] \text{ , by definition, } \dot{\rho} = 0$$

We now put $\hbar = 1$ for convenience.
If we take the form of ρ_F to be:

$\rho_F = f e^{st}$ and writing $H_1 = -e E_\alpha^0 x_\alpha$
we get:

$$\cancel{i\rho_F =}\quad i s f = [H_1, \rho] + [H_0 + H', f]$$

Derivation of $i\dot{\rho}_F = [H_F, \rho] + [H_0 + H', \rho_F]$

$$i\dot{\rho}_T = [H, \rho_T] = [H + H_F, \rho + \rho_F]$$

$$i\dot{\rho}_F = [H, \rho] = 0$$

We also neglect $[H_F, \rho_F]$ as it is of second order in the field. K & L show that retention of this term leads to Joule heating.

We now show or choose a representation. Choose one such that: $H'_{kk} = 0$, by just shifting origin of energy.

Notation: $f_{kk} \to f_k$

We want to write: $isf = [H, \rho] + [H_0 + H', f]$ in components or matrix elements. Must watch diagonal terms:

$$-is f_k = C_k + \sum_{k'}{}' \left(f_{kk'} H'_{k'k} - H'_{kk'} f_{k'k} \right)$$

ρ represents state of system in absence of applied field and must be taken as boundary condition: Take:

$$t = -\infty, \quad \rho = K e^{-H/kT}, \quad \frac{1}{K} = \mathrm{Tr}\left(e^{-H/kT}\right)$$

For the operator $C = [H, \rho]$, the diagonal elements are of order zero, while the off-diagonal terms are of order λ. That is:

$$C^0_{kk'} = ie E^0_\alpha \frac{\partial \rho_k}{\partial k_\alpha} \delta_{kk'}$$

$$f_k \sim \lambda^{-2}$$
$$f_{kk'} \sim \lambda^{-1}$$

For the off diagonal elements:

$$\overset{(\lambda^{-1})}{(\epsilon_k - \epsilon_{k'} - is) f_{kk'}} = \overset{(\lambda^{-1})}{C_{kk'}} + (f_k - f_{k'}) H'_{kk'} + \overset{(1)}{\sum_{k''}{}'} \left(f_{kk''} H'_{k''k'} - H'_{kk''} f_{k''k'} \right)$$

If we make the assumption $f_k \sim \lambda^{-2}$, $f_{kk'} \sim \lambda^{-1}$ we find that these will give us a consistent set of equations. Making these approximations, letting $s \to 0$ slowly or slowly turn on field:

$$f_{kk'} = \frac{(f_k - f_{k'})\, H'_{kk'}}{\epsilon_k - \epsilon_{k'} - is}$$

$$0 = C_k + \sum_{k'}{}' \frac{(f_k - f_{k'})\, |H'_{kk'}|^2}{\epsilon_k - \epsilon_{k'} - is} - \sum_{k'} \frac{(f_{k'} - f_k)\, |H'_{kk'}|^2}{\epsilon_{k'} - \epsilon_k - is}$$

$$-is f_k = ie E_\alpha^0 \frac{\partial \rho_k}{\partial k_\alpha} + \sum_{k'}{}' |H_{kk'}|^2 \left\{ (f_k - f_{k'}) \left(\frac{1}{\epsilon_k - \epsilon_{k'} - is} - \frac{1}{\epsilon_k - \epsilon_{k'} + is} \right) \right\}$$

putting the s back in momentarily.

Let $s \to 0$, using the relation:

$$\lim_{s \to 0^+} \frac{1}{x - is} = P\left(\frac{1}{x}\right) + i\pi\, \delta(x)$$

and get:

$$0 = e E_\alpha^0 \frac{\partial \rho_k}{\partial k_\alpha} + 2\pi \sum_{k'} \frac{N\, |\varphi_{kk'}|^2}{\Omega^2}\, \delta(\epsilon_k - \epsilon_{k'})\, (f_k - f_{k'})$$

where we have replaced $|H'_{kk'}|^2$ by its original definition after taking an ensemble average to get rid of the sum over impurities. The above is the Boltzmann equation; ϵ_k are solutions for H_0. This is first order in f_k, consistent with the assumptions above that $f_k \sim \lambda^{-2}$ and $f_{kk'} \sim \lambda^{-1}$.

Since ρ_k depends on E but not on k, some further simplification can be had.

This equation is for only diagonal elements of density matrix or Boltzmann equation is in terms of diagonal elements. We eventually want current which is proportional to $\mathrm{Tr}\,[\rho_E v_\alpha]$ where v_α is of the form:

$$\langle k | v_\alpha | k' \rangle = k_\alpha\, \delta_{kk'}/m \quad \text{or } v_\alpha \text{ is diagonal}$$

hence $\mathrm{Tr}\,\{\rho_E v_\alpha\} = \sum_k \langle k | \rho_E | k \rangle \langle k | v_\alpha | k \rangle$

thus only diagonal elements of density matrix are involved. This is not true for magnetic fields. These diagonal elements represent state occupation.

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The correction due to neglected second order terms in deriving the Boltzmann equation are of the form: $\frac{n r_0^6}{\hbar}$ $\frac{n \bar{\Phi}}{\hbar^2}$ for the collision term, r_0 is range of potential of scatterer ϕ is depth of potential $\bar{\hbar}$ is average impurity. For ionized impurity scattering in semiconductors the range is quite long and is not usually mentioned in the literature. The Boltzmann equation is:

$$0 = e E_\alpha^{(0)} \frac{\partial \rho_k}{\partial k_\alpha} + 2\pi \sum_{k'} \frac{N |\phi_{kk'}|^2}{\Omega} \delta(\epsilon_{k'} - \epsilon_k)(f_k - f_{k'})$$

This, however, is for electron in a box. What about Bloch electrons? Start as before:

$$H_0 = \frac{p^2}{2m} + V \quad , \quad H' \quad , \quad H_F$$

Define quantum number $l = (\nu, k)$ where ν indexes bands, k the reduced zone. Also:

$$H_0 \psi_l = \epsilon_l^{(0)} \psi_l \quad ; \quad \epsilon_l = \epsilon_l^{(0)} + H'_{ll}$$

Proceeding as before: $C = [H_1, \rho]$,

$$C_{ll'} = C_{ll'}^{(0)} + C_{ll'}^{(1)} + \dots$$

Difference between this and free electron is that here we have off diagonal terms of the same order as the diagonal.

Before: $C^{(0)}_{kk'} = C_k = ie\,E_\alpha^{(0)} \frac{\partial \rho_k}{\partial k_\alpha}\,\delta_{kk'}$

Now: $C^{(0)}_{ll'} = ie\,E_\alpha (\rho_l - \rho_{l'})\,J_\alpha^{\nu\nu'}(k)\ \delta_{kk'}$

where: $\psi_l = \frac{1}{\sqrt{\Omega}}\,e^{ik\cdot r}\,w_l(r)$

$$J_\alpha^{\nu\nu'} = \frac{1}{\Omega_0}\int_{\Omega_0} w^*_{\nu k}\,\frac{\partial w_{\nu' k}}{\partial k_\alpha}\,dr$$

Calculation of $Tr[\rho_F v]$: Before: off diagonal elements vanish. Now: off diagonal elements do not vanish, however, to first or lowest order in λ, K & L show that off diagonal elements vanish. Hence, Boltzmann equation is same as above except that $|\phi_{kk'}|^2$ in between Bloch states. Does not work for bands close together.

Magnetic Field Case: Approach is to use free electron wave functions. Use $H_0 + H' + H_F$ where H_0 contains the vector potential. Then get the Landau potential levels and Landau wave functions. Get three quantum numbers for asymmetric gauge, n, k_y, k_z:

$\nu = (n\,k_y\,k_z)$; $\nu \pm 1\ (n \pm 1\ k_y\ k_z)$

$$H_0 = \frac{1}{2m}\left[p_x^2 + (p_y + m\omega_0 x)^2 + p_z^2\right]$$

$$\epsilon_{nk} = (n+\tfrac{1}{2})\hbar\omega_0 + \frac{\hbar^2 k_z^2}{2m}, \quad \omega_0 = \frac{eH}{mc}$$

$\hbar\omega_0 << kT$ can treat magnetic field as part of field operator since quantization is weak. For $\hbar\omega_0 \sim kT$, one gets Shubnikov effect or oscillations in magnetoresistance. Current which is found from $[\rho_F v]$ is the product of off diagonal elements since there are no diagonal elements.

We now take up the question of the distribution function or only the diagonal elements of the density matrix. Consider:

$f(k,r)$: spatial dependence needs concept of wave packets.

Meaning is the number of electrons with wave vector k at position r. Now consider:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{fields}} + \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = 0$$

Then change in the f due to fields uses the expression: $\hbar \frac{dk}{dt} = eE + \frac{e}{c}(v \times H)$ or a variation of Ehrenfest's theorem.

$$-\left(\frac{\partial f}{\partial t}\right)_{\text{Field}} = e\left[E + \frac{1}{c} v \times H\right] \cdot \frac{1}{\hbar} \nabla_k f(k,r)$$

$$+ \underset{\substack{\downarrow \\ \frac{1}{\hbar}\nabla_k E(k)}}{v} \cdot \nabla_r f(k,r) = \left(\frac{\partial f}{\partial t}\right)_{\text{coll.}}$$

$$= \int \left\{ P(k'k)\, f(k')\left[1 - f(k)\right] - P(kk')\, f(k)\left[1 - f(k')\right] \right\} dk'$$

$f(k,r)$ should really describe the probability of occupation of state k at position r.

$P(k'k)\, f(k')\left[1 - f(k)\right]$	$P(kk')\, f(k)\left[1 - f(k')\right]$
rate of transfer from k' to k	rate of transfer out of k to k'

The above is a logical expression rather than a physical one. Equation using density matrix was only for inelastic scattering, but this is not.

Principle of Detailed Balance: In no field, rates of transfer to and from are equal. Also true under constant applied fields.

We then have:

$$P(k'k)\,\frac{f_0(k')}{1-f_0(k')} = P(k\,k')\,\frac{f_0(k)}{1-f_0(k)}$$

for the equilibrium case.

If we set up:

$$P(k',k) = \frac{1-f_0(k')}{f_0(k')}\,H(k',k)$$

$$P(k,k') = \frac{1-f_0(k)}{f_0(k)}\,H(k,k')$$

Then $H(k',k) = H(k,k')$ or we have a symmetric distribution. We get:

$$\left\{\frac{1-f_0(k')}{f_0(k')}\,f(k')\left[1-f(k)\right] - \frac{1-f_0(k)}{f_0(k)}\,f(k)\left[1-f(k')\right]\right\} H(k'k)$$

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Boltzmann Equation:

$$\left(\frac{\partial f}{\partial t}\right)_{drift} + \left(\frac{\partial f}{\partial t}\right)_{coll} = 0$$

where:

$$\left(\frac{\partial f}{\partial t}\right)_{drift} = -e\left[E + \frac{1}{c}\,v\times H\right]\cdot\frac{1}{\hbar}\nabla_k f(k,r) + v\cdot\nabla_r f(k,r)$$

$$\left(\frac{\partial f}{\partial t}\right)_{collision} = \sum_{k'}\left\{P(k'k)\,f(k')\left[1-f(k)\right] - P(k\,k')\,f(k)\left[1-f(k')\right]\right\}$$

where we could make $\sum_{k'} \rightarrow \frac{\Omega}{4\pi^3}\int dk'$

Actually if we talk about entire crystal we must include phonon transitions.

Thus we should write for scattering:

$$P(k' \to k,\ n_\sigma \to n_\sigma + 1)$$

$$P(k \to k',\ n_\sigma + 1 \to n_\sigma)$$

where the phonon transition is $n \to n+1$ and the electron is $k' - k = \sigma$. Also we need a new distribution for the lattice vibrations.

$$\left(\frac{\partial f}{\partial t}\right)_{collision} = \sum_{k', n} \Big\{ P(k' \to k,\ n \to n+1)\, f(k') \left[1 - f(k)\right] g(n_\sigma)$$

$$- P(k \to k',\ n+1 \to n)\, f(k) \left[1 - f(k')\right] g(n_\sigma + 1) \Big\}$$

where we consider that in thermal equilibrium each of the terms is equal. We take for the distribution functions.

$$f_0(k) = \frac{1}{1 + e^{\frac{\epsilon(k) - \zeta}{kT}}} \qquad \text{Fermi} \qquad \frac{f_0}{1 - f_0} = e^{\frac{\zeta - \epsilon}{kT}}$$

$$g_0(n) = \frac{e^{-\frac{n\hbar\omega}{kT}}}{1 - e^{-\frac{\hbar\omega}{kT}}} \qquad \text{Einstein}$$

Then we get:

$$P(k'k,\ n\ n+1)\, \frac{f_0(k')}{1 - f_0(k')}\, g_0(n) = P(kk',\ n+1\ n)\, \frac{f_0(k)}{1 - f_0(k)}\, g_0(n+1)$$

From which we can see $\epsilon(k') - \epsilon(k) = \hbar\omega$

It is a good approximation to assume that distribution of phonons at any time is given by equilibrium distribution as lattice relaxes from non-equilibrium quickly. Not so for phonon drag where at low temperatures phonons tend to move in direction of applied field.

For the distribution of electrons we write:

$f(k) = f_0(k) + f_1(k)$

Define as an average over phonon states:

$$\bar{P}(k'k) = \sum_n P(k'k,\ n\ n+1)\, g_0(n)$$

Thus we have for non-equilibrium:

$$\sum_{k'} \bar{P}(k'k) \Big\{ f_1(k') \left[1 - f_0(k) + e^{-\frac{\hbar\omega}{kT}} f_0(k) \right]$$

$$- f_1(k) \left[(1 - f_0(k'))\, e^{-\frac{\hbar\omega}{kT}} + f_0(k') \right] \Big\}$$

or:

$$\sum_{k'} \bar{P}(k'k)\, f_1(k')\, f_0(k) \left[e^{\frac{\epsilon(k) - \zeta}{kT}} + e^{-\hbar\omega/kT} \right]$$

$$- \sum_{k'} P(k'k)\, f_1(k)\, f_0(k') \left[e^{\frac{\epsilon(k) - \hbar\omega - \zeta}{kT}} + 1 \right]$$

Finally; for the collision term:

$$\left(\frac{\partial f}{\partial t} \right)_{coll.} = \sum_{k'} P(k'k) \left\{ \frac{f_1(k')}{f_0(k')} f_0(k)\, e^{-\frac{\hbar\omega}{kT}} - \frac{f_1(k)}{f_0(k)} f_0(k') \right\}$$

Now consider the field term:

We will make $f_1(k)$ of the form:

$f_1(k) = e E_\alpha \frac{1}{\hbar} \frac{\partial f_0(k)}{\partial k_\alpha} \tau(k)$ which we use

in $\left(\frac{\partial f}{\partial t} \right)_{drift} = e E_\alpha \frac{1}{\hbar} \frac{\partial f_0(k)}{\partial k_\alpha}$, no spatial dependence.

Recall $\frac{1}{\hbar} \frac{\partial f_0(k)}{\partial k_\alpha} = \hbar^{-1} \frac{\partial f_0}{\partial \epsilon} \frac{\partial \epsilon}{\partial k_\alpha}$; $v_\alpha = \frac{1}{\hbar} \frac{\partial \epsilon}{\partial k_\alpha}$

$= v_\alpha \frac{\partial f_0}{\partial \epsilon}$

When priming must write $v_\alpha' \frac{\partial f_0}{\partial \epsilon'}$

Then: $f_1(k) = e E_\alpha \frac{\partial f_0}{\partial \epsilon} v_\alpha \tau(k)$

Finally, for the Boltzmann equation:

$$v_\alpha \frac{\partial f_0}{\partial \epsilon} = \sum_{k'} \bar{P}(k'k) \left\{ \frac{1}{f_0(\epsilon')} \frac{\partial f_0}{\partial \epsilon'} f_0(\epsilon) v_\alpha' \tau(k') e^{-\frac{\hbar\omega}{kT}} - \frac{1}{f_0(\epsilon)} \frac{\partial f_0}{\partial \epsilon} f_0(\epsilon') v_\alpha \tau(k) \right\}$$

If we work with semiconductors, can change f_0 to Boltzmann distribution. The Boltzmann equation is essentially an integral equation in $\tau(k)$.

For the case of Elastic scattering, $e^{\frac{\hbar\omega}{kT}} = 0$, $f_0(\epsilon') = f_0(\epsilon)$, we then get:

$$v_\alpha = \sum_{k'} \bar{P}(k'k) v_\alpha' \tau' - \sum_{k'} \bar{P}(k'k) v_\alpha \tau$$

$$1 = \sum_{k'} \bar{P}(k'k) \left[\frac{v_\alpha'}{v_\alpha} \tau' - \tau \right]$$

(sign mistake between k k' terms)

or:

$$\frac{1}{\tau(k)} = \sum_{k'} \bar{P}(k'k) \left[1 - \frac{v_\alpha' \tau'}{v_\alpha \tau} \right]$$

or:

$$\frac{1}{\tau} = \sum_{k'} \bar{P}(k'k) \left[1 - \frac{v_\alpha'}{v_\alpha} \right]$$ (isotropic scattering)

Now; for the current density:

$$j_\alpha = \sum_k e v_\alpha f_1(k) = e^2 E_\alpha \sum_k v_\alpha^2 \tau(k) \frac{\partial f_0}{\partial \epsilon}$$

$$v_\alpha = \sum_{k'} \bar{P}(k'k) \left[v_\alpha \tau - v_\alpha' \tau' \right]$$

Then:

$$j_\alpha = e^2 E_\alpha \sum_{k,k'} \bar{P}(k'k) v_\alpha \tau(k) \frac{\partial f_0}{\partial \epsilon} \left[v_\alpha \tau - v_\alpha' \tau' \right]$$

The conductivity is defined from $j_\alpha = \sigma E_\alpha$

Then: $$\frac{1}{\sigma} = \frac{e^2 \sum_{kk'} \bar{P}(k'k) \frac{\partial f_0}{\partial \epsilon} \left[v_\alpha^2 \tau^2 - v_\alpha v_\alpha' \tau \tau' \right]}{e^4 \left\{ \sum_k v_\alpha^2 \tau \frac{\partial f_0}{\partial \epsilon} \right\}^2} = \rho$$

If we vary τ we will be lead back to the original integral equation.

