

THE OPTICAL PROPERTIES OF GRAPHITE

by

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
CHAPTER 1	
THE BAND STRUCTURE OF GRAPHITE	3
(a) The Graphite Structure	3
(b) The Tight Binding Approximation	4
CHAPTER 2	
THE REFLECTION COEFFICIENT AS A FUNCTION OF THE COMPLEX DIELECTRIC CONSTANT	7
(a) Formulae for the Complex Dielectric Constant	7
(b) The Matrix Element $\langle u_+ \frac{\partial}{\partial x} u_- \rangle$	10
CHAPTER 3	
THE COMPLEX DIELECTRIC CONSTANT	13
(a) The Imaginary Part	13
(b) The Real Part	14
SUMMARY	18
APPENDIX 1	19
APPENDIX 2	24
REFERENCES	28

INTRODUCTION

A study of the electronic properties of a substance usually requires the knowledge of its band structure. The starting point when trying to determine the band structure of a crystalline material is to employ one or another type of approximation to obtain the general form of the structure of energy bands. This general form usually contains certain parameters whose theoretical calculation is difficult or prohibitive. Thus we resort to experiments to determine the values of these parameters and consequently the exact band structure.

To establish the validity of an approximation we have to show that the model based on this approximation can explain the physical properties of the material. In this present work we rely on the model developed by P.R. Wallace⁽¹⁾ using the tight binding approximation for single crystal graphite. Our task is to examine whether the optical properties of graphite as calculated using this model conform with experimental measurements in the infrared region of radiation.

With the knowledge of the structure of energy bands and the crystal wave functions we can calculate the complex dielectric constant $\epsilon = \epsilon_1 + i\epsilon_2$ making use of the formulae derived by Ehrenreich and Cohen⁽²⁾ for this quantity. From ϵ we can obtain the reflection coefficient R and make comparison between experimental values and the theoretically derived values.

The same problem has been dealt with by Boyle and Nozieres⁽³⁾. In order to obtain reliable data, rather than measure the optical constants directly, they measured the reflection coefficient for graphite in the case of monochromatic, linearly polarized radiation at liquid helium temperature for wavelengths $\lambda = 1 - 30\mu$ (Fig. 3). In their theoretical work they rely on the band structure of graphite developed by Slonczewsky and Weiss⁽⁴⁾ using group theory and perturbation methods to calculate the general topology of bands. This model gives rise to a number of adjustable parameters. B. and N.'s work is concerned with the determination of one of these parameters from the experiment mentioned above.

Our purpose is to try to fit the experimental data on the reflection coefficient using P.R. Wallace's model. It is interesting to see whether this model, despite its simplicity, can give a fair agreement with the experiment in question.

CHAPTER 1

THE BAND STRUCTURE OF GRAPHITE

In this section we give a short account of the derivation of the structure of the energy bands and electronic wave functions for single crystal graphite using the tight binding approximation⁽¹⁾.

(a) Crystal Structure of Graphite

In graphite the carbon atoms are arranged in parallel layers in such a way that atoms in each layer form a hexagonal network (Fig. 1). The hexagonal spacing in the layer (1.42Å) is small compared with the spacing of the lattice planes ($d = 3.37\text{Å}$). This suggests that in first approximations we neglect the interaction between layers and treat graphite as a two dimensional crystal structure.

Graphite has four valence electrons, three of which form tight bonds with neighbouring atoms in the layer. The fourth electron is considered to be in the $2p_z$ state with its axis of symmetry perpendicular to the lattice plane. Since the electrons forming bonds in the plane do not play a part in the electrical properties of graphite, we will assume that graphite has one conduction electron in the $2p_z$ state.

The unit cell in the hexagonal layer contains two atoms: A and B (Fig. 1).

The fundamental lattice displacement vectors are:

$$\bar{a}_1 = (\frac{\sqrt{3}a}{2}, \frac{a}{2}, 0), \quad \bar{a}_2 = (0, a, 0), \quad \bar{a}_3 = (0, 0, d).$$

The corresponding reciprocal lattice vectors:

$$\bar{b}_1 = (\frac{4\pi}{\sqrt{3}a}, 0, 0), \quad b_2 = (-\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}, 0) \quad b_3 = (0, 0, \frac{2\pi}{d}).$$

The first Brillouin zone for a layer of graphite is depicted in Fig. 2.

(b) The Tight Binding Approximation

In the tight binding approximation the wave function is of the form:

$$\psi = \phi_1 + \phi_2$$

where

$$\phi_1 = \sum_A \exp(i\bar{k} \cdot \bar{r}_A) X(\bar{r} - \bar{r}_A)$$

$$\phi_2 = \sum_B \exp(i\bar{k} \cdot \bar{r}_B) X(\bar{r} - \bar{r}_B)$$

$X(\bar{r})$ is the normalized $2p_z$ wave function for an isolated atom and the sums are taken over all sites occupied by A or B type atoms respectively. Using the variational method and assuming that the $X(\bar{r})$'s centered on different atoms do not overlap, that is

$$\int X(\bar{r} - \bar{r}_A) X(\bar{r} - \bar{r}_{A'}) = 0$$

we obtain for the energies and wave functions:

$$E_{\pm} = H_{11} \pm |H_{12}|$$

$$\psi_{\pm} = \frac{1}{\sqrt{2}} (\phi_1 \pm \lambda \phi_2)$$

where the \pm sign applies if \bar{k} is ^{outside}_{inside} of the hexagonal zone. The factor $1/\sqrt{2}$ has been inserted in order to normalize the periodic part of the wave function over the unit cell. H_{11} , H_{12} and λ are given by the expressions:

$$H_{11} = \int \phi_1^* H \phi_1 d^3r$$

$$H_{12} = \int \phi_1^* H \phi_2 d^3r$$

$$\lambda = \frac{H_{12}^*}{|H_{12}|} = \exp(i\delta(\bar{k}))$$

Calculating H_{11} and H_{12} as an approximation, only exchange integrals connecting nearest neighbours amongst the A type atoms, and integrals connecting nearest neighbours between different types (A and B) of atoms are retained. In this approximation we obtain:

$$H_{11} = E_0 - 2\gamma_0' \left[\cos(ak_y) + 2\cos\left(\frac{ak_y}{2}\right) \cos\left(\frac{3ak_y}{2}\right) \right]$$

$$H_{12} = -\gamma_0 \left[\exp\left(-\frac{iak_x}{3}\right) + 2\cos\left(\frac{ak_y}{2}\right) \exp\left(\frac{iak_x}{2 \cdot 3}\right) \right]$$

$$|H_{12}| = \gamma_0 \sqrt{1 + 4\cos^2\left(\frac{ak_y}{2}\right) + 4\cos\left(\frac{ak_y}{2}\right) \cos\left(\frac{3ak_x}{2}\right)}$$

and

$$\tan \delta(\bar{k}) = \frac{\sin\left(\frac{ak_x}{3}\right) - 2\sin\left(\frac{ak_x}{2 \cdot 3}\right) \cos\left(\frac{ak_y}{2}\right)}{\cos\left(\frac{ak_x}{3}\right) - 2\cos\left(\frac{ak_x}{2 \cdot 3}\right) \cos\left(\frac{ak_y}{2}\right)}$$

We notice that in the reduced wave vector representation $\Delta E = 2|H_{12}|$ gives the energy difference between levels corresponding to the same \bar{k} in the conduction and valence bands respectively. We can see that the bands do not overlap and there are degeneracies at the corners of the Brillouin Zone. Near the corners the following expression is valid:

$$|H_{12}| = \frac{\sqrt{3}}{2} a\gamma_0 |\bar{k}|$$

where \bar{k} is measured from the respective corner.

Previous theoretical estimates and fitting of the model to various physical properties of graphite give the value $\gamma_0 = 2.6$ Ev.

CHAPTER 2

THE REFLECTION COEFFICIENT AS A FUNCTION OF THE COMPLEX DIELECTRIC CONSTANT

As stated in the introduction, we want to calculate the reflection coefficient R of graphite at normal incidence of radiation. In this case R can be expressed in terms of the optical constants n and k in the following way⁽⁵⁾.

$$R = \frac{(n+ik-1)^2}{(n+ik+1)^2} = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \quad (2.1)$$

The relationship between the complex dielectric constant and the optical constants is:

$$\epsilon = \epsilon_1 + i\epsilon_2 = (n+ik)^2$$

Hence
$$n^2 - k^2 = \epsilon_1, \quad 2nk = \epsilon_2$$

and
$$2n^2 = \epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2} \quad (2.2)$$

$$2k^2 = -\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}$$

(a) Formulae for the Dielectric Constant

Ehrenreich and Cohen⁽²⁾ derived expressions for the complex dielectric constant for solids in the case when the electron-lattice interaction is negligible. The criterion for the relaxation effects to be negligible is that $\omega\tau \gg 1$. Since

the measurements of the reflection coefficient were done at liquid helium temperature in the infrared region, this condition is fulfilled in our case. (Soule⁽⁶⁾ gives the estimate $\tau \approx 3 \times 10^{-11}$ cm. for $T = 4.2$ K. For the angular frequencies considered $\omega > \frac{6\pi}{30} 10^{14} = 0.63 \times 10^{14}$. Hence $\omega\tau \approx 2 \times 10^3$.)