Important: a) Since ρ is stationary under variation in τ, approximate values of τ give accurate values of ρ.

b) ρ is a minimum

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(Paul) Recall last time: $(p = \hbar k)$

$$f_1(k) = \frac{eE}{\hbar} \frac{\partial f_0}{\partial k} \tau(k) = \tau(k)\, eE \cdot \nabla_p \epsilon \frac{\partial f_0}{\partial \epsilon}$$

$$f_1(p) = \tau(p)\, eE \cdot \nabla_p \epsilon \frac{\partial f_0}{\partial \epsilon}$$

$$f(p) = f_0(p) + f_1(p)$$

For the Magnetic Field:

$$\frac{f_1(p)}{\tau(p)} = \left(eE + \frac{e}{c} v \times H \right) \cdot \nabla_p (f_0 + f_1)$$

$$= eE \cdot \nabla_p \epsilon \frac{\partial f_0}{\partial \epsilon} + \underbrace{\frac{e}{c} (v \times H) \cdot \nabla_p \epsilon \frac{\partial f_0}{\partial \epsilon}}_{0} + eE \cdot \nabla_p f_1$$

$$+ \frac{e}{c} (v \times H) \cdot \nabla_p f_1$$

Now: $eE \cdot \nabla_p f_1 = eE \cdot \nabla_p \left(\tau(p) eE \cdot \nabla_p \epsilon \frac{\partial f_0}{\partial \epsilon} \right)$ which is second order in E so we drop.

now: $$\frac{f_1(p)}{\tau(p)} = eE\cdot\nabla_p\epsilon\frac{\partial f_0}{\partial\epsilon} + \frac{e}{c}(v\times H)\cdot\nabla_p\left(\tau(p)\,eE\cdot\nabla_p\epsilon\frac{\partial f_0}{\partial\epsilon}\right)$$

or, for a better approximation:

$$\frac{f_1(p)}{\tau(p)} = eE\cdot\nabla_p\epsilon\frac{\partial f_0}{\partial\epsilon} + \frac{e}{c}(v\times H)\cdot\nabla_p\Big\{\tau(p)\,eE\cdot\nabla_p\epsilon\frac{\partial f_0}{\partial\epsilon} + \tau(p)\frac{e}{c}(v\times H)$$

$$\cdot\nabla_p\left(\tau(p)\,eE\cdot\nabla_p\epsilon\frac{\partial f_0}{\partial\epsilon}\right)\Big\}$$

We will not solve for the magnetic field case but only for electric:

now: $$J = -e\sum_{\substack{\text{all}\\\text{states}}} v = -\frac{2e}{\hbar^3}\int v(p)\Big(\underbrace{f_0(p)}_{\downarrow\ 0} + f_1(p)\Big)\,dp$$

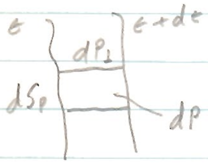
since F-D term

Thus: $$\underline{J} = -\frac{2e^2}{\hbar^3}\,\underline{E}\cdot\int\frac{\partial f_0}{\partial\epsilon}\nabla_p\epsilon\,\nabla_p\epsilon\;\tau(p)\,dp$$

since $\underline{J} = \underline{\underline{\sigma}}\,\underline{E}$;

$$\underline{\underline{\sigma}} = -\frac{2e^2}{\hbar^3}\int\frac{\partial f_0}{\partial\epsilon}\nabla_p\epsilon\,\nabla_p\epsilon\;\tau(p)\,dp$$

Can also be written in terms of a surface integral over a constant energy surface:

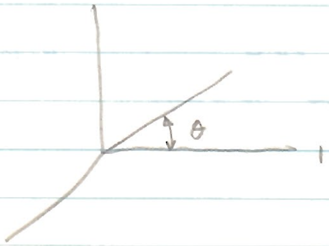


$$\underline{\underline{\sigma}} = -\frac{2e^2}{h^3}\int\frac{\partial f_0}{\partial\epsilon}\,d\epsilon\int\frac{\nabla_p\epsilon\,\nabla_p\epsilon}{|\nabla_p\epsilon|}\,\tau(p)\,dS_p$$

$$dP = dP_\perp\,dS_p = \frac{d\epsilon}{|\nabla_p\epsilon|}\,dS_p$$

We will solve for two simple cases. Take spherical band edges.

(1) $\epsilon = \frac{p^2}{2m}$, $\epsilon_0 = p_0 = 0$



$$\sigma_{\parallel} = \frac{-2e^2}{h^3}\int\frac{\partial f_0}{\partial\epsilon}\,d\epsilon$$

$$\cdot\int\tau(p)\left(\frac{p_\parallel}{m}\right)^2\frac{2\pi p\sin\theta\,p\,d\theta}{p/m}$$

or: $$\sigma_{11} = \frac{2e^2}{h^3}\int \frac{\partial f_0}{\partial \epsilon}\,d\epsilon \int_1^{-1} \tau(p)\,\frac{p^2\cos^2\theta}{m^2}\,\frac{2\pi p}{p/m}\,p\,d(\cos\theta)$$

Assume $\tau(p)$ can be written as $\tau(\epsilon)$:

$$\sigma_{11} = -\frac{2e^2}{h^3}\int \frac{\partial f_0}{\partial \epsilon}\,d\epsilon\;\tau(\epsilon)\,\frac{4\pi}{3m}\,(2m\epsilon)^{3/2}$$

This is as far as we can go without a function for the relaxation time $\tau(\epsilon)$.

(2) Ellipsoidal Constant Energy Surfaces:
Treatment is same in essentials:

$$\epsilon = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{p_3^2}{2m_3} \quad ; \quad \epsilon_0 = p_0 = 0$$

Let $a = \sqrt{2m_1\epsilon}$; $b = \sqrt{2m_2\epsilon}$, $m_2 = m_3$

Then: $$1 = \frac{p_1^2}{a^2} + \frac{p_2^2 + p_3^2}{b^2}$$

Let $p_1 = a\cos\theta$, $p_2 = b\sin\theta\cos\varphi$, $p_3 = b\sin\theta\sin\varphi$

$\nabla_p\epsilon$: $\frac{p_1}{m_1}$, $\frac{p_2}{m_2}$, $\frac{p_3}{m_3}$

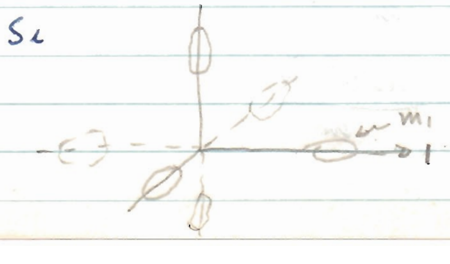
$$|\nabla_p\epsilon| = \sqrt{\left(\frac{p_1}{m_1}\right)^2 + \left(\frac{p_2}{m_2}\right)^2 + \left(\frac{p_3}{m_3}\right)^2} = 2\epsilon\sqrt{\frac{\cos^2\theta}{a^2} + \frac{\sin^2\theta}{b^2}}$$

Surface Element $= (a^2\sin^2\theta + b^2\cos^2\theta)^{1/2}\, b\sin\theta\, d\theta\, d\varphi$

$\tau(p) = \tau(\epsilon)$

$$\sigma_{11} = -\frac{2e^2}{h^3}\int d\epsilon\,\frac{\partial f_0}{\partial \epsilon}\,\tau(\epsilon)\,\frac{4\pi}{3}\,2^{3/2}\,\frac{(m_1 m_2^2)^{1/2}}{m_1}\,\epsilon^{3/2}$$

This contribution to conductivity is from one of the ellipsoids: the total contribution can be written:



$$\sigma_{11}^{total} = \frac{-2e^2}{h^3}\int d\epsilon\,\frac{\partial f_0}{\partial \epsilon}\,\tau(\epsilon)\,\frac{4\pi}{3}\,2^{3/2}\,\frac{(m_1 m_2^2)^{1/2}}{m_1}\,\epsilon^{3/2}\left\{\frac{2}{m_1} + \frac{4}{m_2}\right\}$$

If in the spherical case, we get same if we take:

$$\frac{1}{m'_{eff}} = \frac{1}{3}\left(\frac{1}{m_1} + \frac{2}{m_2}\right)$$ (conductivity effective mass)

$\left(\frac{m_1 m_2^2}{m_1}\right)^{1/2}$ is called density of states effective mass. Expression for 6e not easy to obtain but same result is obtained.

Particularize to case of Boltzmann Statistics:

$$f_0 = e^{\frac{\epsilon_F - \epsilon}{kT}} \; ; \quad \frac{\partial f_0}{\partial \epsilon} = -\frac{1}{kT} e^{\frac{\epsilon_F - \epsilon}{kT}}$$

no. of electrons $= 2\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2} e^{\epsilon_F/kT}$; $\epsilon_0 = 0$

set $x = \frac{\epsilon}{kT}$

Then: $$\sigma_{\parallel} = \frac{e^2 n_0}{m'} \frac{4}{3\sqrt{\pi}} \int_0^\infty \tau(\epsilon)\, x^{3/2} e^{-x}\, dx$$

n_0 = Total no. of electrons.

$\sigma = n_0 e \mu$; $\mu_{\parallel} = \frac{e}{m'} \langle \tau \rangle$. Then:

$$\boxed{\langle \tau \rangle = \frac{4}{3\sqrt{\pi}} \int_0^\infty e^{-x} x^{3/2} \tau(\epsilon)\, dx}$$

Consider some solution of the scattering problem; to get $\tau(\epsilon)$:

(1) $\tau = \tau_0$ (constant)

$$\langle \tau \rangle = \frac{4}{3\sqrt{\pi}} \tau_0 \int_0^\infty e^{-x} x^{3/2}\, dx = \frac{4}{3\sqrt{\pi}} \tau_0 \Gamma\left(\frac{5}{2}\right)$$

$= \tau_0$ since:

$\Gamma(p) = (p-1)\Gamma(p-1)$ $\quad \Gamma(\frac{1}{2}) = \sqrt{\pi}$

$\Gamma(\frac{5}{2}) = \frac{3}{4}\sqrt{\pi}$

$\Gamma(2) = 1$

$\Gamma(1) = 1$

$\Gamma(\frac{3}{2}) = 1/2\sqrt{\pi}$

$$\mu = \frac{e}{m'} \tau_0$$

$$\sigma = \frac{n_0 e^2 \tau_0}{m'}$$

(2) $\tau(\epsilon) = \frac{l_0}{kT} \epsilon^{-p}$ p is number

$$\langle \tau \rangle = \frac{4}{3\sqrt{\pi}} (kT)^{-p} \int_0^\infty \frac{l_0}{kT} e^{-x} x^{3/2} x^{-p} dx$$

$$= \frac{4}{3\sqrt{\pi}} kT^{-(1-p)} l_0 \Gamma(\tfrac{5}{2} - p)$$

For longitudinal waves, $p = 1/2$

$$\langle \tau \rangle = \frac{4}{3\sqrt{\pi}} l_0 kT^{-3/2}$$

or $\mu = \frac{4e}{3\sqrt{\pi}\, m'} l_0 (kT)^{-3/2}$

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$$\langle \tau \rangle = \frac{4}{3\sqrt{\pi}} \int_0^\infty e^{-x} x^{3/2} \tau(\epsilon) dx$$

For ionized impurities - simplest form: $\tau = l_0 \epsilon^{3/2}$

$$\langle \tau \rangle = \frac{4(kT)^{3/2}}{3\sqrt{\pi}} \int_0^\infty e^{-x} x^{3/2} l_0 x^{3/2} dx = \frac{4}{3\sqrt{\pi}} (kT)^{3/2} l_0 \, 6$$

$$= \frac{8}{\sqrt{\pi}} l_0 (kT)^{3/2}$$

$$\frac{1}{\tau(\epsilon)_{TOT}} = \frac{1}{\tau_1(\epsilon)} + \frac{1}{\tau_2(\epsilon)} + \dots$$

$$\frac{1}{\mu_{TOT}} = \frac{1}{\mu_1} + \frac{1}{\mu_2} + \dots$$

$$\frac{1}{\sigma} = \frac{1}{\sigma_1} + \frac{1}{\sigma_2} + \dots$$

Must watch addition laws as they may not hold if scattering is evenly divided among several mechanisms.

Galvanomagnetic Effects:

Reference: Brook's article

Take field in x direction:

$$\left.\begin{aligned} \dot{v}_x &= \frac{e}{m} E_x + \frac{e}{mc} H_z v_y \\ \dot{v}_y &= \frac{e}{m} E_y - \frac{e}{mc} H_z v_x \end{aligned}\right\} \quad \omega = \frac{e H_z}{mc}$$

$$\dot{v}_x + i\dot{v}_y = \frac{e}{m}(E_x + iE_y) - i\omega(v_x + iv_y)$$

$$v_x + iv_y = A e^{-i\omega t} + \frac{\frac{e}{m}(E_x + iE_y)}{i\omega}$$

At $t=0$, $v_x + iv_y = (v_x + iv_y)_0$ which averages out in final result.

$$v_x + iv_y = e^{i\omega t}\left\{(v_x + iv_y)_0 - \frac{e}{m}\frac{E_x + iE_y}{i\omega}\right\} + \frac{e}{m}\frac{E_x + iE_y}{i\omega}$$

Acquired $v_x + iv_y = \frac{e}{i\omega m}(E_x + iE_y)(1 - e^{-i\omega t})$

We first average over initial velocities.

The probability that an electron has lasted a time t is $\frac{1}{\tau(t)} e^{-t/\tau(t)}$

Average acquired velocity for particles of same starting velocity is:

$$\int_0^\infty \frac{1}{\tau(t)} e^{-t/\tau} \frac{e}{i\omega m}(E_x + iE_y)(1 - e^{-i\omega t})\,dt$$

$$\bar{v}_x + i\bar{v}_y = \frac{e}{m}(E_x + iE_y)\frac{\tau}{1 + i\omega\tau}$$

This must now be averaged over all electrons and all initial velocities.

This is not a trivial calculation as must use $\int_0^\infty e^{-x} x^{3/2} \tau \, dx$. See Dingle, Physica, Aug. 1956.

We will have then for the current:

$$\bar{J}_x + i\bar{J}_y = \frac{ne^2}{m}(E_x + iE_y)\left\langle \frac{\tau}{1+i\omega\tau} \right\rangle_{AV}$$

Now: $\left\langle \frac{\tau}{1+i\omega\tau} \right\rangle = \left\langle \frac{\tau}{1+\omega^2\tau^2} \right\rangle - i\omega \left\langle \frac{\tau^2}{1+\omega^2\tau^2} \right\rangle$

Then:

$$\bar{J}_x = \frac{ne^2}{m}\left[E_x \left\langle \frac{\tau}{1+\omega^2\tau^2} \right\rangle + E_y \omega \left\langle \frac{\tau^2}{1+\omega^2\tau^2} \right\rangle \right]$$

$$\bar{J}_y = \frac{ne^2}{m}\left[E_y \left\langle \frac{\tau}{1+\omega^2\tau^2} \right\rangle - E_x \omega \left\langle \frac{\tau^2}{1+\omega^2\tau^2} \right\rangle \right]$$

If we take as boundary condition that $\bar{J}_y = 0$

$$\frac{E_y}{E_x} = \frac{\omega \left\langle \frac{\tau^2}{1+\omega^2\tau^2} \right\rangle}{\left\langle \frac{\tau}{1+\omega^2\tau^2} \right\rangle}$$

$$\therefore \bar{J}_x = \frac{ne^2}{m} E_x \left[\left\langle \frac{\tau}{1+\omega^2\tau^2} \right\rangle + \frac{\omega^2 \left\langle \frac{\tau^2}{1+\omega^2\tau^2} \right\rangle^2}{\left\langle \frac{\tau}{1+\omega^2\tau^2} \right\rangle} \right]$$

(a) Constant τ_0: $\frac{E_y}{E_x} = \omega\tau_0$

$$\bar{J}_x = \frac{ne^2}{m} E_x \tau_0$$

Under this case there is no magnetoresistance.

(b) $\omega\tau \ll 1$: $E_y = \omega \frac{\langle \tau^2 \rangle}{\langle \tau \rangle} E_x = \frac{eH_z}{mc} \frac{\langle \tau^2 \rangle}{\langle \tau \rangle}$

$$\cdot \frac{m J_x}{ne^2 \langle \tau \rangle} = \frac{1}{nec} \frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} H_z J_x = R_H H_z J_x$$

Therefore: $R_H = \frac{1}{nec} \frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2}$

which is different from metals. Usually have spread in τ but usually $\frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2}$ is close to 1, and gives at least the right order of magnitude of carrier density.

(c) If we can identify the scattering mechanism:

$$\tau = a\,\epsilon^{-1/2} \; ; \quad \frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} = \frac{3\pi}{8} \approx 1.17$$

However, this is not usually the case in Germanium and Silicon

(d) For ionized impurity scattering: $\tau \sim \epsilon^{3/2}$ get:

$$\frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} = \frac{315\,\pi}{512}$$

(e) Note: $R_H = \frac{1}{nec} \frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2}$; $\sigma = \frac{ne^2}{m} \langle \tau \rangle$

$R_H \sigma = \frac{e}{mc} \frac{\langle \tau^2 \rangle}{\langle \tau \rangle}$ called Hall mobility

This is usually not the same as the drift mobility.

More than one type of current carrier present:

$$\bar{J}_x + i \bar{J}_y = (E_x + i E_y) \sum_i \frac{n_i e_i^2}{m_i} \left\langle \frac{\tau_i}{1 + i \omega_i \tau_i} \right\rangle$$

with $\omega_i = \frac{e_i H_z}{m_i c}$

Special case: $\frac{e_i H_z \tau_i}{m_i c} = \omega_i \tau_i \ll 1$ for all i.

Call $\frac{e_i \tau_i}{m_i} = \mu_i$ (unaveraged)

$$\bar{J}_x = E_x \sum_i |e|\, n_i \langle \mu_i \rangle + E_y \sum_i n_i \langle \mu_i^2 \rangle \frac{e_i H}{c}$$

Boundary condition: $\bar{J}_y = 0 = - E_x \sum_i \frac{n_i e_i}{c} H \langle \mu_i^2 \rangle$

$+ E_y \sum_i n_i |e| \langle \mu_i \rangle$

Then: $$R_H = \frac{E_y}{H J_x} = \frac{\sum_i n_i \frac{e_i}{c} \langle \mu_i^2 \rangle}{\left[\sum_i n_i |e| \langle \mu_i \rangle \right]^2}$$

Suppose electrons and holes, one type of each.

$$R_H = \frac{1}{ec} \left[\frac{p \langle \mu_p^2 \rangle - n \langle \mu_n^2 \rangle}{(p \langle \mu_p \rangle + n \langle \mu_n \rangle)^2} \right]$$

Could write expression for two types of holes in valence band. Note that because of $\langle \mu \rangle^2$, low carrier concentrations can still lead to the high R_H. Happens with light mass holes in valence band of Ge which can lead to error of 2 in R_H if present in concentration of only 2%.

Have not considered:
- Magnetoresistance
- High Fields
- Ellipsoidal Energy Surfaces.

Will find this in book by Smith or articles by Brooks.

LECTURE XLII 5-20-61

Boltzmann Equation: calculation for specific type of scattering:

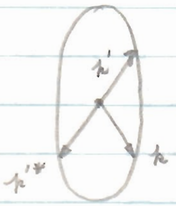
Reference: C. Herring and E. Vogt, P.R. 101, 944 (1956)

Randomizing Mechanisms;
Energy Conserving Mechanisms:

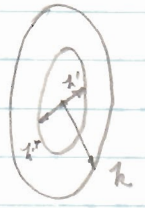
$$\frac{\partial f(k)}{\partial t} = \left.\frac{\partial f(k)}{\partial t}\right|_{\text{field}} + \int\left\{ f(k')\, S(k' \to k) - f(k)\, S(k \to k') \right\} dk'$$

S is scattering mechanism.

$$S(k \to k') = S(k \to k'^{*}) = S(k^{*} \to k')$$



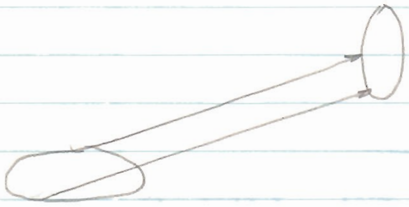
Energy
Conserved



Energy
not Conserved

k^{*} is same magnitude as k but opposite in direction

Get for above integral; $\dfrac{f(k) - f_0(k)}{\tau}$



Ellipsoids are so small that wave vectors between them can be considered the same.

All scattering except electron-electron can be described by the two above mechanisms.