For monochromatic radiation of angular frequency ω and polarization in the μ direction, the real and imaginary parts of the complex dielectric constant are given by the expressions:

$$\begin{aligned} \epsilon_1 = 1 + \frac{e^2}{\pi^2 m} \sum_{\ell, \ell'}^1 \int d^3 k \frac{f_o(E_{\vec{k}\ell}) f_{\ell\ell'}^\mu}{\omega_{\ell\ell'}^2 - \omega^2} - \frac{e^2}{\pi^2 \hbar \omega^2} \sum_{\ell} \int d^3 k f_o(E_{\vec{k}\ell}) \frac{\partial^2 E_{\vec{k}\ell}}{\partial k_\mu^2} \\ \epsilon_2 = \frac{e^2}{\pi m^2 \omega^2} \sum_{\ell, \ell'}^1 \int d^3 k \left[f_o(E_{\vec{k}\ell}) - f_o(E_{\vec{k}\ell'}) \right] |P_{\ell\ell'}^\mu|^2 \delta(E_{\vec{k}\ell'} - E_{\vec{k}\ell} - \hbar\omega) \\ + \frac{e^2}{\pi} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{\ell} \int d^3 k f_o(E_{\vec{k}\ell}) \left[\delta(E_{\vec{k}+\vec{q}, \ell} - E_{\vec{k}\ell} - \hbar\omega) - \right. \\ \left. - \delta(E_{\vec{k}-\vec{q}, \ell} - E_{\vec{k}\ell} + \hbar\omega) \right] \end{aligned}$$

where $\hbar\omega_{\ell\ell'} = E_{\vec{k}\ell'} - E_{\vec{k}\ell}$

$$P_{\ell\ell'}^\mu = \int_{\text{unit cell}} u_{\vec{k}\ell'}^* p^\mu u_{\vec{k}\ell} d^3 r, \quad p^\mu = -i\hbar \frac{\partial}{\partial x_\mu}$$

$$f_{\ell\ell'}^\mu = \frac{2}{\hbar m \omega_{\ell\ell'}} |P_{\ell\ell'}^\mu|^2$$

Since the measurements were done at such a low temperature, we may calculate ϵ for zero temperature by setting the distribution function $f_0(E)$ equal to a step function. In the simple two dimensional model upon which we base our calculations, graphite has one valence and one conduction band. Since the bands do not overlap, the valence band will be completely filled. In order to give an explanation for the diamagnetic susceptibility of graphite, Haering and Wallace⁽⁷⁾ assumed that the conduction band is filled up to 0.06 eV from the degeneracy corners even at very low temperatures.

If the electric radiation is directed perpendicularly to the layer and polarized in the x direction, we obtain with the above assumptions:

$$\epsilon_1 = 1 + \frac{4e^2\hbar}{\pi m^2 d} \int_{\hbar\omega_{+-} > 2E_F} d^2k \frac{|\langle u_+ | \frac{\partial}{\partial x} | u_- \rangle|^2}{\omega_{+-}(\omega_{+-}^2 - \omega^2)} - \frac{2e^2}{\pi \hbar^2 d} \int_{\hbar\omega_{+-} < 2E_F} d^2k \frac{\partial^2 E_+(\bar{k})}{\partial k_x^2} \quad (2.3)$$

$$\epsilon_2 = \frac{2e^2\hbar^2}{m^2 d} \int_{\hbar\omega_{+-} > 2E_F} d^2k \left| \langle u_+ | \frac{\partial}{\partial x} | u_- \rangle \right|^2 \delta(\hbar\omega_{+-} - \hbar\omega) \quad (2.4)$$

(The second term in ϵ_2 dropped since at zero temperature it is different from zero only when $\omega = 0$.)

d = inter-layer distance

$$\hbar\omega_{+-} = E_+(\bar{k}) - E_-(\bar{k}) = 2|H_{12}|$$

E_F = Fermi energy.

(b) The Matrix Element $\langle u_+ | \frac{\partial}{\partial x} | u_- \rangle$.

In order to calculate the complex dielectric constant we have to evaluate the matrix element

$$\langle u_+ | \frac{\partial}{\partial x} | u_- \rangle = \int d^3 r_0 u_+^* \frac{\partial}{\partial x} u_-$$

where $\int d^3 r_0$ indicates integration over the unit cell.

$$\begin{aligned} \langle \psi_+ | \frac{\partial}{\partial x} | \psi_- \rangle &= \int d^3 r e^{-i\vec{k} \cdot \vec{r}} u_+^* \frac{\partial}{\partial x} e^{i\vec{k} \cdot \vec{r}} u_- \\ &= \int d^3 r u_+^* (ik_x + \frac{\partial}{\partial x}) u_- d^3 r \end{aligned}$$

$\int u_+^* ik_x u_- d^3 r$ drops since u_+ and u_- are orthogonal.

$\int u_+^* \frac{\partial}{\partial x} u_- d^3 r = N \int u_+^* \frac{\partial}{\partial x} u_- d^3 r_0$ since u_+ and u_- have the periodicity of the lattice. (N is the number of cells in the crystal.)

Hence $\langle u_+ | \frac{\partial}{\partial x} | u_- \rangle = \frac{1}{N} \langle \psi_+ | \frac{\partial}{\partial x} | \psi_- \rangle$

Now we have:

$$\begin{aligned} \langle \psi_+ | \frac{\partial}{\partial x} | \psi_- \rangle &= \frac{1}{2} \langle \phi_1 + e^{i\delta} \phi_2 | \frac{\partial}{\partial x} | \phi_1 - e^{i\delta} \phi_2 \rangle \\ &= \frac{1}{2} \langle \phi_1 | \frac{\partial}{\partial x} | \phi_1 \rangle - \frac{e^{i\delta}}{2} \langle \phi_1 | \frac{\partial}{\partial x} | \phi_2 \rangle \\ &\quad + \frac{e^{-i\delta}}{2} \langle \phi_2 | \frac{\partial}{\partial x} | \phi_1 \rangle - \frac{1}{2} \langle \phi_2 | \frac{\partial}{\partial x} | \phi_2 \rangle \end{aligned}$$

The first and last terms on the right hand side cancel each other, thus we have to evaluate only the second and third terms.

$$\begin{aligned}\langle \phi_1 | \frac{\partial}{\partial \mathbf{x}} | \phi_2 \rangle &= \int \sum_A \exp(-i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}_A) X^*(\bar{\mathbf{r}} - \bar{\mathbf{r}}_A) \frac{\partial}{\partial \mathbf{x}} \sum_B \exp(i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}_B) X(\bar{\mathbf{r}} - \bar{\mathbf{r}}_B) d^3\mathbf{r} \\ &= \sum_{A,B} \exp i\bar{\mathbf{k}} \cdot (\bar{\mathbf{r}}_B - \bar{\mathbf{r}}_A) \int X^*(\bar{\mathbf{r}} - \bar{\mathbf{r}}_A) \frac{\partial}{\partial \mathbf{x}} X(\bar{\mathbf{r}} - \bar{\mathbf{r}}_B) d^3\mathbf{r}\end{aligned}$$

Setting $\bar{\mathbf{r}} - \bar{\mathbf{r}}_A = \bar{\mathbf{r}}'$ and $\bar{\mathbf{r}}_B - \bar{\mathbf{r}}_A = \bar{\mathbf{r}}_L$

$$\begin{aligned}&= \sum_{A,L} \exp(i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}_L) \int X^*(\bar{\mathbf{r}}) \frac{\partial}{\partial \mathbf{x}} X(\bar{\mathbf{r}} - \bar{\mathbf{r}}_L) d^3\mathbf{r} \\ &= N \sum_L \exp(i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}_L) \int X^*(\bar{\mathbf{r}}) \frac{\partial}{\partial \mathbf{x}} X(\bar{\mathbf{r}} - \bar{\mathbf{r}}_L) d^3\mathbf{r}\end{aligned}$$

And similarly

$$\langle \phi_2 | \frac{\partial}{\partial \mathbf{x}} | \phi_1 \rangle = N \sum_L \exp(-i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}_L) \int X^*(\bar{\mathbf{r}} - \bar{\mathbf{r}}_L) \frac{\partial}{\partial \mathbf{x}} X(\bar{\mathbf{r}}) d^3\mathbf{r}$$

Let us set the origin of the coordinate system on an A type atom. Then evaluating the sums we make the approximation in which only terms connecting nearest neighbours amongst atoms of different types are taken into account. This approximation seems to be justified, for, on account of the negative exponential character of $X(\bar{\mathbf{r}})$, the integrals fall off very rapidly as r_L increases. Thus both sums will consist of three terms corresponding to $\bar{\mathbf{r}}_L = \bar{\mathbf{r}}_{B_1}, \bar{\mathbf{r}}_{B_2}, \bar{\mathbf{r}}_{B_3}$ (see Fig. 1).