We now transform the ellipsoids into spheres and then expand everything in Boltzmann equation in terms of spherical harmonics.

$$f_1 = f - f_0 = \sum_{l,m} F_{lm}(q)\, Y_{lm}(\Phi/\varphi)$$

$$q_\alpha = \frac{\hbar\,(k_\alpha - k_\alpha^{(\alpha)})}{(m_\alpha^*)^{1/2}} \quad ; \quad \Delta\epsilon = \frac{1}{2} q^2$$

$$\frac{1}{2} q_\alpha^2 = \frac{\hbar^2}{2 m_\alpha^*} (k_\alpha - k_\alpha^{(\alpha)})^2$$

$$\left.\frac{\partial F_{lm}}{\partial t}\right|_{\text{scattering}} = \sum_{l'm'} (lm|s|l'm')\, F_{l'm'}(q)$$

$$\left.\frac{\partial F_{lm}}{\partial t}\right|_{\text{field}} = \text{elect. Field} + \sum_{m'} C_{mm'} F_{lm'}$$

from : $\left.\frac{\partial f}{\partial t}\right|_{\text{field}} = e E_\alpha \frac{\partial f_0}{\partial q_\alpha} \longrightarrow F_{1m}$

The effect of the magnetic field on F_0 is zero but on higher terms conserves l. We assume that distribution F_{lm} contains only $l = 1$ or independent of scattering so only have left matrix elements.

Take then:

F_{1x} have symmetry like $\sin\theta \cos\varphi$

F_{1y} " $\sin\theta \cos\varphi$

F_{1z} " $\cos\theta$

$$f_1 = F_{1x} \sin\theta\cos\varphi + F_{1y} \sin\theta \sin\varphi + F_{1z} \cos\theta$$

$$\left.\frac{\partial F_{1x}}{\partial t}\right|_{\text{scattering}} = (1x|s|1x)\, F_{1x} + (1y|s|1y)\, F_{1y} + (1z|s|1z)\, F_{1z}$$

$$\frac{\partial F_{1x}}{\partial t} = -\frac{F_{1x}}{\tau_x} = -F_{1x}\left\{ \frac{1}{\tau_{rx}} + \frac{1}{\tau_{cx}} \right\}$$

r - random

c - conserved

$$\frac{1}{\tau_{rx}} = \frac{\iint \varphi_x^2 \, S_r(\varphi \to \varphi') \, d\Omega_{\varphi'} \, d\Omega_\varphi}{\int \varphi_x^2 \, d\Omega_\varphi}$$

$$\frac{1}{\tau_{cx}} = \frac{\iint \varphi_x (\varphi_x - \varphi_x') \, S_c(\varphi \to \varphi') \, d\Omega_{\varphi'} \, d\Omega_\varphi}{\int \varphi_x^2 \, d\Omega_\varphi}$$

now equate this to field term. Can be done from equations for spherical case, with appropriate changes:

$$\mu_{\alpha\alpha} = \frac{e}{m_\alpha} \frac{\langle \Delta\epsilon \, \tau_\alpha \rangle}{\langle \Delta\epsilon \rangle} \equiv \frac{e}{m_\alpha} \langle \tau_\alpha \rangle$$

$\frac{\tau_\alpha}{m_\alpha}$ replaces $\frac{\tau}{m}$ for spherical case.

For Hall Effect:

$$\frac{\mu_H}{\mu} = \frac{3\left\{ 2 \frac{\langle \tau_\parallel \tau_\perp \rangle}{m_\parallel m_\perp} + \frac{\langle \tau_\perp^2 \rangle}{m_\perp^2} \right\}}{\left(\frac{\langle \tau_\parallel \rangle}{m_\parallel} + 2 \frac{\langle \tau_\perp \rangle}{m_\perp} \right)^2}$$

LECTURE XLIII 5-23-61

Acoustical scattering : Schockley, Bardeen, PR 80, 72 (1950)

$$f - f_0 = \sum_{lm} F_{lm}(\varphi)\, Y_{lm}(\varphi)$$

$$\varphi_\alpha = \frac{\hbar\,(k_\alpha - k_\alpha^{(i)})}{m_\alpha^{1/2}}$$

$$\left.\frac{\partial F_{1\alpha}}{\partial t}\right]_{\text{scattering}} = -F_{1\alpha}\,\varphi\left(\frac{1}{\tau_{\Lambda x}} + \frac{1}{\tau_{cx}}\right)$$

Today we consider scattering that conserves energy, or scattering about a constant energy ellipsoid, not from one to another.

$$\frac{1}{\tau_{c\alpha}(\varphi)} = \frac{\iint \varphi_\alpha(\varphi_\alpha - \varphi_{\alpha'})\, S_c(\varphi - \varphi')\, d\Omega_{\varphi'}\, d\Omega_\varphi}{\int \varphi_\alpha^2\, d\Omega_\varphi}$$

Equation (11) in Herring and Vogt.

$$S_c(\varphi \to \varphi') = \frac{2\pi}{\hbar}\Big(\sum_{\text{branches}} |M|^2\Big)\, \underset{\substack{\downarrow \\ \text{conservation} \\ \text{of energy}}}{\delta(\epsilon' - \epsilon)}\, dV_{\varphi'}\, \underset{\substack{\downarrow \\ \text{number of states in} \\ \text{a unit volume of} \\ \varphi \text{ space}}}{N_1}$$

Now: $$dV_{\varphi'} = \frac{dS_{\varphi'}}{|\nabla_\varphi \epsilon'|}\, d\epsilon$$

$$dS_\varphi = \varphi^2\, d\Omega_\varphi \quad ; \quad |\nabla_\varphi \epsilon'| = \varphi \text{ from } \Delta\epsilon = \tfrac{1}{2}\varphi^2$$

Then:

$$S_c(\varphi \to \varphi') = \frac{2\pi}{\hbar}\Big(\sum |M|^2\Big)\, N_1\, \varphi'\, d\Omega_{\varphi'}$$

To find N_1, take sphere in φ space, radius φ_0. Ellipsoidal semi-axes in k space are

$$\frac{m_\alpha^{1/2}\varphi_0}{\hbar}$$

The volume of this ellipsoid is $\frac{4\pi}{3}\frac{\varphi_0^3}{\hbar^3}(m_1 m_2 m_3)^{1/2}$

No. of states (unit volume of k space) $= \frac{1}{8\pi^3}$

Volume of φ space $= \frac{4}{3}\pi\varphi_0^3$

$$N_1 = \frac{1}{8\pi^3\hbar^3}(m_1 m_2 m_3)^{1/2}$$

$$\varphi' = (2\Delta\epsilon)^{1/2}$$

$$\therefore \quad S_c(\varphi \to \varphi') = C\left(\Sigma |M|^2\right)(\Delta\epsilon)^{1/2}$$

$$C = \frac{(m_1 m_2 m_3)^{1/2} V}{2^{3/2}\pi^2\hbar^4}$$, V is unit of crystal volume

Deformation Potential Theory:

Valid when considering long wavelengths so that small regions are homogeneously strained. However in going from one region we stipulate that a change in lattice constant occurs. These regions are big enough for Bloch functions to exist. The change in the band edge can be written:

$$\delta\epsilon = \sum_{s=1}^{6} \Xi_s u_s$$

s is one of six stain directions.

Ξ_s is the deformation potential, u_s = strain Eq.

We can get $V(r)$ which is change in lattice potential due to shift in band edge.

Now:

$$M = \int u^*(k',r)\,e^{-ik'r}\,V(r)\,u(k,r)\,e^{ikr}\,dr$$

$$= \int e^{-iqr}\sum_{s=1}^{6}\Xi_s u_s(r)\,dr \qquad q = k'-k$$

from $V(r) = \sum_{s=1}^{6} \Xi_s u_s(r)$

$$\int e^{-iq\cdot r} u_s(r) = u_s(q,\alpha)$$

$$M(q\alpha) = \sum_s \Xi_s u_s(q,\alpha)$$

$$|M(q,\alpha)|^2 = \sum_{r,s} \Xi_r \Xi_s \langle u_r(q,\alpha)\, u_s(q,\alpha)\rangle$$

which in equation (44) from Herring and Vogt

We need lattice vibration spectrum to determine deformation potentials by evaluting $\langle\ \rangle$ above and using SE. Get six Ξ.

Let amplitude of vibration $\propto \sqrt{\frac{kT}{2}}$.

Local energy density $= \sum_{r,s} c_{rs} u_r u_s$

$$V \sum_{r,s} C_{rs} \langle u_r(q,\alpha)\, u_s(q,\alpha)\rangle = kT \qquad (43)$$

$$u_r(q,\alpha) = A(q,\alpha) \underbrace{f_r(q,\alpha)} \qquad (42)$$

polarization factors which are known if spectrum is known.

From (43):

$$V[A(q,\alpha)]^2 \sum_{r,s} C_{rs} f_r f_s = kT$$

or $$[A(q,\alpha)]^2 = \frac{kT}{V} \frac{1}{\sum_{r,s} C_{rs} f_r f_s}$$

$$[M(q,\alpha)]^2 = \frac{kT}{V} \frac{1}{\sum_{r,s} f_r f_s C_{rs}} \sum_{r,s} \Xi_r \Xi_s f_r f_s \qquad (44)$$

Can redefine deformation potentials to fit better into ellipsoid model: For (111) direction:

$$\Xi_{1,2,3} = \Xi_d + \frac{1}{3}\Xi_u$$

$$\Xi_{456} = \frac{1}{3}\Xi_u$$

Values of $|M(\alpha, q)|^2$ is given in Herring and Vogt. Will not do averaging here, see H and V. We will look at results.

Can describe τ along directions of effective mass, so would have $\frac{1}{\tau_\parallel}$ and $\frac{1}{\tau_\perp}$.

$$\frac{1}{\tau_\parallel} = \frac{3\pi C kT (\Delta\epsilon)^{1/2}}{V c_l}\left[\xi_\parallel \Xi_d^2 + \eta_\parallel \Xi_d \Xi_u + \zeta_\parallel \Xi_u^2\right]$$

$$\frac{1}{\tau_\perp} = \quad '' \quad \left[\xi_\perp \Xi_d^2 + \text{etc.}\right.$$

ξ, η, ζ are numerical coefficients obtained from averaging over angular directions.

In Ge: $\frac{1}{\tau_\parallel} \simeq \frac{1}{\tau_\perp}$

but Herring and Vogt point out that this is accident and could very well have turned out different.

JONES: ORTHOGONALIZED PLANE WAVE METHOD (OPW)

This approximation involves the correction of the free electron wave function near an atomic core in the lattice by the subtraction of the core wave functions expressed as Bloch functions, that is:

(1) $\psi(K,k,r) = e^{i(k+K)\cdot r} - \sum_n \mu_n(K)\, b_n(k,r)$

We assume that:

(2) $\int b_{n'}^*(k,r)\, b_n(k,r)\, d^3r = \delta_{nn'}$

The $\mu_n(K)$ can be determined by making $\psi(K,k,r)$ and $b_n(k,r)$ orthogonal. The sum on n is a sum of all the core states lower than the valence band.

(3) $\int b_n^*(k,r)\, \psi(K,k,r)\, d^3r = 0$

or $\int b_n^*(k,r)\, e^{i(k+K)\cdot r}\, d^3r - \sum_n \int b_n^*(k,r)\, \mu_n(K)\, b_n(k,r)\, d^3r = 0$

(4) $\mu_m(K) = \int b_n^*(k,r)\, e^{i(k+K)\cdot r}\, d^3r$

We take the $\psi(K,k,r)$ to form a complete set in K on the reciprocal lattice and may expand the desired wave function in terms of them; and then regard this as a variation function upon which the Hamiltonian will act and whose resultant energy will be minimized after the operation by minimizing with respect to the variation parameter which is the coefficient in the following expansion:

(5) $\Psi(k,r) = \sum_K \beta(K)\, \psi(K,k,r)$

As the terms in the sum are increased, the expansion converges to the correct value of the wave function.

It should be noted that $\psi(K,h,r)$ and $\psi(K';h,r)$ are not orthogonal, that is:

(6) $\int \psi^*(K';h,r)\,\psi(K,h,r)\,d^3r$

$$= \int \psi^*(K';h,r)\,e^{i(h+K)\cdot r}\,d^3r - \sum_n u_n(K)\int \psi^*(K';h,r)\cdot b_n(h,r)\,d^3r$$

$$= \int e^{-i(h+K)\cdot r}\,e^{i(h+K)\cdot r}\,d^3r - \int \sum_{n'} u^*_{n'}(K')\,b^*_{n'}(h,r)\,e^{i(h+K)\cdot r}\,d^3r$$

$$- \int \sum_n u_n(K)\,b_n(h,r)\,e^{-i(h+K')\cdot r}\,d^3r$$

$$+ \int \sum_{nn'} u^*_{n'}(K')\,u_n(K)\,b^*_{n'}(h,r)\,b_n(h,r)\,d^3r$$

Recall: $u_n(K) = \int b^*_n(h,r)\,e^{i(h+K)\cdot r}\,d^3r$

$u^*_n(K) = \int b_n(h,r)\,e^{-i(h+K)\cdot r}\,d^3r$

Then, if $K \neq K'$:

(7) $\int \psi^*(K';h,r)\,\psi(K,h,r)\,d^3r = -\sum_{n'} u^*_{n'}(K')\,u_{n'}(K)$

$$- \sum_n u_n(K)\,u^*_n(K') + \sum_n u^*_n(K')\,u_n(K)$$

$$= -\sum_n u^*_n(K')\,u_n(K) \equiv A_{KK'}$$

Now the variational principle requires that:

(8) $\delta \int \Psi^*(h,r)\{H-\epsilon\}\Psi(h,r)\,d^3r = 0$

(9) $\int \Psi^*(h,r)\{H-\epsilon\}\Psi(h,r)\,d^3r$

$$= \int \sum_{K'} \beta^*(K')\,\psi^*(K';h,r)\{H-\epsilon\}\sum_K \beta(K)\,\psi(K,h,r)\,d^3r$$

$$= \sum_{KK'} \int \Big\{ \beta^*(K')\beta(K)\,\psi^*(K';h,r)\,H\,\psi(K,h,r)$$

$$- \epsilon\,\beta^*(K')\beta(K)\,\psi^*(K';h,r)\,\psi(K,h,r)\Big\}\,d^3r$$

$$(9) \quad \int \Psi^*(k,r)\left\{H-\epsilon\right\}\Psi(k,r)\,d^3r$$

$$= \sum_{KK'} \beta^*(K')\beta(K)\left\{\int \psi^*(K',k,r)\,H\,\psi(K,k,r)\,d^3r - \epsilon\int \psi^*(K',k,r)\,\psi(K,k,r)\,d^3r\right\}$$

$$= \sum_{KK'} \beta^*(K')\beta(K)\left\{H_{KK'} - \epsilon A_{KK'}\right\}$$

where $H_{KK'} = \int \psi^*(K',k,r)\,H\,\psi(K,k,r)\,d^3r$

We now perform the variation with respect to $\Psi^*(k,r)$:

$$(10) \quad \delta\Psi = \sum_K \delta\beta(K)\,\psi(K,k,r)$$

$$(11) \quad \delta\int \Psi^*\left\{H-\epsilon\right\}\Psi\,d^3r$$

$$= \sum_{K'} \delta\beta^*(K')\sum_K \beta(K)\left\{\ \right\} + \sum_K \delta\beta(K)\sum_{K'}\beta(K')\left\{\ \right\} = 0$$

Thus, since the coefficient of each variation must vanish,

$$(12) \quad \sum_K \beta(K)\left\{H_{KK'} - \epsilon A_{KK'}\right\} = 0, \quad K' = 1, 2, 3, \ldots$$

Hence the determinant of the coefficients of $\beta(K)$ must vanish.

$$(13) \quad \det\left|H_{KK'} - \epsilon A_{KK'}\right| = 0$$

It is seen that the number of terms in this determinant (order of K, K') determines the accuracy of the result and a perfect result is in theory obtainable if an infinite number of terms is considered. The usual practice is to express the Bloch functions in terms of the LCAO approximation as follows:

$$(14) \quad b_n(k,r) = \sum_l e^{ik\cdot R_l}\,a_n(r-R_l)$$

The φ_n's are the orbital wave functions. We now have all the information needed to solve the determinant (13) for the band structure.

Difficulties of the OPW method:

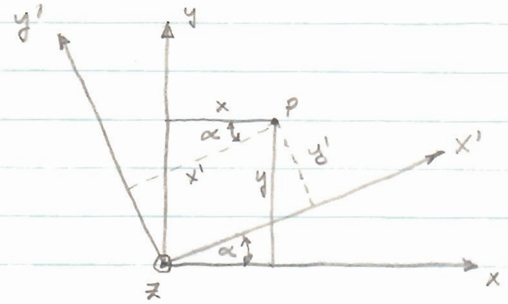
1) Cannot use Hartree functions for the core orbitals as they are not orthogonal, and thus many terms in the variational function are required.
2) A difficulty arises at symmetry points of the BZ where the plane waves are symmetrized and the μ's vanish. Then it is the usual practice to choose the form of the trial function to approach, near the nuclei, the expected crystal wave function, instead of making them orthogonal.

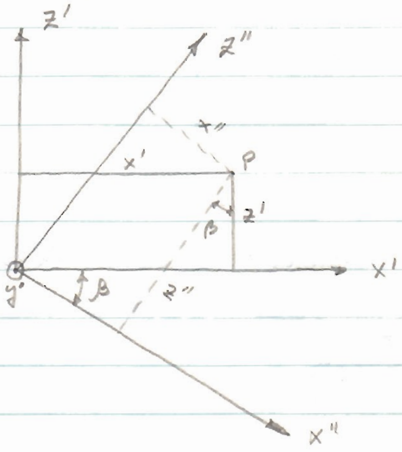
NOTES ON GROUP THEORY FROM JONES

Space Group: The space group of a particular crystal is defined as the product of the translation group with the complex of operations of rotation, reflection, glide reflections and screw displacements.

Point Group: The point group is defined as the complex of above operations multiplying the translation group when it contains only rotation and reflection operations.

Consider the following rotation operations:



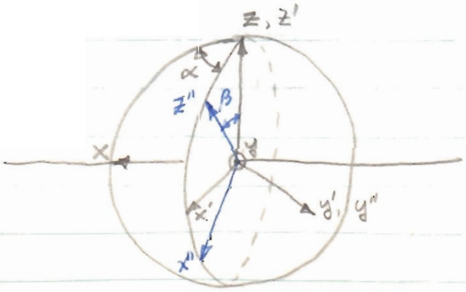


$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} = \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$$

or:

$$\begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} = \underbrace{\begin{pmatrix} \cos\alpha\cos\beta & \sin\alpha\cos\beta & -\sin\beta \\ -\sin\alpha & \cos\alpha & 0 \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix}}_{R} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$



In the original rectangular coordinate system a lattice point was specified by a vector An:

$$An = \begin{pmatrix} a_{1x} & a_{1y} & a_{1z} \\ a_{2x} & a_{2y} & a_{2z} \\ a_{3x} & a_{3y} & a_{3z} \end{pmatrix} \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix}$$

In the new coordinate system, the same point is: $A'n$ where $A' = RA$.

Now rotate the crystal thru an angle γ about Oz''; by applying the matrix S on $A'n$,

$$S = \begin{pmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

We show that this is a rotation of the crystal and not the coordinate system by writing:

$$SA'n = A'n'$$

If n' is an integral vector like n, then the rotation through γ about Oz' is a symmetry operation of the crystal lattice.

We now transform back the coordinate system to its original position by applying R^{-1}:

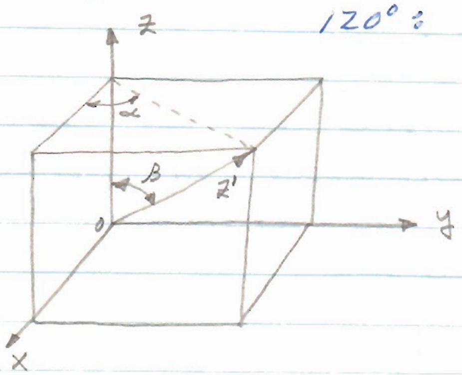
$$(R^{-1}SR)An = An' \quad \text{or} \quad (R'SR)An = An'$$

since R is orthogonal. Thus the matrix specifying a rotation about any axis can be found from R and S.

The matrix of a reflection in a plane thru the origin at right angles to the directions specified by α and β is $R'MR$ where:

$$M = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Examples: rotation around cube diagonal of 120°:



$\alpha = 45°$

$\cos\beta = 1/\sqrt{3}$

$\gamma = 120°$

$$R'SR = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

For the reflection in the plane $x = -z$, $\alpha = 0$, $\beta = 45°$ and:

$$R'MR = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$$

Important: Both of these operations belong to the point group of the cubic system.

That is, given the matrix A of that system, solutions of:

$$(R'SR)\,An = An'$$

when both n and n' have integer values.

An improper rotation is defined as a rotation about a particular axis and a reflection in the plane perpendicular to that axis and the matrix is given by:

$$R'(MS)R$$

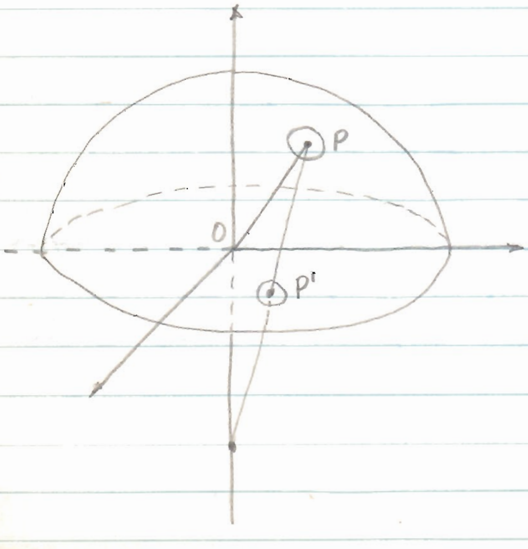
The traces are the same for all rotation matrices (independent of α, β) and are equal to: $1 + 2\cos\gamma$. The traces of all reflection matrices are equal to $+1$.

The point groups determined by taking into account only the nature of the translation lattice are known as the holosymmetric point groups.

The order of a group is defined as the number of symmetry operations it contains. In the cubic system the holosymmetric point group is of order 48.

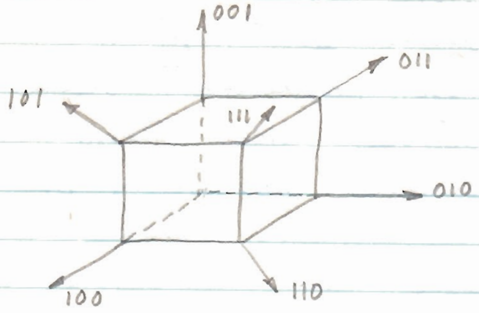
Stereographic Projections:

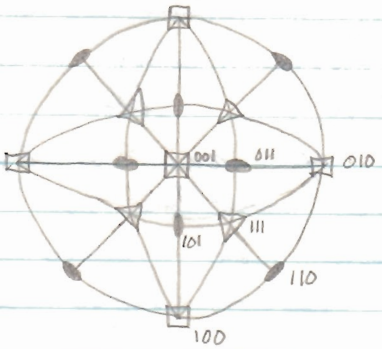
One can represent as points on a plane different directions in space by circumscribing a unit sphere about the system of direction axes and projecting the intersections of the space directions with the sphere onto the equatorial plane of the sphere via a polar line intersection with this plane which connects a pole of the sphere to the desired intersection of direction and sphere surface.



A small circle in the plane ⊥ to OP about P is projected as a small circle about P' on the equatorial plane, although not with P' as center. Thus, rotations about a symmetry axis can be represented as circles in the stereogram.

Stereogram of a Cube:





The multiplication table of the point group defines the results of successive applications of the symmetry operations of the point group in terms of the basic symmetry operations of the group.

The Regular Representation:

If we take any solution of the equation:

$$\left(H_0 + \frac{\hbar}{m} k\cdot p\right) u_n(k,r) = \epsilon_n(k)\, u_n(k,r)$$

that does not possess any particular symmetry about $k=0$, and operate on it with all the symmetry operations of the point group, we will generate a series of g functions, where g is the order of the group, which yield the same eigenvalues as above.

It is now desirable to find linear combinations of these new wave functions such that Bloch functions of a specific symmetry can be constructed. If we take as one the sum of all the new wave functions, this one is invariant under any operation of the group and thus corresponds to an atomic s-state.

Construction of other symmetries is more difficult. Consider operating on each one of the new wave functions with an element

element of the group, considering the set of wave functions as a column vector. The result is obviously the same set of wave functions, but arranged in different order or permuted. These permutations can then be thought of as g by g matrices operating on the column vector of wave functions. These matrices can be seen to contain all 0's and one 1 in each row and column.

The representation of the group by these matrices is called the regular representation (after regular permutations, Cayley). Obviously, the trace is either zero for the general matrix or g for the identity.

Class:

A class is a complex of operations determined as follows: Take A as an operation of the point group. Form $X^{-1}AX$ where X is an operation of the point group. The set of operations formed when X takes on all operations of the point group in turn form a class. For example, if A represents a rotation C_3 about a triad axis of the holosymmetric cubic point group, then $X^{-1}AX$ will be a rotation about another triad axis and the totality of operations $X^{-1}AX$ will form the class $8C_3$, 8 because of symmetry rotations $2\pi/3$ and $-2\pi/3$. Some of the operations may be repeated, that is, $X^{-1}AX = A$ occurs. If there are, say, h_c different operations, then each one will be repeated g/h_c times. In the above example $g = 48$ so each element of the class will be repeated 6 times.

Important: When the operations of a group are represented by matrices, the traces of the matrices of a given class are all equal.

That this is true follows directly from the fact that a similitude transformation leaves the trace invariant. Also, it is known that the trace of a matrix of equivalent rotation about any axis independent of its direction is the same as other matrices of rotation regardless of the sense of rotation and the direction of the axis. This is another motivation for the fact the trace of the operations of a class is a constant.

If we denote a class by the symbol C_i and represent it by a sum of its constituent operations, then clearly:

$$C_i = \frac{h_i}{g} \sum_X X^{-1} A X$$

and also a transformation of the entire class by an operation of the point group leaves the class invariant;

$$X^{-1} C_i X = C_i$$

Since this is possible for any class, the classes commute amongst themselves:

$$C_i C_j = C_j C_i$$

Irreducible Forms: Group Characters

The regular representation consists of g matrices, $g \times g$, each representing an operation of the point group. Each matrix permutes the wave functions at $k = 0$ into a different arrangement.

Since the operations of the point group do not commute, each matrix of the regular representation cannot be brought into diagonal form by the same similitude transformation.

However, the following form can be found for each member of the regular representation:

$$\begin{pmatrix} \times & & & & & & & & \\ & \times & & & & & 0 & & \\ & & \times & \times & & & & & \\ & & \times & \times & & & & & \\ & & & & \times & \times & & & \\ & & & & \times & \times & & & \\ & 0 & & & & & \times & \times & \times \\ & & & & & & \times & \times & \times \\ & & & & & & \times & \times & \times \end{pmatrix}\ddots$$

A single diagonal element implies a wave function which is a linear combination of the ψ's which transforms into plus or minus itself under the operations of the point group. The 2×2 sub-matrix implies that two linear combinations of the ψ's exist such that they transform either into themselves or each other under the operations of the point group. Thus the two linear combinations must be Bloch waves and degenerate at $k=0$. This degeneracy depends only on the crystal symmetry and not on the form of the potential (example, degeneracy with respect to magnetic quantum number in a central field of force).

The above sub-matrices are called <u>irreducible representations</u>. For the crystallographic group, the order of a sub-matrix is never greater than three.

It is necessary to distinguish between equivalent and inequivalent sub-matrices. Equivalent sub-matrices can be transformed into each other and thus their traces are equal.
In the holosymmetric cubic point group, there are four irreducible representations of the third degree. One of these has symmetries of x, y, z. For a particular operation of the group, say a rotation about a diad axis we have $xyz \rightarrow yx\bar{z}$ and the corresponding

matrix is: $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} y \\ x \\ -z \end{pmatrix}$, Tr = -1

For another of the irreducibles of third degree, take for the symmetry of the degenerate wave functions xy, yz, zx , performing the same operation on the group as before, that is, $xyz \rightarrow yx\bar{z}$:

$$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} yz \\ zx \\ xy \end{pmatrix} = \begin{pmatrix} -zx \\ -yz \\ xy \end{pmatrix} \quad , \quad Tr = +1$$

These are thus not equivalent sub-matrices.

Calculation of Character Tables

I. The number of irreducible representations is equal to the number of classes.

II. The number of equivalent matrices of an irreducible representation, in the regular representation, is equal to their degree.

The traces of the matrices of an irreducible representation are called the *characters*. A character is represented by the symbol χ_i^ν where ν is the irreducible representation and i the class of the operation to which the matrix refers. All operations of one class have the same character. It will be found that a knowledge of the characters is sufficient to obtain the symmetry types.

In any irreducible representation, the matrix which represents the identity matrix is the unit matrix. The character of the νth irreducible representation is χ_E^ν and is seen to be the order of this matrix. Because of II, the number of diagonal places occupied in the regular representation by the equivalent matrices of the νth irreducible representation is the order of the νth matrix squared, or in the terms of the characters: $(\chi_E^{\nu})^2$ since the number of diagonal elements and the order of the regular representation are equal, we have, using I:

$$(\chi_E^{1})^2 + (\chi_E^{2})^2 + \cdots + (\chi_E^{r})^2 = g$$

where r is the number of classes: For the holosymmetric cubic point group, there are 10 classes and the order of the group is 48. It is easily verified that:

$$1^2 + 1^2 + 1^2 + 1^2 + 2^2 + 2^2 + 3^2 + 3^2 + 3^2 + 3^2 = 48$$

so that there are four distinct non-degenerate states, two distinct doubly degenerate states and four distinct triply degenerate states.

We now derive relations between the characters of the other classes. Consider a representation where an operation of the group is represented by a set of matrices of the degree χ_E^{ν}. Recall the invariant relation of the classes, viz:

$$X^{-1} C_i X = C_i \quad \text{or} \quad C_i X = X C_i$$

thus C_i must be represented by a diagonal matrix with constants in the diagonal. Let each element be denoted by x_i^{ν} and the trace of each operator in the class will be χ_i^{ν} and the trace of matrix for the class will be $x_i^{\nu} \chi_E^{\nu}$. However, there are h_i operators in the class, hence the relation:

$$(3.29) \qquad h_i \chi_i^{\nu} = x_i^{\nu} \chi_E^{\nu}$$

and the matrix representing the class can be written:

$$x_i^{\nu} \mathbb{I} = \frac{h_i \chi_i^{\nu}}{\chi_E^{(\nu)}} \mathbb{I}$$

where $\mathbb{I}$ is a unit matrix of order χ_E^{ν}.

Now, it may be shown that the product of two classes may expressed as a linear combination of classes:

$$C_i C_j = \sum_{s=1}^{r} c_{ij,s} C_s$$

where the $c_{ij,s}$ are positive integers or zero. Also, by use of the stereogram, a multiplication table of classes can be constructed which indicates the above relation.

Thus we have between the elements of the class matrix:

$$h_i h_j \chi_i^\nu \chi_j^\nu = \chi_E^\nu \sum_{s=1}^{r} c_{ij,s} h_s \chi_s^{(\nu)}$$

Because we have the results of the multiplication table on hand along with other items, we can consider the only unknowns to be χ_i^ν. We consider the equation in terms of χ_i^ν:

$$\chi_i^\nu \chi_j^\nu = \sum_{s=1}^{r} c_{ij,s} \chi_s^\nu$$

or

$$\sum_{s=1}^{r} \left\{ c_{ij,s} - \delta_{is} \chi_j^\nu \right\} \chi_s^\nu = 0 \quad , \quad i = 1, 2, \cdots r$$

which has non-trivial χ_s^ν only if the determinant of coefficients vanishes:

$$\det \left\{ c_{ij,s} - \delta_{is} \chi_j^\nu \right\} = 0 \quad , \quad i, s = 1, 2, \cdots r$$

Now, the r values of the roots χ_j are the values of the diagonal elements in each of the r irreducible representations. The c_{ij} can be found from the multiplication table for the classes of the group. These roots can be arranged in a column for each class, however, there is as yet no way of telling which root belongs to which irreducible representation.

We now assume the following orthogonality relations among the characters of the different classes and irreducible representations to be true (see Jones for proof).

$$(3.38) \qquad \sum_{\nu=1}^{r} \chi_i^\nu \chi_j^\nu = \begin{cases} 0 & j \neq i' \\ g/h_i & j = i' \end{cases}$$

where i' means the inverse of the operations of the class:

$$C_i = A + B + C + \cdots$$
$$C_{i'} = A^{-1} + B^{-1} + C^{-1} + \cdots$$

$$(3.46) \qquad \sum_{i=1}^{r} h_i \chi_i^\nu = \begin{cases} 0 & \nu \neq 1 \\ g & \nu = 1 \end{cases}$$

$$(3.47) \qquad \sum_{i=1}^{r} \chi_i^\nu = \begin{cases} 0 & \nu \neq 1 \\ g & \nu = 1 \end{cases}$$

Thus we must rearrange the roots such that the first row of our columns adds to g and all others to zero. We have now found a table which gives the elements of the diagonal for each irreducible representation in each class. Now (3.38) can be written:

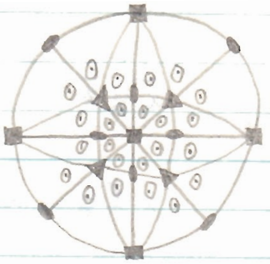
$$\sum_{\nu=1}^{r} \chi_E^\nu \chi_i^\nu = \begin{cases} 0 & i \neq E \\ g/h_i & i = E \end{cases}$$

Using relation (3.29) $h_i \chi_i^\nu = \chi_E^\nu \chi_i^\nu$:

$$(3.48) \qquad \sum_{\nu=1}^{r} (\chi_E^\nu)^2 \chi_i^\nu = \begin{cases} 0 & i \neq E \\ g & i = E \end{cases}$$

This is now a rule for the columns of our root table and enables us to find the characters since χ_E^ν is known, but not yet. The multiplication of the rows by $(\chi_E^\nu)^2$, must be done in such a way that all columns but the first add to zero and the first adds to g. The use of (3.29) to calculate the characters then follows immediately, that is, divide each by $\chi_E^\nu h_i$.

Character Table of the Holosymmetric Point Group (Cubic)

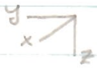
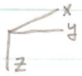


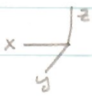
This group is characterized by the following classes: There three 4-fold rotation axis, each with a symmetry operation of $+\pi$ or $-\pi$ rotation or a $\pm \pi/2$ rotation. For the former, $+\pi$ and $-\pi$ are the same and this rotation is denoted C_4^2. Since there are three axis, the class is $3C_4^2$. For the latter, $+\pi/2$ and $-\pi/2$ are separate operations, so there are six elements in this class which is denoted by $6C_4$. About the diad axis, there are rotations of $+\pi$ and $-\pi$ which are the same. As there are 6 diad axes, the class is denoted by $6C_2$. About a triad axis, there are rotations of $2\pi/3$ and $4\pi/3$ where $4\pi/3$ is the same as $-2\pi/3$. Since there are 4 triad axes, the class is $8C_3$. Also, the group contains identity and inversion symmetry.

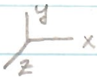
Class:	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$
Representation:										
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	-1	-1	1	1	1	-1	-1	1
Γ_{12}	2	2	0	0	-1	2	2	0	0	-1
Γ'_{15}	3	-1	1	-1	0	3	-1	1	-1	0
Γ'_{25}	3	-1	-1	1	0	3	-1	-1	1	0
Γ_1'	1	1	1	1	1	-1	-1	-1	-1	-1
Γ_2'	1	1	-1	-1	1	-1	-1	1	1	-1
Γ'_{12}	2	2	0	0	-1	-2	-2	0	0	1
Γ_{15}	3	-1	1	-1	0	-3	1	-1	1	0
Γ_{25}	3	-1	-1	1	0	-3	1	1	-1	0

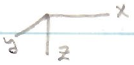
Classes in terms of coordinate substitutions:

E $\quad xyz$ 

$3C_4^2$ $\quad \bar{x}\bar{y}z$  $x\bar{y}\bar{z}$  $\bar{x}y\bar{z}$ 

$6C_4$ $\quad \bar{y}xz$  $y\bar{x}z$  $x\bar{z}y$, $xz\bar{y}$, $zy\bar{x}$, $\bar{z}yx$

$8C_3$ $\quad zxy$  yzx, $z\bar{x}\bar{y}$, $\bar{y}\bar{z}x$, $\bar{z}\bar{x}y$, $\bar{y}z\bar{x}$, $\bar{z}x\bar{y}$, $y\bar{z}\bar{x}$

$6C_2$ $\quad yx\bar{z}$  $z\bar{y}x$, $\bar{x}zy$, $\bar{y}\bar{x}\bar{z}$, $\bar{z}\bar{y}\bar{x}$, $\bar{x}\bar{z}\bar{y}$

If we look for s-type symmetry at Γ, the middle of the zone, it is immediately apparent that Γ_1 has this type of symmetry. For p-type symmetry, Γ_{15} has the required form, as can be seen from a combination of the character table and coordinate substitutions. For example, a p-state wave function would be $x f(r)$. It is seen that at least one element of each class except $8C_3$ preserves the position of x in the symmetry operation and the sign of the class character preserves the sign of x. Other symmetry types can be found from this same reasoning.

States at Points of High Symmetry within the Brillouin Zone

Suppose k is a point in the BZ which lies on some axis of symmetry. The product $k \cdot r$ is clearly unchanged for a rotation A about this axis. If we have a solution of the Schroedinger equation, viz, a Bloch function:

$$b_n(k,r) = e^{ik\cdot r} u_n(k,r)$$
$$u_n(k,r) = u_n(k, r+R_l)$$

where u has no other specified symmetry, we may generate other wave functions by the operations of the sub-group of the point group which applys to the axis of symmetry, which then can be formed into a linear combination with the symmetry of the sub-group.

For points on the boundary of the BZ, not only those operations which leave k invariant but those that transform k into an equivalent vector must be considered. Let Q be an operation of the point group. Then:

$$Qk \cdot Qr = k \cdot r \quad , \quad k \cdot Qr = Q^{-1}k \cdot r$$

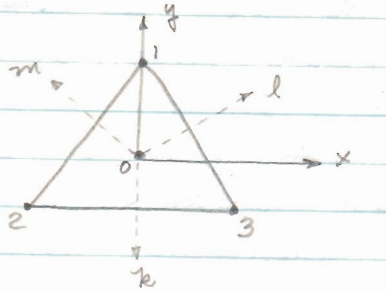
Now, if $Q^{-1}k = k + K$, then Q is an operation which transforms a wave function at k into another wave function belonging to the same state. All these operations belonging to group G form a sub-group G_K of the wave vector k. The operations of G_K applied to an unsymmeterized solution of the wave equation form a set of functions from which the symmeterized Bloch functions can be found. The obtaining of irreducibles and character tables at these points of symmetry follows from those procedures for Γ. The classification of states at Γ is dependent only on the point group of the crystal. The classification of states at symmetry points on the BZ depends upon the shape of the BZ (because of K) and thus on the form of the Bravais lattice.