Making use of the form of the atomic orbital $X(\bar{\mathbf{r}})$ it is easily seen that the integrals of interest will be:

$$\int x(\bar{r}) \frac{\partial}{\partial x} x(\bar{r}-\bar{r}_{B_1}) d^3r = - \int x(\bar{r}-\bar{r}_{B_1}) \frac{\partial}{\partial x} x(\bar{r}) d^3r = \alpha$$

$$\int x(\bar{r}) \frac{\partial}{\partial x} x(\bar{r}-\bar{r}_{B_2}) d^3r = - \int x(\bar{r}-\bar{r}_{B_2}) \frac{\partial}{\partial x} x(\bar{r}) d^3r = \beta$$

$$\int x(\bar{r}) \frac{\partial}{\partial x} x(\bar{r}-\bar{r}_{B_3}) d^3r = - \int x(\bar{r}-\bar{r}_{B_3}) \frac{\partial}{\partial x} x(\bar{r}) d^3r = \beta$$

Then we obtain in our approximation:

$$\begin{aligned} \langle \psi_+ | \frac{\partial}{\partial x} | \psi_- \rangle &= - \frac{Ne^{i\delta}}{2} \left[\alpha \exp(i\bar{k} \cdot \bar{r}_{B_1}) + \beta \exp(i\bar{k} \cdot \bar{r}_{B_2}) + \beta \exp(i\bar{k} \cdot \bar{r}_{B_3}) \right] \\ &\quad - \frac{Ne^{-i\delta}}{2} \left[\alpha \exp(-i\bar{k} \cdot \bar{r}_{B_1}) + \beta \exp(-i\bar{k} \cdot \bar{r}_{B_2}) + \beta \exp(-i\bar{k} \cdot \bar{r}_{B_3}) \right] \\ &= -N \left[\alpha \cos\left(\frac{ak_x}{3} + \delta\right) + 2\beta \cos\left(\frac{ak_x}{2 \cdot 3} - \delta\right) \cos\left(\frac{ak_y}{2}\right) \right] \end{aligned}$$

It is shown in Appendix 1 that:

$$\alpha > 0, \quad \beta < 0 \quad \text{and} \quad |\alpha| = 2|\beta|$$

Hence we have

$$\left| \langle u_+ | \frac{\partial}{\partial x} | u_- \rangle \right|^2 = \alpha^2 \left[\cos\left(\frac{ak_x}{3} + \delta\right) - \cos\left(\frac{ak_x}{2 \cdot 3} - \delta\right) \cos\left(\frac{ak_y}{2}\right) \right]^2.$$

CHAPTER 3

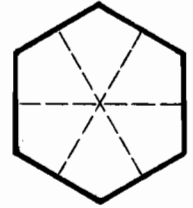
THE COMPLEX DIELECTRIC CONSTANT

(a) The Imaginary Part

As we saw in the previous section, the contribution of the intra-band term to ϵ_2 is zero and the imaginary part of the complex dielectric constant is given by the expression (2.4):

$$\epsilon_2 = \frac{2e^2\hbar^2}{m^2\omega^2} \int d^2k \left| \langle u_+ | \frac{\partial}{\partial \mathbf{x}} | u_- \rangle \right|^2 \delta(\hbar\omega_{+-} - \hbar\omega)$$

$\hbar\omega_{+-} > 2E_F$



Substituting for $\langle u_+ | \frac{\partial}{\partial \mathbf{x}} | u_- \rangle$ and ω_{+-}

$$\epsilon_2 = \frac{2e^2\hbar^2}{m^2\omega^2} \int d^2k \left[\cos\left(\frac{ak_x}{3} + \delta\right) - \cos\left(\frac{ak_x}{2} - \delta\right) \cos\left(\frac{ak_y}{2}\right) \right]^2 \delta(2|H_{12}| - \hbar\omega)$$

In order to perform the integration we break up the Brillouin zone into sections as indicated in the figure. For each section we shift the origin of the coordinate system in the corresponding corner of the Brillouin zone. For small values of $k = |\bar{k}|$ (where k is now measured from the corner of the zone corresponding to the section over which we integrate), we have to first order in k ; $|H_{12}| = (\sqrt{3}/2) a\gamma_0 k$. Since the k values for which the argument of the delta function vanishes are small, we can use this approximate expression for $|H_{12}|$ through the entire section. (For the frequencies

considered the energy of the radiation $E < 2 \times 10^{-12}$ erg and $2|H_{12}| < 2 \times 10^{-19}$ kerg. Hence $k < 10^7$ or $ak < 0.25$).