Compatibility Relations:

There is a rule which determines the symmetry types along an axis which are compatable with the symmetry types at the end of the axis. That is, that the sum of the characters of the compatible representations along the axis must be equal to the character of the representation at the end point.

HEINE : GROUP THEORY IN QUANTUM MECHANICS

Consider the following figure,



Which is an equilateral triangle. Sides of length a.

The following are the symmetry operations or rotations of the triangle:

A : 120° about z
B : 240° or 120° about z
K : 180° about 0k
L : 180° about 0l
M : 180° about 0m
E : 0 or 360° about any axis

These are the element of the group.

We can quickly construct the multiplication Table of the above group:

(Applied first)

Applied second	E	A	B	K	L	M
E	E	A	B	K	L	M
A	A	B	E	M	K	L
B	B	E	A	L	M	K
K	K	L	M	E	A	B
L	L	M	K	B	E	A
M	M	K	L	A	B	E

Note that each operation has its inverse, that is, $PP^{-1} = E$. In some cases $P = P^{-1}$. It can be shown that associative multiplication holds, viz, $(PQ)R = P(RQ)$. Note also that the elements do not commute.

Definition of a Group:

A group G is a collection of elements A, B, C, . . . that have the following properties:

(a) It must be possible to construct a multiplication table such that the results are elements of the group.

(b) If the elements of the group commute, the group is called Abelian.

(c) One of the group elements must be unitary, that is, be E.

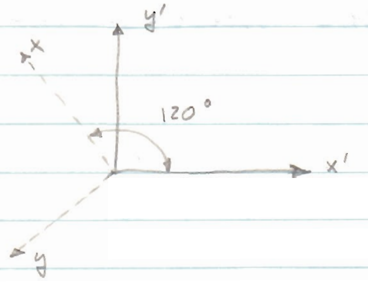
(d) Every element P must have an inverse P^{-1} which is also an element of G such that $PP^{-1} = P^{-1}P = E$.

(e) The multiplication must be associative.

Symmetry Transformations of a Hamiltonian

We can reduce the elements of the group to coordinate substitutions:

A :



$$x, y, z \longrightarrow -\tfrac{1}{2}x + \tfrac{\sqrt{3}}{2}y, -\tfrac{\sqrt{3}}{2}x - \tfrac{1}{2}y, z$$

B : $x, y, z \longrightarrow -\tfrac{1}{2}x - \tfrac{\sqrt{3}}{2}y, \tfrac{\sqrt{3}}{2}x - \tfrac{1}{2}y, z$

K : $x, y, z \longrightarrow -x, y, -z$

L : $x, y, z \longrightarrow \tfrac{1}{2}x + \tfrac{\sqrt{3}}{2}y, \tfrac{\sqrt{3}}{2}x - \tfrac{1}{2}y, -z$

M : $x, y, z \longrightarrow \tfrac{1}{2}x - \tfrac{\sqrt{3}}{2}y, -\tfrac{\sqrt{3}}{2}x - \tfrac{1}{2}y, -z$

If we consider protons situated at all three corners of the Triangle, the Hamiltonian for an electron moving in the field produced by them is:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \sum_{i=1}^{3}\frac{e^2}{|\vec{r}-\vec{r}_i|}$$

If we select a point in space and hold it constant as the triangle undergoes a symmetry rotation, the Hamiltonian obviously remains invariant as it depends upon only the distance from the protons, which is always the same after a symmetry operation.

Now the table of coordinate substitutions multiplies the same way as the set of rotations. Thus, the two groups are <u>isomorphous</u> as might be expected.

Group Representations

Transformation of Wave Functions: If we have the Schroedinger equation $H(x,y,z)\,\psi_1(x,y,z) = F_1\,\psi_1(x,y,z)$ and apply a symmetry operation which leaves the Hamiltonian invariant, we will generate a new wave function $\psi_2(x,y,z)$ which is an eigenfunction of H. Thus we have: $R\,\psi_1(x,y,z) = \psi_2(x,y,z)$. The mechanics of this are to make the coordinate substitutions of R on $\psi_1(x,y,z)$ to get $\psi_2(x,y,z)$. Obviously, the set of wave functions generated by the elements of a group are degenerate. Thus if we denote a symmetry transformation by T, the following equations are true:

$$T\psi(q_i) = \psi(T_{ij}\,q_j)$$

$$T H(q_i) = H(q_i)$$

Representations of a Group: Consider the function:

$$x\,f(r)\,,\quad y\,f(r)$$

and operate on them with the group element A:

$$A\,x\,f(r) = -\tfrac{1}{2}\,x\,f(r) + \tfrac{\sqrt{3}}{2}\,y\,f(r)$$
$$A\,y\,f(y) = -\tfrac{\sqrt{3}}{2}\,x\,f(r) - \tfrac{1}{2}\,y\,f(r)$$

We see that we have generated the following matrix from A:

$$D_{xy}(A) \equiv \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -1/2 \end{pmatrix}$$

(Actually $D_{xy}(A)$ refers to an element of $D(A)$, but sometimes the notation is used interchangeably.)

which is actually the transpose written because of future convenience. We can generate $D_{xy}(B)$, etc. also by operating on $x\,f(r)$, $y\,f(r)$, which will obey the same multiplication rules as the elements themselves, viz., $D_{xz}(K)\,D_{xy}(A) = D_{xy}(L)$ corresponding to $KA = L$. These matrices form a representation of the group which we call Γ. If we operate on the function $z\,f(r)$ we generate another representation which we will call $\mathcal{A}$. Finally, if we operate on the function $(x^2+y^2)\,f(r)$ we obtain the identity representation called $\mathcal{A}$.

	E	A	B	K	L	M
Γ	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -1/2 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$
$\mathcal{A}$	1	1	1	−1	−1	−1
$\mathcal{A}$	1	1	1	1	1	1

Although we have used functions to obtain the matrices, the representation is just a group of matrices that multiply together properly consistent with the original multiplication table.

The functions are not needed at all and the representation can be deduced from the coordinate substitutions. Take A for example:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} \longrightarrow \begin{pmatrix} -\frac{1}{2}x + \frac{\sqrt{3}}{2}y \\ -\frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z \end{pmatrix}$$

or $$\begin{pmatrix} -\frac{1}{2}x + \frac{\sqrt{3}}{2}y \\ -\frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$= (x \;\; y \;\; z) \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \sqrt{3}/2 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Thus we that Γ and A for A can be generated without the use of functions, and the matrices of the representation are uniquely determined. However, the use of functions to introduce the group representation leads to interesting observation: suppose we have a linearly independent set of functions $\varphi_1, \ldots, \varphi_n$ and the group G, of which T is a typical linear transformation. If the functions and transformations are such that $T\varphi_i$ can be expressed as:

$$T\varphi_j = \varphi_i D_{ij}(T) \qquad \left\{ \sum_i \text{ implied} \right\}$$

then we have immediately the set of matrices $D_{ij}(T)$. The functions $\varphi_1, \ldots, \varphi_n$ are said to form a basis for the representation. Other sets of basis functions can give rise to the same representation, so the basis is not unique. However, only special sets of functions can form a basis.

Suppose we have of functions $\varphi_1, \ldots, \varphi_n$ which could be the eigenfunctions of a particular Hamiltonian. Then we say the vector space $R(\varphi_1, \ldots, \varphi_n)$ consists of all functions:

$$c_1\varphi_1 + c_2\varphi_2 + \cdots + c_n\varphi_n$$

Transformations in Vector Space:

We take the base vectors of the space such that the transformation $T\varphi_j$ is expressible as a linear combination of the φ_i:

$$T\varphi_j = \sum_i^n \varphi_i D_{ij}(T)$$

or we say that $T\varphi_j$ belongs to the space R.
For $\varphi = c_j \varphi_j$:

$$T\varphi = c_j T\varphi_j = c_j \sum_i^n \varphi_i D_{ij}(T)$$

so that $T\varphi$ belongs to R. Clearly this can be done for any constant c and for each term in a general vector expressed as a linear combination of the basis vectors. therefore, the operation of T on any vector of R results in another vector of R and we say that the space R is invariant under the group G of transformations.

now, if we choose a new set of basis function $\varphi_1', \ldots, \varphi_n'$, what representation do they transform according to? We express φ_i' in terms of φ_i:

$$\varphi_j' = \sum_i \varphi_i P_{ij} \quad \text{and} \quad \varphi_j = \sum_i \varphi_i' P_{ij}^{-1}$$

Then: $$T\varphi_j' = T\sum_l \varphi_l P_{lj} = \sum_{kl} \varphi_k D_{kl}(T) P_{lj}$$

$$= \sum_{ikl} \varphi_i' P_{ik}^{-1} D_{kl}(T) P_{lj} = \sum_i \varphi_i' D_{ij}'(T)$$

Then: $$D'(T) = P^{-1} D(T) P$$

Definition: Two representations are said to be equivalent if a matrix P exists that relates the matrices of the two representations as above.

Reducibility of a Representation:

In general, a representation $D_{ij}(T)$ of a group G is reducible into the representations $D^{(1)}$, $D^{(2)}$, ... $D^{(s)}$ if a similitude transformation of the type above exists which brings every matrix $D_{ij}(T)$ into the form as shown in the notes from Jones. We write the representation for a particular element as:

$$D(T) = D^{(1)}(T) + D^{(2)}(T) + \cdots + D^{(s)}(T)$$

and D is said to contain the $D^{(\alpha)}$. This is not a sum in the usual sense. The reason that the above table of representations is already reduced is because the proper basis functions were chosen to begin with.

Reducibility of a Vector Space:

If we have a vector space $R(\varphi_1, \ldots, \varphi_n)$ whose basis vectors transform according to the reducible representation D, there exists some similitude transformation which brings D into reduced form. This is equivalent to choosing new basis vectors φ_i' so that D can be represented as an irreducible transformation. Let $R^{(1)}$ be the sub-space spanned by the first n_1 vectors and which thus transforms according the $D^{(1)}$. We see from the form of the reduced D that the vectors in the sub-space $R^{(\alpha)}$ transform among themselves by $D^{(\alpha)}$ without mixing in vectors of other sup-spaces.

If we consider the eigenfunctions of a given Hamiltonian as defining some big space R, then it will be found that the functions associated with different $R^{(\alpha)}$ belong to different eiginvalues. Also, the function belonging to the different subspaces can always be made orthogonal to each other.

Applications to Quantum Mechanics:

I. If a Hamiltonian is invariant under a group G of symmetry transformations, then the eigenfunctions belonging to one energy level form a basis for a representation of G.

II. If the group G includes all possible symmetry transformations of the Hamiltonian, then the eigenfunctions of each energy level transform irreducibly under G, apart from accidental degeneracy.

III. A perturbation will cause a degenerate level to split into as many levels as the degree of degeneracy, that is, at a maximum. This result from group theory does not make assumptions about the magnitude of the perturbation.

The Representation of Finite Groups

Classes: A class is defined as in Jones. From the Triangle example, the classes are three in number and are $E, (A,B), (K,L,M)$.

Character: The character $\chi(T)$ is defined as the trace of $D(T)$:

$$\chi(T) = \sum_i D_{ii}(T)$$

Let S be any matrix whose inverse S^{-1} exists. Form $S\,D(T)\,S^{-1}$, then:

$$\sum_i \{S\,D(T)\,S^{-1}\}_{ii} = \sum_{ijk} S_{ij}\,D_{jk}(T)\,S^{-1}_{ki}$$

$$= \sum_{ijk} S^{-1}_{ki}\,S_{ij}\,D_{jk}(T) = \sum_{jk} \delta_{kj}\,D_{jk}(T)$$

$$= \sum_k D_{kk}(T) = \chi(T)$$

thus the character of a representation is invariant under a similitude transformation. The characters of the elements of a class are equal as are those of equivalent irreducible representations.

Character Table of Equilateral Triangle

	E	A	B	K	L	M
χ^{Π}	2	-1	-1	0	0	0
$\chi^{\mathcal{A}}$	1	1	1	-1	-1	-1
$\chi^{\mathcal{S}}$	1	1	1	1	1	1

The classes are now evident.

Reduction of a Representation:

If $D(T)$ is reducible by $P^{-1}D(T)P$ into components $D = D^{(\alpha)} + D^{(\beta)} + \cdots + D^{(\epsilon)}$, then the character is obviously:

$$\chi(T) = \chi^{(\alpha)}(T) + \chi^{(\beta)}(T) + \cdots + \chi^{(\epsilon)}(T)$$

$$\text{or} \quad \chi(T) = \sum_{\lambda} C_\lambda \chi^{(\lambda)}(T)$$

where C_λ denotes the number of times the irreducible $D^{(\lambda)}$ appears in the representation. This equation enables the calculation of the number of equivalent irreducibles in the representation.

Orthogonality Relation and Products:

Product relation: consider the representation form by the product of the irreducibles $D^{(\lambda)}(T)$ and $D^{(\mu)}(T)$:

$$D(T) = D^{(\lambda)}(T) \times D^{(\mu)}(T).$$

Then it can be shown that:

$$\chi(T) = \chi^{(\lambda)}(T)\,\chi^{(\mu)}(T)$$

Orthogonality Relation: It can be shown that:

$$\sum_T \chi^{(\lambda)*}(T)\,\chi^{(\mu)}(T) = h\,\delta_{\lambda\mu}$$

where h is the order of the group. This can be seen from the equilateral triangle character table.

Projection Operators:

$$\varphi_i^{(\lambda)} = \sum_T D_{ij}^{(\lambda)*}(T)\,T\varphi$$

Then: $$S\varphi_i^{(\lambda)} = \sum_T D_{ij}^{(\lambda)*}(T)\,ST\varphi$$

$$= D_{i\alpha}^{(\lambda)*}(S^{-1}) \sum_T D_{\alpha j}^{(\lambda)*}(ST)\,ST\varphi$$

$$= D_{\alpha i}^{(\lambda)}(S)\,\varphi_\alpha^{(\lambda)}$$

which shows that the $\varphi_i^{(\lambda)}$ are vectors in R transforming according to $D^{(\lambda)}(T)$. Putting $i = j$:

$$\varphi^{(\lambda)} = \sum_T \chi^{(\lambda)*}(T)\,T\varphi$$

These are called projection operators because they pick out from φ the part lying in a particular subspace.

Solid State Applications

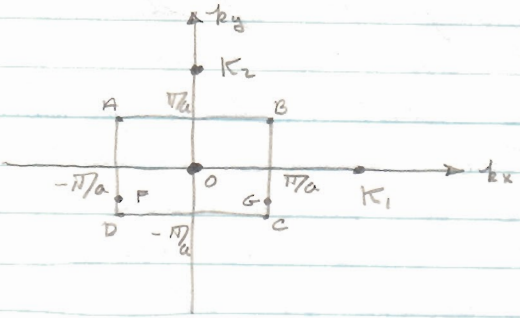
The space group of a crystal lattice consists of the translation and rotation groups. The translation operator is defined as $t_n = e^{ik\cdot t_n}$, such that:

$$t_n\,\psi(k,r) \equiv \psi(k, r+t_n) = e^{ik\cdot t_n}\,\psi(k,r)$$

this defines the Bloch functions.

Corrollary: $e^{iK\cdot t_n} = 1$ for all t_n.

Consider the first BZ for a square lattice.



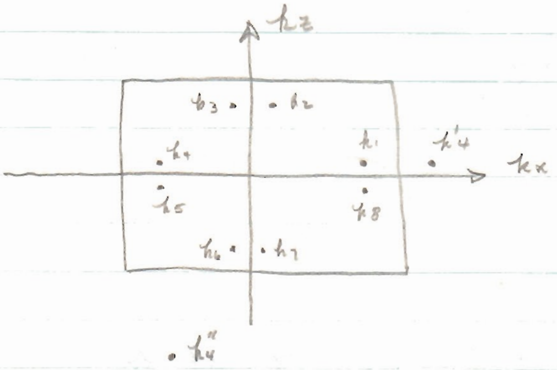
We always take opposite ends of the BZ to be equivalent points, that is: $k_F = k_G + K_1$

We denote the operations of the space group as $\{R \mid t_n\}$ for crystals which do not have glide planes or screw axis. The translation t_n or any translation for that matter does not change the k-vector of $\psi(k, r)$. However, the rotation R changes $\psi(k, r)$ to $\psi(k', r)$ where k' is derived from k by applying the rotation in k space. Note that the product $k \cdot t_n$ remains invariant under R when it is applied to real and k space simultaneously.

Let $\psi(k_1, r)$ represent an energy eigenstate with k_1 some general point in the BZ. The rotation operations will generate $\psi(k_1, r)$, $\psi(k_2, r)$ etc. and since the Hamiltonian is invariant:

$$E(k_1) = E(k_2) = E(k_3) = \cdots$$

such that the energy possesses the full symmetry of the point group of the BZ. This can be seen for the square lattice:



the energy at each one of these points will be the same.

The Bloch functions form a basis of the vector space R for the space group of the crystal.

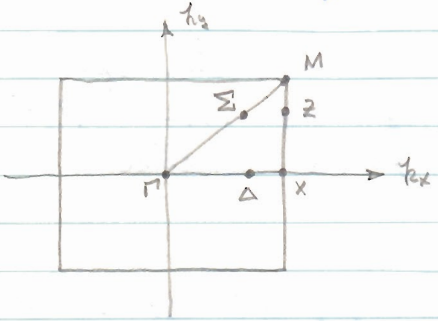
We have shown that the Bloch functions are invariant (except for $e^{i k \cdot t_n}$) under the operation of translation. Now we find the representations of the point group P of the rotations. We form a set of $\psi(k_i)$ as above. We must first prove that these form a representation. This is true since each operation of P on $\psi(k_i)$ gives a new wave function of the original set. Thus the $\psi(k_i)$ form an irreducible representation for the group P.

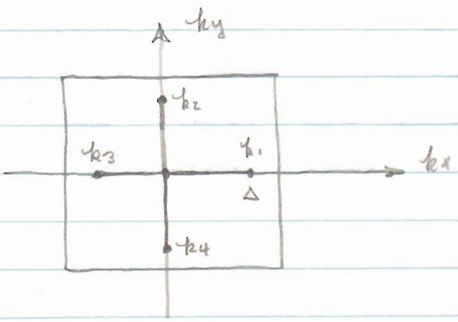
Special Points in the BZ:

The above argument fails if k_0 is taken at a special point in the zone because the operations of P give two or more identical k_i.

Reasons: (1) k_i identical if lying on rotation axis or mirror plane
(2) by being separated by a reciprocal lattice vector from each other,
(3) Both (1) and (2).

Consider the following special points:





Type (1): Γ, Σ, Δ
Type (2): Z
Type (3): M, X

Consider the Bloch function $\psi(k_1)$ at k_1 at Δ. We divide the elements of P into two classes, those that leave k_1 invariant and those that change it.

I: k_1 invariant: E, my
II: k changed: 4z, 2z, $4z^3$, mx, md, md'

The II operations change k_1 into k_2, k_3, k_4. The functions with these k's form the star of Δ. The operations of class I leave k_1 invariant and thus form the point group of Δ, usually denoted by K. Here it is my with two representations, symmetric and antisymmetric called Δ_1 and Δ_2. Having a $\psi(k_1)$ that satisfies these conditions, we use class II to generate $\psi(k_2)$, $\psi(k_3)$, $\psi(k_4)$ which transforms into one another and hence give an irreducible representation.