In what follows, the expression in the square bracket is expressed in polar coordinates, then expanded about $k = 0$ to first order in k (see Appendix 2). Performing the integration in each section over the angle variable and summing over the sections we obtain:

$$\begin{aligned}\epsilon_2 &= \frac{2e^2 \hbar^2 \alpha^2}{m^2 d \omega^2} \int (Ak + Bk^2) \delta(\sqrt{3} a \gamma_0 k - \hbar \omega) \\ &= \frac{2e^2 \hbar^2 \alpha^2 \Omega^2}{m^2 d} \left[\frac{1}{\omega} + \frac{B\Omega}{A} \right]\end{aligned}$$

where

$$A = \frac{a}{2}(\pi - \frac{3\sqrt{3}}{8}) \quad B = -\frac{27a}{4} \quad \Omega = \frac{\hbar}{\sqrt{3} a \gamma_0}$$

Substituting the numerical values for e , \hbar , etc. and writing ϵ_2 as function of wavelength (expressed in microns):

$$\epsilon_2 = 5.25 (\lambda - 0.16) \quad (3.1)$$

(b) The Real Part

The real part of the complex dielectric constant (2.1a) is made up of two parts, ϵ_{1a} corresponding to the contribution of band to band transitions and ϵ_{1b} corresponding to the contribution of free electrons.

$$\epsilon_{1a} = \frac{4e^2\hbar}{\pi m^2 d} \int_{\hbar\omega_{+-} > 2E_F} d^2k \frac{|\langle u_+ | \frac{\partial}{\partial x} | u_- \rangle|^2}{\omega_{+-}(\omega_{+-}^2 - \omega^2)}$$

$$= \frac{4e^2\hbar\alpha^2}{\pi m^2 d} \int d^2k \frac{\left[\cos\left(\frac{ak_x}{2} + \delta\right) - \cos\left(\frac{ak_x}{2} - \delta\right) \cos\left(\frac{ak_y}{2}\right) \right]^2}{\frac{2|H_{12}|}{\hbar} \left[\frac{4|H_{12}|^2}{\hbar^2} - \omega^2 \right]}$$

Evaluating this integral we go ahead in a similar way as we did in the case of ϵ_2 .

The main contribution to the integral comes from \bar{k} values for which the denominator is small. These values are near the corners as we explained before. We express the integrand in polar coordinates and expand it to first order in k (again, k is measured from the corners). Moreover, since the small k values give the large contribution to the integral we use a cut-off for k . We will perform the integration for $k < K = 2 \times 10^7$ and neglect the contribution of k values for which $k > K$.

Substituting $|H_{12}| = (\sqrt{3}/2) a\gamma_0 k$ and performing the integration over the angle variable:

$$\epsilon_{1a} = \frac{4e^2\hbar\alpha^2\Omega^3}{\pi m^2 d} \int_{k_F}^K dk \frac{A + Bk}{k^2 - \Omega^2\omega^2}$$

where A , B and Ω were defined in section (a) and k_F is defined by $E_F = (\sqrt{3}/2)a\gamma_0 k_F$.

Carrying out the integration and substituting numerical values for the constants we obtain for ϵ_{1a} as a function of wavelength:

$$\epsilon_{1a} = 1.67 \left[\lambda \ln \frac{(20\lambda-11)(11+18E_F\lambda)}{(20\lambda+11)(11-18E_F\lambda)} - 0.16 \ln \left(\frac{400\lambda^2 - 121}{121 - 324E_F^2\lambda^2} \right) \right] \quad (3.2a)$$

(E_F is measured in electron-volts, λ in microns and K has been taken to be 2×10^7 .)

The contribution of free electrons ϵ_{1b} is given by:

$$\epsilon_{1b} = - \frac{2e^2}{\pi \hbar^2 d \omega^2} \int d^2 k \frac{\partial^2 E_+(\vec{k})}{\partial k_x^2}$$

where the integration is taken over the occupied states of the conduction band.

Near the corners (setting the energy level to zero at the corners):

$$E_+(\vec{k}) = \frac{\sqrt{3}}{2} a \gamma_0 |\vec{k}|$$

Hence

$$\epsilon_{1b} = - \frac{\sqrt{3} e^2 a \gamma_0}{\pi \hbar^2 d \omega^2} \int_{|\vec{k}| < k_F} d^2 k \frac{\partial^2}{\partial k_x^2} \sqrt{k_x^2 + k_y^2}$$

Introducing polar coordinates and performing the integration

$$\epsilon_{1b} = - \frac{2\sqrt{3} e^2 a \gamma_0}{\hbar^2 d} k_F \frac{1}{\omega^2}$$

And as a function of wavelength:

$$\epsilon_{1b} = -11.3 E_F \lambda^2 \quad (3.2b)$$

From (2.3), (3.2a), (3.2b) and (3.1) we finally have for the complex dielectric constant:

$$\epsilon_1 = 1 + 1.67 \left[\lambda \ln \frac{(20\lambda - 11)(11 + 18E_F \lambda)}{(20\lambda + 11)(11 - 18E_F \lambda)} - 0.16 \ln \left(\frac{400\lambda^2 - 121}{121 - 324E_F^2 \lambda^2} \right) \right] - 11.3 E_F \lambda^2 \quad (3.3)$$

$$\epsilon_2 = 5.25(\lambda - 0.16) \quad (3.4)$$

SUMMARY

We obtain the numerical values of the reflection coefficient from Equations (2.1), (2.2), (3.3) and (3.4).

Curves for the reflection coefficient for different values of the Fermi energy are plotted against wavelength in Fig. 3. Comparison of our graphs with the experimental graph shows that the agreement between the experimental and theoretically calculated values of R is rather poor. The reason for this discrepancy is thought to lie in the simplicity of the model upon which we have based our calculations. It is very likely that using P.R. Wallace's three dimensional model instead of the two dimensional, we would have gotten a much better agreement with experiment.

APPENDIX 1

As wave function for an isolated atom, we use the normalized $2p_z$ Slater-Zener orbital⁽⁸⁾:

$$X(\bar{r}) = NZe^{-k|\bar{r}|} \quad (A.1)$$

where $k = 1.625$, $N = (\frac{k^5}{\pi})^{1/2}$ and distances are measured in Bohr radii a_0 .

In general

$$\frac{\partial}{\partial x} \int X(\bar{r})X(\bar{r}-\bar{r}_L)d^3r = 0$$

Hence

$$\int X(\bar{r}) \frac{\partial}{\partial x} X(\bar{r}-\bar{r}_L)d^3r = - \int X(\bar{r}-\bar{r}_L) \frac{\partial}{\partial x} X(\bar{r})d^3r$$

Consequently

$$\int X(\bar{r}) \frac{\partial}{\partial x} X(\bar{r}-\bar{r}_{B_1})d^3r = - \int X(\bar{r}-\bar{r}_{B_1}) \frac{\partial}{\partial x} X(\bar{r})d^3r = \alpha \quad (A.2)$$

And since \bar{r}_{B_3} is the mirror image of \bar{r}_{B_2} with respect to the x axis (Fig. 1)

$$\int X(\bar{r}) \frac{\partial}{\partial x} X(\bar{r}-\bar{r}_{B_2})d^3r = \int X(\bar{r}) \frac{\partial}{\partial x} X(\bar{r}-\bar{r}_{B_3})d^3r = \beta \quad (A.3)$$

Combining (A.2) and (A.3) we obtain the expressions given on page 12.

(a) Calculation of α

From (A.1) and (A.2) we have for α ,

$$\alpha = N^2 \int Z^2 e^{-k|\bar{r}|} \frac{\partial}{\partial x} e^{-k|\bar{r}-\bar{r}_{B_1}|} d^3r$$

Introducing the notation $\bar{B}_1 = k\bar{r}_{B_1}$, $B = |\bar{B}|$ and the transformation $k\bar{r} = \bar{r}'$

$$\begin{aligned}\alpha &= \frac{N^2}{k^4} \int Z^2 e^{-|\bar{r}|} \frac{\partial}{\partial x} e^{-|\bar{r}-\bar{B}_1|} d^3r \\ &= -\frac{N^2}{k^4} \int (x-B) Z^2 e^{-|\bar{r}|} \frac{e^{-|\bar{r}-\bar{B}_1|}}{|\bar{r}-\bar{B}_1|} d^3r\end{aligned}$$

Transforming to polar coordinates with the x axis as polar axis,

$$\begin{aligned}x &= r \cos\vartheta \\ y &= r \sin\vartheta \cos\varphi \\ z &= r \sin\vartheta \sin\varphi\end{aligned}$$

$$\alpha = -\frac{N^2}{k^4} \int (r \cos\vartheta - B) \sin^3\vartheta \sin^2\varphi r^4 e^{-r} \frac{e^{-R}}{R} dr d\vartheta d\varphi$$

where $R = |\bar{r}-\bar{B}_1|$ and $0 < \vartheta \leq \pi$, $0 < \varphi \leq 2\pi$.