At Γ, k=0 and the group of Γ is the point group of the crystal

Energy Level Splittings in Crystal:

Consider the plane wave functions:

$$e^{i\pi/a(x+y)} \qquad e^{i\pi/a(x-y)}$$
$$e^{i\pi/a(-x+y)} \qquad e^{i\pi/a(-x-y)}$$

These functions have the point group symmetry of M so that at this point in the crystal, there will be four consecutive degenerate bands touching. It can be shown that this degeneracy is split into two singlet levels and a doubly degenerate one thru use of character relations, when V(r) is applied.

Compatibility Relations:

As the wave functions are continous throughout k space, the symmetries along different lines and points in the B.Z. must meld into each other continuously as they approach. From this condition, a compatibility table between the different representations can be constructed.

Degeneracy:

(1) Essential degeneracy: due to symmetry properties and cannot be split by $V(r)$.

(2) Degeneracy between two inequivalent representations as shown by two crossing energy bands. It is conventional to take a band as consisting of all points lower in energy than the next highest, whether they originally crossed or not. This type of degeneracy is obtained by a consideration of the compatibility relations along an axis of symmetry in the B Z.

Direct Product:

Consider the transformations:

$$T \varphi_j^{(\lambda)} = \sum_i \varphi_i D_{ij}^{(\lambda)}(T)$$

$$T \varphi_k^{(\mu)} = \sum_l \varphi_l D_{lk}^{(\mu)}(T)$$

$$T(\varphi_j^{(\lambda)} \varphi_k^{(\mu)}) = \sum_i \sum_l \varphi_i \varphi_l D_{ij}^{(\lambda)}(T) D_{lk}^{(\mu)}(T) = \sum_i \sum_l \varphi_i \varphi_l D_{ij,lk}(T)$$

or $$D^{(\lambda)}_{(T)} \times D^{(\mu)}_{(T)} = D(T)$$

and $$\chi^{(\lambda)}(T) \chi^{(\mu)}(T) = \chi(T)$$

Matrix Elements and Selection Rules:

We wish to examine matrix elements of the form:

$$M_{ij} = \int \psi_i^* Q \psi_j \, d\tau$$

where ψ_i belongs to a complete orthonormal set which is φ_n.

If we sort out the functions in the integrand according to the irreducible representations $D^{(\mu)}$, $D^{(\nu)}$, $D^{(\lambda)}$, we have for the matrix element:

$$M_{ij} = \int \psi_i^{(\lambda)*} Q_k^{(\mu)} \psi_j^{(\nu)} \, d\tau$$

The following theorems then exist:

A. M_{ij} is non-zero only if the reduction of $D^{(\mu)} \times D^{(\nu)}$ contains $D^{(\lambda)}$

M_{ij} is non-zero only if the reduction of $D^{(\lambda)*} \times D^{(\mu)} \times D^{(\nu)}$ contains the identity representation.

B. If $D^{(\lambda)}$ is contained once (or n times), then the M_{ij} are uniquely determined by the symmetry properties of the ψ's and Q's, apart from a constant factor.

If the identity representation is contained once (or n times), then the M_{ij} are uniquely determined by the symmetry properties of the ψ's and Q's, apart from a constant factor.

APPLIED PHYSICS 297

Professor Brooks
Professor Paul

February 23, 1961

PROBLEMS

1. Using the character tables in Koster (SS Physics 5, 173-256, 1957) find the correspondence between the representations of the space group at Γ in the diamond and zincblende structures. Include the relations for the extra representations of the double group. Carry out the same procedure for the point L in the two structures (see p. 230 of Koster for symmetry of L). When two representations which are different in the diamond structure become identical in the zincblende structure what happens to the energies of the corresponding states?

2. Using the character tables in Koster, obtain the correspondence between the irreducible representations at X in the FCC, diamond, and zincblende structures, including the extra representations of the double group.

3. By looking up the articles by Elliott (PR 96, 280, 1954) and Dresselhaus (PR 100, 580, 1955) tabulate which of the single irreducible representations are further split by spin-orbit interaction.

APPLIED PHYSICS 297

Impurities in Semiconductors

1961

1. (a) Rederivation of effective mass equation for a band edge at $k = 0$, using Bloch waves.

   (b) Justification of selection of small region of k space near $k = 0$, and of neglect of band edges other than nearest one (ignoring degeneracies, multiple minima)

   (c) Justification of use of (static) dielectric constant

2. (a) Derivation of effective mass equation in multiple minima case(e.g. Ge)

   (b) Consideration of lifting of ground state degeneracies by corrections to effective mass Hamiltonian. Reduction in terms of irreducible representations of group T_d.

   (c) Solution of equation discussed.

   Discussion of labelling of levels as S, 2S, etc.

   (d) Discussion of nature of wave functions (a) the envelope function, (b) the Bloch function (c) the multiplying coefficients.

3. Modifications for acceptor shapes.

4. Experimental

   (a) Ionization and excitation energies. (i) thermal (ii) optical.

   (b) Spin resonance (i) general spectrum

   (ii) spectrum of P, As, Sb, in Si - determination of $[\psi(0)]^2$ from ΔH

   (iii) line widths - influence of Si^{29}

   (iv) Endor technique

5. First comparison with experiment

   (a) Energies - ionization and excitation

   (b) Matrix elements for radiative transitions

- (c) Wave-functions
  - (i) observation of h.f. interaction identifies ground state.
  - (ii) asymmetry of envelope functions leads to anisotropy in stress induced impurity conduction
  - (iii) study of relaxation rate also gives $[\Psi(0)]^2$

6. Corrections to theory
   - (a) Central cell corrections
   - (b) Fixed-up agreement with experiment

7. Further discussion of wave functions
   - (a) Effect of h.f. interaction of donor electron with Si^{29} - Feher experiment
   - (b) Width of e. s. r. due to h.f. interaction of Si^{29} and donor electron

8. Other effects
   - (a) Magnetic fields
     - (i) effect on continuum - done
     - (ii) effect on impurity - Hall effect, RRE tunable detector
     - (iii) splitting of optical transitions
   - (b) Strain effects
     - (i) lifting of degeneracies
     - (ii) effect on impurity banding

9. Deep lying impurities from theoretical standpoint

10. If time,
    - (a) Impurity banding
    - (b) Excitons
    - (c) Stark effect
    - (d) Interaction with lattice vibrations

REFERENCES

1-3 Kohn SSP Vol. 5 for all references before 1957, some of which are also listed below

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8. Fan and Fisher JPCS8, paper J2; absorption in Ge and magnetic field

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Price P.R 104, 1223; strain effects

9. Tyler JPCS, paper C2; review of experiments on deep lying impurities

Kôhn SSP5, p. 319; appendix on deep lying impurities

10. Lax and Burstein P.R. 100; interaction with lattice vibrations

Kohn SSP5; Stark effect theory

33. Optical Properties of Solids

General Quantum Mechanical Theory

Represent oscillating electricifield by vector potential

$$\underline{A} = -\frac{c}{2i\omega}\underline{F}\,(e^{i\omega t} - e^{-i\omega t}) \tag{33.1}$$

For electrons the perturbing potential is given by:

$$\frac{e}{m_o c}\,\underline{A}\cdot\underline{p} = -\frac{e}{2im_o\omega}\,\underline{F}\cdot\underline{p}\,(e^{i\omega t} - e^{-i\omega t}) \tag{33.2}$$

Now, assume the wave function can be expanded in the form:

$$\Psi(\underline{r},t) = \sum_n a_n(\underline{k},t)\,b_n(\underline{k},\underline{r}) \tag{33.3}$$

where n refers to different bands and $\underline{k}$ is reduced wave vector. Since $\underline{p} = \frac{\hbar}{i}\nabla$ is a periodic operator only states with same $\underline{k}$ interact through the vector potential. The time-dependent Schrödinger equation reduces to:

$$-\frac{\hbar}{i}\dot{a}_n(\underline{k},t) = a_n(\underline{k},t)\,\varepsilon_n(\underline{k}) - \frac{e}{2i\omega m_o}\,e^{i\omega t}\sum_{n'}(n|\underline{F}\cdot\underline{p}|n')a_{n'}(\underline{k},t)$$

$$+\frac{e}{2i\omega m_o}\,e^{-i\omega t}\sum_{n'}(n|\underline{F}\cdot\underline{p}|n')a_{n'}(\underline{k},t) \tag{33.4}$$

where

$$(n|\underline{F}\cdot\underline{p}|n') = \int b_n^*(\underline{k},\underline{r})\,\underline{F}\cdot\underline{p}\,b_{n'}(\underline{k},\underline{r})d\underline{r}$$

and $\varepsilon_n(\underline{k})$ is the energy in the n'th band. Attempt solution of (33.4) on the assumption that the perturbation is small. Use successive approximations, replacing a's on right of (33.4) by their unperturbed values:

$$a_{n'}^{(o)}(\underline{k},t) = \delta_{n'}{}^{o}\,e^{-\frac{i}{\hbar}\varepsilon_o(\underline{k})t} \tag{33.5}$$

and let

$$a_n^{(1)}(\underline{k},t) = b(\underline{kt})e^{-\frac{i}{\hbar}\varepsilon_n(\underline{k})t}$$

Eq. (33.4) then reduces to:

$$-\frac{\hbar}{i}\dot{b}_n(\underline{k},t) = -\frac{e}{2i\omega m_0}e^{i(\omega_n+\omega)t}(n|\underline{F}\cdot\underline{p}|o) + \frac{e}{2i\omega m_0}e^{i(\omega_n-\omega)t}(n|\underline{F}\cdot\underline{p}|o) \tag{33.6}$$

where $\hbar\omega_n = \varepsilon_n(\underline{k}) - \varepsilon_o(\underline{k})$ = absorption or emission energy. Integrate (33.6) with the initial condition

$$b_n(\underline{k},o) = \delta_n^{\,o}$$

We have:

$$b_n(\underline{k},t) = +\frac{e}{2m_o\hbar\omega}\left\{\frac{e^{i(\omega_n+\omega)t}-1}{i(\omega_n+\omega)} - \frac{e^{i(\omega_n-\omega)t}-1}{i(\omega_n-\omega)}\right\}(n|\underline{F}\cdot\underline{p}|o) \tag{33.7}$$

Using (33.7) and (33.5) in (33.3) we obtain:

$$\Psi(\underline{r},t)e^{\frac{i}{\hbar}\varepsilon_o(\underline{k})t} = b_o(\underline{k},\underline{r}) + \frac{e}{2m_o\hbar\omega}\sum_n(n|\underline{F}\cdot\underline{p}|o)b_n(\underline{k},\underline{r})$$

$$\left\{\frac{e^{i\omega t}-e^{-i\omega_n t}}{i(\omega_n+\omega)} - \frac{e^{-i\omega t}-e^{-i\omega_n t}}{i(\omega_n-\omega)}\right\} \tag{33.8}$$

We use (33.8) to calculate the current density according to the usual relation:

$$\underline{J} = -\frac{e}{m_o}\int\Psi^*\underline{p}\,\Psi\,d\underline{r} - \frac{e^2}{m_o c}\int\Psi^*\underline{A}\,\Psi\,d\underline{r} \tag{33.9}$$

We are interested only in the forced part of the current, i.e. that which depends on $e^{i\omega t}$ and $e^{-i\omega t}$. We obtain:

$$\underline{J} = -\frac{e^2\underline{F}\cdot}{2m_o^2\hbar\omega}\sum_n(o|\underline{p}|n)(n|\underline{p}|o)\left\{\frac{e^{i\omega t}}{i(\omega_n+\omega)} - \frac{e^{-i\omega t}}{i(\omega_n-\omega)} - \frac{e^{-i\omega t}}{i(\omega_n+\omega)} + \frac{e^{i\omega t}}{i(\omega_n-\omega)}\right\}$$

$$+\frac{e^2}{m_o}\frac{\underline{F}}{2i\omega}(e^{i\omega t}-e^{-i\omega t}) \tag{33.10}$$

$$= \left\{ - \frac{1}{i} \frac{e^2 \underline{F} \cdot}{m_o^2 \hbar\omega} \sum_n (o|\underline{p}|n)(n|\underline{p}|o) \frac{\omega_n}{\omega_n^2 - \omega^2} + \frac{1}{2i} \frac{e^2}{m_o \omega} \underline{F} \right\} (e^{i\omega t} - e^{-i\omega t}) \tag{33.11}$$

Integrate (33.11) to obtain the polarization $\underline{P}$. This gives the result:

$$\underline{P} = \left\{ \frac{e^2 \underline{F} \cdot}{m_o} \sum_n 2 \frac{(o|\underline{p}|n)(n|\underline{p}|o)}{m_o \hbar \omega_n} \frac{\omega_n^2}{\omega^2} \frac{1}{\omega_n^2 - \omega^2} - \frac{e^2 \underline{F}}{m_o \omega^2} \right\} \cos \omega t \tag{33.12}$$

We collect separately terms which diverge as ω ⟶ 0 and those which do not. This gives us:

$$\underline{P} = \frac{e^2 \underline{F}}{m_o} \cdot \left\{ \sum_{n \neq 0} \frac{2}{m_o \hbar \omega_n} (o|\underline{p}|n)(n|\underline{p}|n) \frac{1}{\omega_n^2 - \omega^2} - \frac{1}{\omega^2} \left[1 - \sum_{n \neq 0} \frac{2}{m_o \hbar \omega_n} (o|\underline{p}|n)(n|\underline{p}|o) \right] \right\} \tag{33.13}$$

The quantity

$$\underset{\sim}{f}_n = \frac{2}{m_o \hbar \omega_n} (o|\underline{p}|n)(n|\underline{p}|o) \tag{33.14}$$

is the f-value or oscillator strength. By analogy the last bracket is:

$$\underset{\sim}{f}_o = 1 - \sum_{n \neq 0} \frac{2}{m_o \hbar \omega_n} (o|\underline{p}|n)(n|\underline{p}|o) \tag{33.15}$$

which is the oscillator strength for zero frequency. The f-values are tensor quantities in general. Equation (33.13) can therefore be written:

$$\underline{D} = \underline{E} + 4\pi \underline{P} = \underset{\sim}{\varepsilon} \cdot \underline{E}$$

$$\underset{\sim}{\varepsilon} = 1 + \frac{4\pi e^2}{m_o} \sum_{n \neq 0} \frac{\underset{\sim}{f}_n}{\omega_n^2 - \omega^2} - \frac{4\pi e^2}{m_o \omega^2} \underset{\sim}{f}_o \tag{33.16}$$

Equation (33.16) is the contribution of one electron. To get the entire constant the polarization must be summed over all occupied Bloch states, whence:

$$\underset{\sim}{\varepsilon} = 1 + \frac{4\pi e^2}{m_o} \sum_{\underline{k},m} f_m(\underline{k}) \left[\sum_{n \neq m} \frac{\underset{\sim}{f}_{mn}}{\omega_{mn}^2 - \omega^2} - \frac{\underset{\sim}{f}_{mn}}{\omega^2} \right. \qquad (33.17)$$

where $f_m(\underline{k})$ is the Fermi factor for the m'th band and reduced wave-vector $\underline{k}$,

$$\hbar\omega_{mn} = \varepsilon_n(\underline{k}) = - \varepsilon_m(\underline{k}), \text{ and } \underset{\sim}{f}_{mn} = \frac{2}{m_o \hbar \omega_{mn}} (m|\underline{p}|n)(n|\underline{p}|m)$$

$$\underset{\sim}{f}_{mn} = 1 - \sum_{n \neq m} \underset{\sim}{f}_{mn} \qquad (33.18)$$

where ω_{mn} and $\underset{\sim}{f}_{mn}$ are both functions of $\underline{k}$.

In ordinary atomic theory the f's obey a sum rule:

$$\sum_{n \neq m} \underset{\sim}{f}_{mn} = \underset{\sim}{1} \quad \text{all } m. \qquad (33.19)$$

In this case $\underset{\sim}{f}_{nn} = 0$. This is no longer true for solids. Instead it can be shown that:

$$\underset{\sim}{f}_{mm} = \frac{m_o}{\hbar^2} \nabla_{\underline{k}} \nabla_{\underline{k}} \varepsilon(\underline{k}) \qquad (33.20)$$

i.e. just the effective mass tensor.

Proof: Schrödinger equation for $b(\underline{k},\underline{r})$ is:

$$- \frac{h^2}{2m_o} \nabla^2 b_n(\underline{k},\underline{r}) + V(\underline{r})\, b_n(\underline{k},\underline{r}) - \varepsilon_n(\underline{k}) b_n(\underline{k},\underline{r}) = 0 \qquad (33.21)$$

Now, consider the energy at a nearby point in $\underline{k}$-space say $\underline{k} + \underline{\sigma}$, and let $b_n(\underline{k} + \underline{\sigma}, \underline{r}) = e^{i\underline{\sigma}\cdot\underline{r}}\, u_n(\underline{k},\underline{r})$. Then u satisfies the equation:

$$-\frac{\hbar^2}{2m_o}\nabla^2 u_n(\underline{k},\underline{r}) + V(\underline{r})u_n(\underline{k},\underline{r}) - \frac{\hbar^2}{m_o} i\underline{\sigma}\cdot\nabla u_n(\underline{k},\underline{r}) = \left[\varepsilon_n(\underline{k}+\underline{\sigma}) - \frac{\hbar^2}{2m_o}\sigma^2\right] u_n(\underline{k},\underline{r}) \qquad (33.22)$$

The eigenvalue $\varepsilon_n(\underline{k} + \underline{\sigma}) - \frac{h^2}{2m_o}\sigma^2$ is the eigenvalue of a Schrödinger equation which is almost identical with (33.21) except for the perturbing term which can be made small as $\underline{\sigma}$. Thus eigenvalue may be computed by perturbation theory in the standard manner:

$$\varepsilon_n(\underline{k} + \underline{\sigma}) - \frac{\hbar^2}{2m_o}\sigma^2 = \frac{\hbar}{m_o}(n|\underline{\sigma}\cdot\underline{p}|n) + \sum_{m\neq n}\frac{\frac{\hbar^2}{m_o^2}\left|(n|\underline{p}\cdot\underline{\sigma}|m)\right|^2}{-\hbar\omega_{nm}} \qquad (33.23)$$

Expanding $\varepsilon_n(\underline{k} + \underline{\sigma})$ in Taylor series about $\underline{k}$ and comparing terms quadratic in the vector $\underline{\sigma}$, we obtain:

$$+\frac{1}{2}(\underline{\sigma}\cdot\nabla_{\underline{k}})^2\,\varepsilon_n(\underline{k}) = \frac{\hbar^2}{2m_o}\sigma^2 - \frac{\hbar^2}{2m_o}\sum_{m\neq n}\frac{2}{m_o\hbar\omega_{nm}}\left|(n|\underline{p}\cdot\underline{\sigma}|m)\right|^2 \qquad (33.24)$$

Since this must be identity for all values of the three components σ_x, σ_y, σ_z, it follows immediately that

$$\frac{m_o}{\hbar^2}\nabla_{\underline{k}}\nabla_{\underline{k}}\,\varepsilon_n(\underline{k}) = \underset{\sim}{1} - \sum_{m\neq n}\frac{2}{m_o\hbar_{nm}}(n|\underline{p}|m)\,(m|\underline{p}|n) \qquad (33.25)$$

which was to be proved.

Note that there is a separate sum rule for each state $\underline{k}$, n, also that strictly speaking the sum rule includes transitions to lower states, with negative f-values, which are forbidden by the exclusion principle.

Classical Theory of Optical Properties:

Equation of motion for harmonically bound electron:

$$\ddot{y} + \gamma \dot{y} + \omega_o^2 y = -eF_o e^{i\omega t} \tag{33.26}$$

where y represents displacement from equilibrium. Solid represented as assembly of harmonic oscillators each bound to a lattice point. Dipole moment zero in equilibrium. For forced oscillation:

$$y = \frac{-\frac{e}{m_o} F_o e^{i\omega t}}{(\omega_o^2 - \omega^2) + i\omega\gamma} \tag{33.27}$$

$$P = -\sum_{i=1}^{N} e y_i = \sum_{i=1}^{N} \frac{e^2 F_i}{m_o} e^{i\omega t} \frac{1}{(\omega_i^2 - \omega^2) + i\omega\gamma_i} \tag{33.28}$$

where P = polarization F_i = effective force and ω_i, γ_i frequency and damping constant of i'th oscillator.

If all oscillators are surrounded by an environment having cubic symmetry, we have:

$$F_i = E_o + \frac{4\pi}{3} P_o \; ; \quad P = P_o e^{i\omega t} \tag{33.29}$$

where E_o is electric field and F_i is the effective field at the i'th oscillator. If there are s distinct types of oscillators we obtain finally:

$$P_o = \left(E_o + \frac{4\pi}{3} P_o\right) \sum_{j=1}^{s} n_j \frac{e^2}{m_o} \frac{1}{(\omega_j^2 - \omega^2) + i\omega\gamma_j} \tag{33.30}$$

Using definition $D_o = E_o + 4\pi P_o = \varepsilon E_o$, we have the Lorentz relation:

$$\varepsilon = \frac{1 + \frac{8\pi}{3}\alpha}{1 - \frac{4\pi}{3}\alpha} \; ; \quad \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\alpha \qquad (33.31)$$

$$\alpha = \frac{e^2}{m_o} \sum_j n_j \frac{1}{(\omega_j^2 - \omega^2) + i\omega\gamma_j}$$

where α = polarizability

n_j = no. of j-type oscillators

Eq. (33.31) reduces to $\varepsilon = 1 + 4\pi\alpha$ if α is small. Main effect of the quantum-mechanical treatment is to introduce the f-values. Eq. (33.31) then takes the final form:

$$\alpha = \frac{e^2}{m_o} \sum_{\underline{k},m} f_m(\underline{k}) \left\{ \sum_n \frac{f_{mn}}{(\omega_{mn}^2 - \omega^2) + i\omega\gamma_{mn}} - \frac{f_{mm}}{\omega^2 - i\omega\gamma_o} \right\}$$

(33.32)

Eq. (33.32) only valid if α is small. The zero frequency term is not subject to the Lorentz condition, because the dipole moment is distributed. Thus

$$\varepsilon = 4\pi\underset{\sim}{\alpha}_o + \frac{1 + \frac{8\pi}{3}\alpha_1}{1 - \frac{4\pi}{3}\alpha_1}$$

$$\alpha_o = -\frac{e^2}{m_o} \sum_{\underline{k},m} f_m(\underline{k}) \frac{f_{mn}}{\omega^2 - i\omega\gamma_o} \qquad (33.33)$$

$$\underset{\sim}{\alpha}_1 = \frac{e^2}{m_o} \sum_{\underline{k},m} f_m(\underline{k}) \sum_{n \neq m} \frac{f_{mn}}{(\omega_{mn}^2 - \omega^2) + i\omega\gamma_{mn}}$$

Using definition $D_o = E_o + 4\pi P_o = \varepsilon E_o$, we have the Lorentz relation:

$$\varepsilon = \frac{1 + \frac{8\pi}{3}\alpha}{1 - \frac{4\pi}{3}\alpha} \;; \quad \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\alpha \tag{33.31}$$

$$\alpha = \frac{e^2}{m_o} \sum_j n_j \frac{1}{(\omega_j^2 - \omega^2) + i\omega\gamma_j}$$

where α = polarizability

n_j = no. of j-type oscillators

Eq. (33.31) reduces to $\varepsilon = 1 + 4\pi\alpha$ if α is small. Main effect of the quantum-mechanical treatment is to introduce the f-values. Eq. (33.31) then takes the final form:

$$\alpha = \frac{e^2}{m_o} \sum_{\underline{k},m} f_m(\underline{k}) \left\{ \sum_n{}' \frac{f_{mn}}{(\omega_{mn}^2 - \omega^2) + i\omega\gamma_{mn}} - \frac{f_{mn}}{\omega^2 - i\omega\gamma_o} \right\} \tag{33.32}$$

Eq. (33.32) only valid if α is small. The zero frequency term is not subject to the Lorentz condition, because the dipole moment is distributed. Thus

$$\varepsilon = 4\pi\underset{\sim}{\alpha}_o + \frac{1 + \frac{8\pi}{3}\alpha_1}{1 - \frac{4\pi}{3}\alpha_1}$$

$$\alpha_o = -\frac{e^2}{m_o} \sum_{\underline{k},m} f_m(\underline{k}) \frac{f_{mn}}{\omega^2 - i\omega\gamma_o} \tag{33.33}$$

$$\underset{\sim}{\alpha}_1 = \frac{e^2}{m_o} \sum_{\underline{k},m} f_m(\underline{k}) \sum_{n \neq m} \frac{f_{mn}}{(\omega_{mn}^2 - \omega^2) + i\omega\gamma_{mn}}$$

Eq. (33.33) has never been proved in general. The damping factors arise from interaction with lattice vibrations. In particular we can identify γ_o with $1/\tau_{\underline{k}}$, where $\tau_{\underline{k}}$ is the relaxation time for electron lattice collisions. Using this result we find:

$$\alpha_o = -\frac{e^2}{m_o} N_{eff} \frac{\tau^2}{1+\omega^2\tau^2} - i\frac{e^2}{m_o\omega} N_{eff} \frac{\tau}{1+\omega^2\tau^2} \qquad (33.34)$$

where

$$N_{eff} = \frac{m_o}{4\pi^3\hbar^2} \int \frac{\left(\frac{\partial \epsilon}{\partial k_x}\right)^2}{|\nabla_{\underline{k}}\epsilon|^2} dS_{\underline{k}}$$

integration being over the surface of the occupied distribution, and τ is the value of $\tau_{\underline{k}}$ at the Fermi surface. Similarly, we may write:

$$\alpha_1 = \frac{e^2}{m_o} \sum_{\underline{k},m} f_m(\underline{k}) \sum_n \left[1-f_n(\underline{k})\right] \frac{f_{mn}(\omega_{mn}^2-\omega^2)}{(\omega_{mn}^2-\omega^2)^2+\omega^2\gamma_{mn}^2}$$

$$-i\frac{e^2}{m_o} \sum_{\underline{k},m} f_m(\underline{k}) \sum_n \left[1-f_n(\underline{k})\right] \frac{f_{mn}\,\omega\gamma_{mn}}{(\omega_{mn}^2-\omega^2)^2+\omega^2\gamma_{mn}^2} \qquad (33.35)$$

The $\underline{k}$ summation can be turned into an integration, considering both spin directions. If this is done, and the Lorentz relation ignored, we obtain finally:

$$\varepsilon' = 1 - \frac{4\pi e^2}{m_o} N_{eff} \frac{\tau^2}{1+\omega^2\tau^2} + \frac{4\pi e^2}{m_o} \sum_{m,n}{}' \int \frac{f_{mn}(\omega_{mn})\rho_{mn}(\omega_{mn})d\omega_{mn}}{\omega_{mn}^2-\omega^2}$$

$$\varepsilon'' = \frac{4\pi e^2}{m_o\omega} N_{eff} \frac{\tau}{1+\omega^2\tau^2} + \frac{4\pi e^2}{m_o} \sum_{m,n}{}' \int \frac{f_{mn}(\omega_{mn})\rho_{mn}(\omega_{mn})\omega\gamma_{mn}}{(\omega_{mn}^2-\omega^2)^2+\omega^2\gamma_{mn}^2} d\omega_{mn} \qquad (33.36)$$

$$\rho_{mn}(\omega_{mn}) = \frac{1}{4\pi^3} \int f_m(\underline{k}) \left[1-f_n(\underline{k})\right] \frac{dS_{\underline{k}}}{|\nabla_{\underline{k}}\omega_{mn}(\underline{k})|}$$

Surface integral in $\underline{k}$ space is taken over a surface of constant frequency $\omega_{mn}(\underline{k})$. The function ρ_{mn} is thus a frequency density. If ω lies within an absorption band, then ε'' may be simplified. Usually f and ρ vary inappreciably over a frequency interval of width $\sim\gamma_{mn}$. Thus all except resonance function may be taken out of integral, and we have:

$$\varepsilon'' = \frac{4\pi\sigma_0}{1+\omega^2\tau^2}\,\frac{1}{\omega} + \frac{2\pi^2 e^2}{m_0\omega}\sum_{m,n}{}' f_{mn}(\omega)\,\rho_{mn}(\omega) \tag{33.37}$$

where

$$\sigma_0 = \frac{N_{eff}e^2}{m_0}\tau = \text{D.C. conductivity}$$

Thus with assumptions made here high frequency dispersion can be directly related to absorption. If ω is outside absorption band there is still some contribution to absorption arising from simultaneous action of electrons and lattice vibrations.

Optical Constants

If complex dielectric constant (33.33) or (33.36) is substituted in Maxwell's equations, the propagation constant for an isotropic medium is given by:

$$\sigma^2 = \frac{\varepsilon\omega^2}{c^2} \qquad \sigma = (n-ik)\frac{\omega}{c}$$

$$(n-ik)^2 = \varepsilon'-i\varepsilon'' \tag{33.38}$$

From (33.38) we have:

$$n^2 - k^2 = \varepsilon' \qquad 2nk = \varepsilon''$$

$$n^2 = \frac{1}{2}\varepsilon' + \frac{1}{2}\sqrt{\varepsilon'^2 + \varepsilon''^2} \qquad k^2 = -\frac{1}{2}\varepsilon'^2 + \frac{1}{2}\sqrt{\varepsilon'^2 + \varepsilon''^2} \tag{33.39}$$

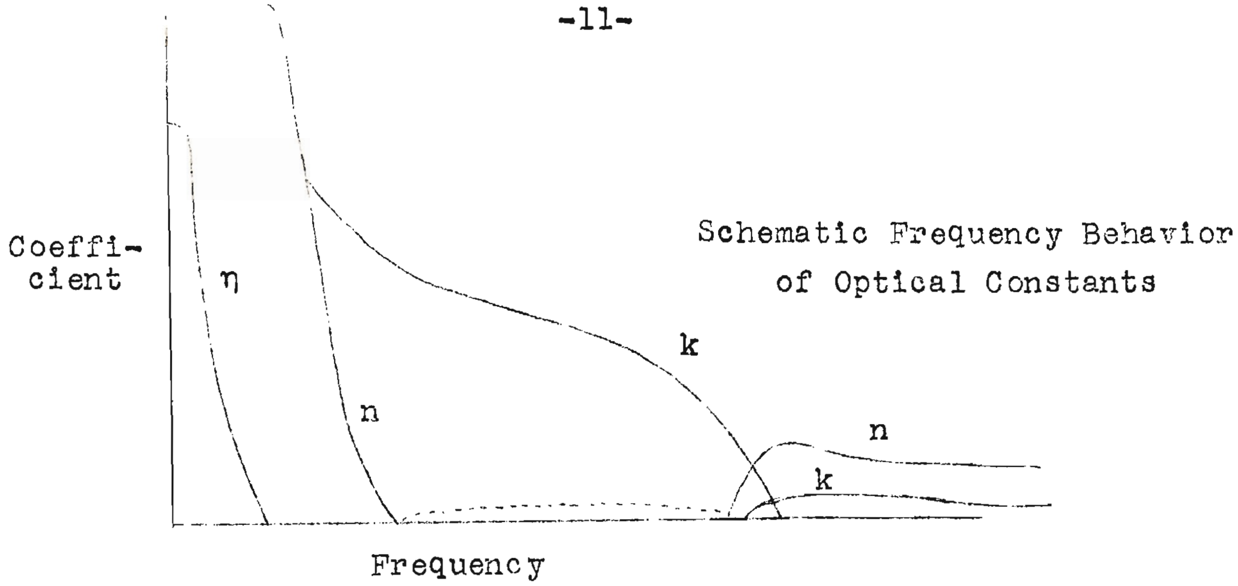

Figure (33.1)

n = refractive index

k = extinction coefficient $\qquad \eta = \frac{8\pi n k\omega}{c}$ = absorption coefficient (thin films)

n,k = optical constants

Figure 33.1 represents case in which DC conductivity terms in ε', ε'' predominate, Three regions:

a. $\omega\tau << 1$, $\tau \sim 10^{-13}$ sec., $n \approx k$ = both large, η large, ε' negative,

$$\varepsilon'' >> |\varepsilon'|. \qquad n = \sqrt{\frac{\varepsilon''}{2}} = \left(\frac{\sigma_o}{\nu}\right)^{\frac{1}{2}}$$

$$n^2 - k^2 = \varepsilon' \sim$$

Normal reflection coefficient $\qquad R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$

$$1 - R = \frac{4n}{(n+1)^2 + k^2} \approx 2\left(\frac{\nu}{\sigma_o}\right)^{\frac{1}{2}} \tag{33.40}$$

This is the Hagen-Rubens relation. In practical units:

$$1 - R = 2(10^{-7}\rho\nu)^{\frac{1}{2}} \tag{33.41}$$

ρ = resistivity in ohm-cm $\qquad \nu$ = frequency

b. $\omega\tau >> 1$, $\varepsilon'' << |\varepsilon'|$. In the general case, we have:

$$1 - R = 2\left(\frac{\nu}{\sigma_0}\right)^{\frac{1}{2}} \left[-\omega\tau + \sqrt{1 + \omega^2\tau^2}\right]^{\frac{1}{2}}$$

$$\approx \left(\frac{1}{\pi\sigma_0\tau}\right)^{\frac{1}{2}} \qquad \omega\tau >> 1 \qquad (33.42)$$

independent of frequency.

c. $\frac{4\pi N_{eff} e^2}{M_0 \omega^2} < 1$; ε' changes from − to +, and roles of n and K interchange, metal becomes transparent usually in ultraviolet. Observed by R. W. Wood on films of alkali metals.

Actually there are several complications of this simple picture, as follows:

1. Extinction distance (or skindepth) comparable with mean free path.

In general $K^2 = \frac{2\pi\sigma_0}{1+\omega^2\tau^2}\frac{1}{\omega}\left[\omega\tau + \sqrt{1+\omega^2\tau^2}\right] \approx \frac{\sigma_0}{\nu}$, $\omega\tau << 1$

$$\approx \frac{\sigma_0}{\pi\nu^2\tau} \qquad , \ \omega\tau >> 1$$

When $\omega\tau << 1$, the condition that mean free path exceeds skin depth may be written:

$$(\nu\sigma_0)^{\frac{1}{2}} > \frac{1}{2\pi}\frac{c}{v_0}\frac{1}{\tau} \qquad (33.43)$$

or $$2\left(\frac{\nu}{\sigma_0}\right)^{\frac{1}{2}} < \frac{2\,v_0}{c}\,\omega\tau$$

where v_0 = velocity of electron at Fermi surface.

The condition (33.43) is reached at a frequency which is proportional to the cube of the resistivity, and which therefore decreases rapidly with temperature, and occurs for good metals at microwave frequencies for liquid air temperature. Above this frequency there is an effective τ which varies with frequency so as to satisfy (33.43) with approximate equality. Thus in this region $\tau \sim \nu^{-1/3}$ and 1-R varies as $\nu^{2/3}$ rather than $\nu^{1/2}$. Thus absorption exceeds classical value by an increasing amount. In the frequency range $\omega\tau >> 1$, which occurs at much higher than the classically calculated frequency, the penetration depth $\frac{c}{\omega}\frac{1}{K} = \left(\frac{4\pi\sigma_o}{c\tau}\right)^{1/2}$ which is independent of frequency and of τ. The effective mean free path is:

$$\lambda_{eff} = \frac{v_o : \tau}{1+\omega^2\tau^2} \qquad (33.44)$$

If $\lambda_{eff} < \left(\frac{4\pi\sigma_o}{c\tau}\right)^{1/2}$, which occurs for sufficiently high frequency, the behavior is normal and τ has the classical value. As the frequency is decreased, λ_{eff} increases until it exceeds the penetration, at which point λ_{eff} can only be made to satisfy the condition by a large decrease in τ into the region where $\omega\tau << 1$. This is accompanied by a corresponding jump in 1-R. Results are sketched in Fig. (33.2) for Ag at liquid helium temperature.

2. Neglect of second-order processes outside fundamental absorption band. The free electron absorption should make the sole contribution in the frequency range below the fundamental absorption band (estimated at 1.7 ev. for Na). This should be

$$\pi = \frac{4\pi N_{eff} e^2}{m_o \omega^2} = \text{absorption coefficient} \qquad (33.45)$$

and should be strongly temperature dependent. Actual absorption is higher and temperature independent, apparently. This has not been explained. May be due to second order process involving simultaneous band absorption and absorption or emission of a phonon. This involves a breakdown of selection rules due to lattice vibrations, or to other crystalline imperfections, or possibly due to electron interactions.

For region c, transition from reflectivity to transparency, the condition is that ε' changes sign,

$$n_c^2 - \frac{N_{eff} e^2 \lambda_o^2}{\pi m c^2} = 0 \qquad (33.46)$$

where n_c^2 is the square of refractive index due to ion cores alone.

Results of Wood for alkali metals shown in table 33.1.

TABLE 33.1

Element	Calculated * Free Electrons	Observed	N_{eff}
Li	1500 Å	2050	0.55
Na	2100	2100	1.10
K	2900	3150	0.97
Rb	3200	3600	0.94
Cs	3600	4400	0.85

* Calculated with $n_c^2 = 1$, N_{eff} = actual electron density.

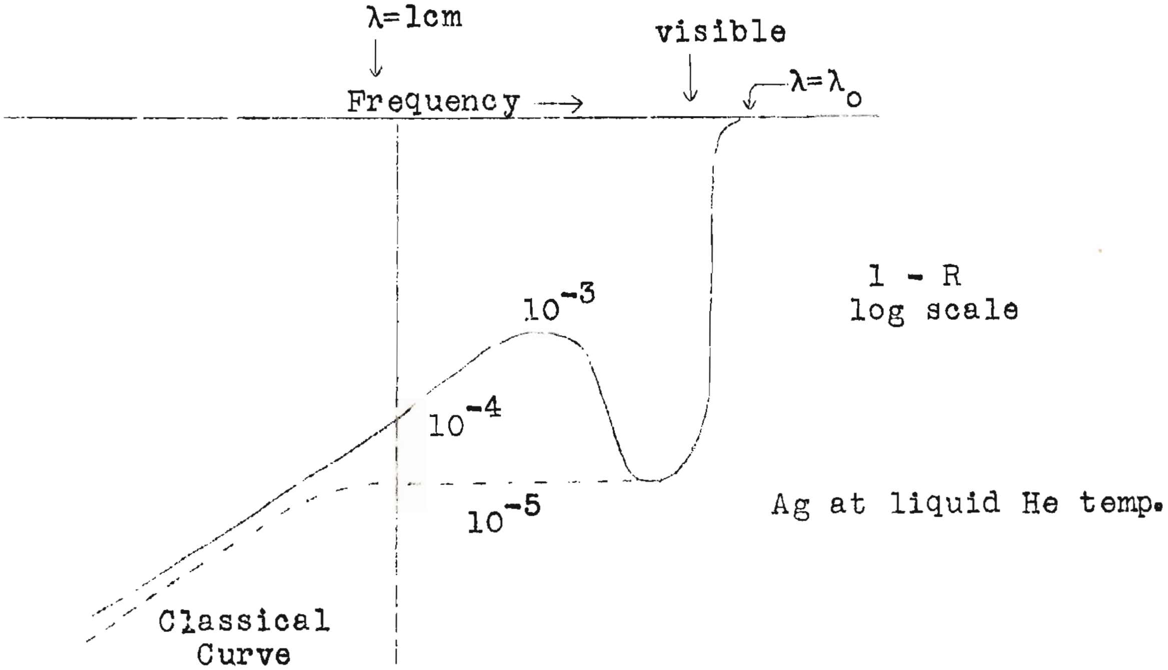

Fig. (33.2)

References:

Mott and Jones, p. 99 - 125

Seitz, p. 629 - 661

E. H. Sondheimer, Advances in Physics, Vol. I, edited by N. F. Mott. (Anomalous skin effect).

A. H. Wilson, Theory of Metals

Applied Physics 297, 1961

Statistics

References

The early references are given in the review article by H. Brooks, Advances in Electronics, Vol. 7. Pages 117-127 of this article should be read; they deal with several points not usually considered in the literature.

Later work can be found by looking first at two reviews by Landsberg (a) in Semiconductors and Phosphors, the proceedings of the Garmisch Conference (b) in Solid State Physics in Telecommunications, the proceedings of the Brussels Conference. Easily identifiable parts of these articles should be read, along with the references given.

These articles also give appropriate references (to Shockley and Read; and to Hall) for recombination via recombination centers.

Other useful articles are by Seitz, in the book "Imperfections in Nearly Perfect Crystals" which discusses the general problem of imperfections; Herring, in the Proceedings of the Photoconductivity Conference. The article by Arthur, Proc. Phys.Soc. B 68, 121 (1955) discusses methods of determining lifetime and gives references, as does that by Many and Bray, Progress in Semiconductors, Vol. 3. The articles in the Physical Review and in the B.S.T.J. by van Roosbroeck are probably unsuitable for the course. A good review article, especially on deep lying impurities, is that by Newman and Tyler, Solid State Physics, Vol. 8.

The G. E. report by H all, 59-RL-2211, is an up-to-date, and clear, report on recombination mechanisms.

Applied Physics 297, 1961

Statistics

1. Derivation of Fermi Dirac distribution, including general case of impurities with degenerate levels.

2. Maxwell Boltzmann approximation, and conditions of validity. Charge balance equation. Approximate solutions in several cases involving impurities. The intrinsic case. Critical assessment of derivation of energy gaps and ionization energies from experiments involving carrier densities.

3. Mechanisms of recombination. Particular consideration of radiative recombination lifetime, and of the phenomenological theory of recombination via impurities.

4. Trapping statistics.

5. Statistics of inhomogeneous semiconductors, simple junctions.

6. Inversion layer at surface, radiation damage islands, dislocation effects.

29. Statistical Mechanics of Semiconductors

Fundamental difference in character of impurity levels and band levels. For band levels occupation probability of a given level is independent of whether other levels are occupied. For localized impurity levels, however, occupation of one level prevents occupation of other levels in the same impurity center because of Coulomb interaction.

Derivation of Fermi statistics from Boltzmann statistics.

$$Z = \sum_r e^{-\frac{W_r}{kT}} \tag{29.1}$$

$$\text{where } W_r = \sum_{s=0}^{\infty} n_s \epsilon_s$$

where $n_s = 0, 1$, i.e. n_s is the occupation number of the energy level s. Index r thus denotes the totality of possible sets $\{n_1, n_2 \ldots n_s \ldots\}$ where s runs over all the energy levels of the system. Actually, partition function is restricted to a fixed total number of particles such that $\sum_{s=0}^{\infty} n_s = n_o$. Thus:

Z = coefficient of x^{n_o} in:

$$\sum_{\ldots n_s \ldots} e^{-\sum_{s=0}^{\infty} \frac{n_s \epsilon_s}{kT}} \, x^{\sum_{s=0}^{\infty} n_s} \tag{29.2}$$

Equation (29.2) may be written as a product:

$$\prod_{s=0}^{\infty} \sum_{n_s} e^{-\frac{n_s \epsilon_s}{kT}} \, x^{n_s} \tag{29.3}$$

For ordinary Fermitstatistics each n_s has the values 0 and 1, so that (29.3) may be written immediately as:

$$\prod_{s=0}^{\infty}\left[1 + x\, e^{-\frac{\varepsilon_s}{kT}}\right] \tag{29.4}$$

The coefficient of x^{n_0} in (29.4) may be obtained by Cauchy's theorem:

$$Z = \frac{1}{2\pi i}\oint \frac{\prod_{s=0}^{\infty}\left[1 + xe^{-\frac{\varepsilon_s}{kT}}\right]}{x^{n_0+1}}\, dx \tag{29.5}$$

where contour surrounds the point x=0. Equation (29.5) is evaluated by steepest descents, i.e. integrand replaced by its maximum value: We let $sx_m = e^{\zeta/kT}$ and determine maximum from the condition:

$$F = -kT \ln Z = n_0\zeta - kT \sum_{s=0}^{\infty} \ln\left[1 + e^{\frac{\zeta-\varepsilon_s}{kT}}\right]$$

$$\frac{\partial F}{\partial \zeta} = 0 \tag{29.6}$$

$$\text{or} \qquad n_0 = \sum_{s=0}^{\infty} \frac{1}{1 + e^{\frac{\varepsilon_s - \zeta}{kT}}}$$

which is the conventional result. However, when impurity levels are present, and spin taken into account a more complicated procedure results:

For band levels $n_s = 0$ with weight 1
$n_s = 1$ with weight 2
$n_s = 1$ with weight 1

$$\sum_{n_s} e^{\frac{-n_s \mathcal{E}_s}{kT}} x^{n_s} = \left[1 + x e^{-\frac{\mathcal{E}_s}{kT}}\right]^2 \qquad (29.7)$$

For localized levels:

$n_i^{(l)} = 1$ with weight g_l, all other $n_i^{(l)}$'s $= 0$

$n_i^{(l)} = 0$ with weight 1

but there are no higher occupation numbers. Thus:

$$\sum_{\ldots n_i^{(l)} \ldots} \prod_l e^{\frac{-n_i^{(l)} \mathcal{E}_i^{(l)}}{kT}} x^{n_i^{(l)}} = 1 + \sum_l g_l x e^{-\frac{\mathcal{E}_i^{(l)}}{kT}} \qquad (29.8)$$

whence:

$$F = n_o \zeta - kT \sum_i \ln\left\{1 + \sum_l g_l e^{\frac{\zeta - \mathcal{E}_i^{(l)}}{kT}}\right\} - 2kT \sum_s \ln\left[1 + e^{\frac{\zeta - \mathcal{E}_s}{kT}}\right] \qquad (29.9)$$

$$n_o = \sum_i \frac{1}{1 + \frac{1}{\sum_l g_l e^{\frac{\zeta - \mathcal{E}_i^{(l)}}{kT}}}} + \sum_s \frac{2}{1 + e^{\frac{\mathcal{E}_s - \zeta}{kT}}} \qquad (29.10)$$

Here $\mathcal{E}_i^{(l)}$ is the l'th energy level in the i'th impurity center and $n_i^{(l)}$ is the corresponding occupation number for this level. First term of (29.10) represents number of electrons in impurity levels, second term represents number of electrons in band levels.

Consider the case of conduction band with single impurity level which can be occupied with either spin direction. Equation (29.10) becomes:

$$n_o = \frac{N_D}{1 + \frac{1}{2} e^{\frac{\mathcal{E}_D - \zeta}{kT}}} + 2Ae^{\frac{\zeta}{kT}} \qquad (29.11)$$

where N_D is the number of donor centers. If there are no acceptors present $n_o = N_D$ to maintain electrical neutrality. Here

$$A = \left(\frac{2\pi mkT}{ah^2}\right)^{3/2} \quad , \quad \text{cf. eq. (18.30), or (15.7)}$$

Eq. (29.11) is derived on assumption the electrons in conduction band have energy $\varepsilon = \frac{a\hbar^2}{2m} k^2$ and that distribution is non-degenerate, i.e. ζ/kt large and negative (origin of energy taken as bottom of conduction band).

$$\text{Let} \qquad x = Ae^{\zeta/kT} \qquad \mu = Ae^{\varepsilon_D/kT} \tag{29.12}$$

Then:

$$x^2 + \frac{1}{2}(\mu + N_D - n_o)x - \frac{1}{4} n_o \mu = 0 \tag{29.13}$$

$$x = \sqrt{\frac{1}{16}(\mu + N_D - n_o)^2 + \frac{1}{4} n_o \mu} - \frac{1}{4}(\mu + N_D - m_o)$$

Case 1: $N_D = n_o$; $\mu \gg N_D$. Corresponds to Ge and Si at room temperature, where $\varepsilon_D \sim kT$. Then:

$$2x = N_D \tag{29.14}$$

i.e. no. of electrons in conduction band is equal to number in impurity centers. Condition for validity equivalent to:

$$\frac{\varepsilon_D}{kT} < \ln \frac{2.6 \times 10^{19}}{N_D}$$

e.g. for $N_D = 4 \times 10^{16}$ cm^{-3} (concentration = 10^{-6} in Ge) gives $\frac{\varepsilon_D}{kT} < 6.5$. Since $\varepsilon_D \sim .01$ev. for Ge this is fulfilled, but not by large margin.

Case 2: $N_D = n_o$; $\mu << N_D$. Then:

$$2x = N_D^{1/2} \mu^{1/2} = N_D^{1/2} A^{1/2} e^{-\frac{|\varepsilon_D|}{2kT}} \qquad (29.15)$$

Case 3: $N_D > n_o$; $\mu << N_D$, n_o $\qquad \mu << N_D - n_o$

Then:

$$2x = n_o \mu = n_o e^{-\frac{|\varepsilon_D|}{kT}} \qquad (29.16)$$

Case 4: $N_D > n_o$; $\mu << N_D$ but $<< N_D - n_o$, then:

$$2x = N_D^{\frac{1}{2}} \mu^{\frac{1}{2}} + \frac{1}{16} \frac{(N_D - n_o)^2}{N_D^{1/2} \mu^{1/2}}$$

$$= (N_D A)^{\frac{1}{2}} e^{-\frac{|\varepsilon_D|}{2kT}} + \frac{1}{16} \frac{(N_D - n_o)^2}{(N_D A)^{1/2}} e^{+\frac{|\varepsilon_D|}{2kT}} \qquad (29.17)$$

In comparing cases 3 and 4, we notice that unless N_D is exactly equal to n_o the condition for 3 is satisfied at low enough temperature. This shows the case 3 is always realized in practice at sufficiently low temperature, and that the position of the Fermi level converges to the impurity levels. In practice there is never an exact balance between donors and acceptors.

Case 5: $N_D > n_o$; $\mu >> N_D$.

$$2x = n_o - \frac{N_D n_o}{\mu}$$

$$= n_o - \frac{N_D n_o}{A} e^{\frac{|\varepsilon_D|}{kT}} \qquad (29.18)$$

When we take acceptor and filled band levels explicitly into account equation (29.11) is replaced by:

$$n_o = \frac{N_D}{1 + \frac{1}{2} e^{\frac{\varepsilon_D - \zeta}{kT}}} + 2A_e e^{\frac{\zeta - \varepsilon_c}{kT}} - 2A_h e^{\frac{\varepsilon_f - \zeta}{kT}} - \frac{N_a}{1 + \frac{1}{2} e^{\frac{\zeta - \varepsilon_a}{kT}}}$$

(29.19)

where:

n_o = excess positive impurity charge over neutral crystal = $N_D - N_A$ in general.

N_D = number of donors

N_A = number of acceptors

ε_C = energy of edge of conduction band

ε_F = energy of top of filled band

$A_e = \left(\frac{2\pi mkT}{\alpha_e h^2}\right)^{\frac{3}{2}}$, α_e = effective mass constant for electrons

$A_h = \left(\frac{2\pi mkT}{\alpha_h h^2}\right)^{\frac{3}{2}}$, α_h = effective mass constant for holes

ε_D = energy of donor levels

ε_A = energy of acceptor levels

Generalization of (29.19) to many donor and acceptor levels is straightforward. If there are several levels for one impurity the summation is inside argument of Fermi function. Middle terms represent, respectively, number of electrons in conduction band and minus number of holes in filled band. Actually it can be shown to be immaterial whether a given level is treated as an acceptor or as a donor in eq. (29.19). Eq. (29.19) is of course, only valid when ζ is not near the edge of either band.

If impurity levels are very near band edges, so that impurities are completely ionized, eq. (29.19) simplifies to:

$$N_D - N_A = n_e - n_h \tag{29.20}$$

where

$$n_e = 2A_e e^{\frac{\zeta - \mathcal{E}_c}{kT}} \qquad n_h = 2A_h e^{\frac{\mathcal{E}_F - \zeta}{kT}} \tag{29.21}$$

From (29.21) it follows that:

$$n_e n_h = 4A_e A_h e^{\frac{\mathcal{E}_F - \mathcal{E}_c}{kT}} \tag{29.22}$$

It follows that product of the number free holes and free electrons is independent of the concentration of donors and acceptors. We can write (29.22)

$$n_e n_h = n_i^2 \tag{29.23}$$

$$n_i = 2(A_e A_h)^{\frac{1}{2}} e^{-\frac{\Delta E_G}{2kT}} \qquad \text{(29}$$

where ΔE_G is energy gap between bands. From (29.23) and (29.20)

$$n_e^2 - n_o n_e - n_i^2 = 0 \tag{29.24}$$

$$n_e = \frac{1}{2}n_o + \sqrt{\frac{1}{4}n_o^2 + n_i^2}$$

$$n_h = -\frac{1}{2}n_o + \sqrt{\frac{1}{4}n_o^2 + n_i^2}$$

Usually $n_i \ll n_o$, then

$$n_e \sim n_o + \frac{n_i^2}{n_o} \tag{29.25}$$

$$n_h \sim \frac{n_i^2}{n_o}$$

In equilibrium increasing electrons suppresses holes and vice-versa. Dynamic argument:

g = rate of generation of hole electron pairs

rn_en_h = rate of recombination

$$g = rn_en_h = rn_i^2 \tag{29.26}$$

r relative temp.-independent, and of order $v\sigma$, where v = av. velocity and σ = cross section. Take $v \sim 10^7$ cm/sec., $\sigma \sim 10^{-15}$ cm^2, $r = 10^{-8}$ cm^3/sec. Then if $\Delta E_G = 0.65$ ev., $n_i \sim 10^{14}$ cm^{-3}, thus

$$g \sim 10^{20} \text{ pairs per cm}^3 \text{ per sec.}$$

at room temperature. From detailed balancing g is high in regions where recombination is rapid.

If impurities remain ionized we may write:

$$\frac{dn_e}{dt} = \frac{dn_h}{dt} = g - rn_en_h$$

$$n_e - n_h = n_o \quad \text{(electrical neutrality)}$$

Thus for electrons in excess: $\frac{dn_h}{dt} = g - rn_h(n_o + n_h)$

$$\frac{dn_h}{dt} = r\left\{n_i^2 - n_h(n_o + n_h)\right\} \qquad (29.27)$$

Life-time of hole is thus $\tau \approx \frac{1}{n_e r} \sim 10^{-8}$ sec.

Actual measured life-times in good bulk materials may be of or order 10^{-4} sec. to 10^{-5} sec. This would make cross section and hence generation rate 1000 times smaller than assumed, i.e.

$$g \sim 10^{17} \text{ pairs/cm}^3\text{/sec.}$$

$$\sigma \sim 10^{-18} \text{cm}^2$$

Degeneracy:

Equation (29.15) may be written:

$$\frac{\zeta}{kT} = -\frac{|\mathcal{E}_D|}{2kT} - \ln 2\sqrt{\frac{A}{N_D}} \qquad (29.28)$$

If $|\mathcal{E}_D|$ very small as in Ge and Si, then $\frac{\zeta}{kT}$ remains large and negative so long as $N_D \ll 4A \sim 10^{20}$ per cc. at room temperature. At a 70°K., $N_D \sim 10^{19}$ and at 10°K. 5×10^{17} per cc. When ζ moves close to the conduction band, it remains much less than given by (29.28). More generally, ζ reaches is maximum point when

$$\frac{N_D}{4A} \sim e^{\frac{3}{2}} = 4.48 \quad \text{or} \left(\frac{Tm}{300}\right) = \left(\frac{N_D}{2.37 \times 10^{20}}\right)^{\frac{2}{3}} \qquad a.$$

$$T = 0.78 \times 10^{-11} N_D^{2/3} \qquad (29.29)$$

so that

$$\zeta = -\frac{|\mathcal{E}_D|}{2} + \frac{3}{4}kT_m \qquad b.$$

If N_D is large, then 29.29 a. is satisfied for a high temperature and ξ becomes large. The degeneracy criterion is usually given as:

$$T_d = 4.2 \times 10^{-11} N_D^{2/3}$$

$$= \frac{h^2}{8mk}\left(\frac{3N_D}{\pi}\right)^{2/3}$$

If temperature above this, there is no degeneracy.

AP 297 1961 Term Paper Topics

Write a critical essay on one of the following topics. Indicate clearly what information can be obtained from experiments involved. Estimate the errors in these cases, and compare them with errors in other experiments measuring the same quantities. Keep any discussion of experimental or calculational details down to a minimum. List your references.

1) Elastoresistance of semiconductors

✓ 2) Recombination mechanisms in semiconductors

3) Magnetic susceptibility of semiconductors

4) Spin resonance in semiconductors

5) Impurity band conduction in semiconductors

6) Mechanisms of photoconductivity

7) Radiation damage in semiconductors

8) Hot electron phenomena

9) Tunneling in semiconductors

10) Phonon drag effect

11) Exciton spectra

12) Specific heat and thermal conductivity of semiconductors

13) Thermoelectric effects in semiconductors

14) Diffusion of impurities in semiconductors

✓ 15) Factors determining lifetime in semiconductors

✓ 16) Trapping in semiconductors

17) Optical properties of impurities in a magnetic field

18) Neutron diffraction and lattice vibration spectra

19) Electrical effects of grain boundaries and dislocations in semiconductors.

✓ 20) Avalanche breakdown in junctions and in homogeneous semiconductors at low temperatures.

21) Group theoretical selection rules on phonon transitions.

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Problem Set II

1) Determine the allowedness of the following transitions for the diamond crystal under the perturbation in brackets (a) $\Gamma_{25}' \rightarrow \Gamma_2'$ (electromagnetic radiation, electric dipole) (b) $\Gamma_{25}' \rightarrow L_1$ (e.d) (c) $\Gamma_{25}' \rightarrow \Delta$ (e.d.) (d) $L_3' \rightarrow L_1$ (e.d.) (e) $\Gamma_{25}' \rightarrow \Gamma_{15}'$ (e.d.) (f) $L_3' \rightarrow L_3$ (e.d.) (g) $\Gamma_2' \rightarrow L_1$ (6 types of phonons) (h) $\Gamma_2' \rightarrow \Delta$ (phonons) (i) $\Gamma_{15}' \rightarrow L_1$ (phonons) (j) $\Gamma_{15}' \rightarrow \Delta$ (phonons), (k) $L_1 \rightarrow L_1$ (phonons)

2. Assume a semiconductor with non-degenerate conduction and valence band edges at $k = 0$, energy gap 0.2 ev and effective masses = 0.04 times the free electron mass. On the assumption that optical transitions between the two bands are allowed, estimate the absorption coefficient 0.05 e.v. above the threshold energy for absorption. Ignore possible phonon effects and exciton effects.