Performing the integration over φ ,

$$\alpha = -\frac{\pi N^2}{k^4} \int (r \cos\vartheta - B) \sin^3\vartheta r^4 e^{-r} \frac{e^{-R}}{R} dr d\vartheta \quad (A.4)$$

We make use of the expression⁽⁹⁾:

$$\frac{e^{-R}}{R} = -\sum_{n=0}^{\infty} (2n+1) P_n(\cos\vartheta) j_n(ir_{<}) h_n(ir_{>})$$

where $\frac{r_{<}}{r_{>}}$ denotes the smaller/larger of r and B .

Substituting we obtain for α ;

$$\alpha = \frac{\pi N^2}{k^4} \sum_{n=0}^{\infty} (2n+1) \int_0^{\pi} \cos \vartheta \sin^3 \vartheta P_n(\cos \vartheta) d\vartheta \int_0^{\infty} r^5 e^{-r} j_n(ir_{<}) h_n(ir_{>}) dr$$

$$- \frac{\pi N^2 B}{k^4} \sum_{n=0}^{\infty} (2n+1) \int_0^{\pi} \sin^3 \vartheta P_n(\cos \vartheta) d\vartheta \int_0^{\infty} r^4 e^{-r} j_n(ir_{<}) h_n(ir_{>}) dr$$

Or, denoting the integrals over ϑ and r by Θ and R respectively;

$$\alpha = \frac{\pi N^2}{k^4} \sum_{n=0}^{\infty} (2n+1) \Theta_n R_n - \frac{\pi N^2 B}{k^4} \sum_{n=0}^{\infty} (2n+1) \Theta'_n R'_n$$

It is easily seen that only certain terms are different from zero in these sums. For instance in the first sum:

$$\Theta_n = \int_0^{\pi} \cos \vartheta \sin^3 \vartheta P_n(\cos \vartheta) d\vartheta = \int_0^{\pi} (\cos^3 \vartheta - \cos \vartheta) P_n(\cos \vartheta) d(\cos \vartheta)$$

$$= - \int_{-1}^1 (\mu - \mu^3) P_n(\mu) d\mu = \frac{2}{5} \int_{-1}^1 (P_1 - P_3) P_n(\mu) d\mu$$

On account of the orthogonality of the Legendre polynomials only Θ_1 and Θ_3 are different from zero;

$$\Theta_1 = \frac{4}{15}, \quad \Theta_3 = -\frac{4}{35}$$

Similarly in the second term only Θ'_0 and Θ'_2 differ from zero,

$$\Theta'_0 = \frac{4}{3}, \quad \Theta'_2 = -\frac{4}{15}$$

To obtain α we now have to evaluate the corresponding R and

R' values. It is accomplished by breaking up the integrals into two parts and substituting the proper spherical Bessel and Hankel functions. (It should be noted that $B = 4.36$ and the symbol is left in the following expressions for sake of convenience). E.g.:

$$\begin{aligned} R_1 &= \int_0^{\infty} r^5 e^{-r} j_1(ir_<) h_n(ir_>) dr \\ &= h_1(iB) \int_0^B r^5 e^{-r} j_1(ir) dr + j_1(iB) \int_B^{\infty} r^5 e^{-r} h_1(ir) dr \\ &= -63.65e^{-B} \end{aligned}$$

Similar calculations give

$$\begin{aligned} R_3 &= -44.13e^{-B} \\ R'_0 &= -17.12e^{-B} \\ R'_2 &= -12.75e^{-B} \end{aligned}$$

Substitution of the ϕ and R values in (A.4) yields $\alpha = 0.203$.

It should be remembered that we carried out our calculations in atomic units. The integral defining α has the dimension $[L]^{-1}$, hence, in order to obtain α in ordinary units, we have to divide 0.203 by the Bohr radius

$$\alpha = \frac{0.203}{a_0} = 3.84 \times 10^7$$

(b) Calculation of β

From (A.1) and (A.3),

$$\beta = N^2 \int z^2 e^{-k|\bar{r}|} \frac{\partial}{\partial x} e^{-k|\bar{r}-\bar{r}_{B_2}|} d^3r$$

With the substitutions $k\bar{r} = \bar{r}'$ and $\bar{B}_2 = k\bar{r}_{B_2}$

$$\beta = -\frac{N^2}{k^4} \int z^2 \left(x + \frac{B}{2}\right) e^{-|\bar{r}'|} \frac{e^{-|\bar{r}'-\bar{B}_2|}}{|\bar{r}'-\bar{B}_2|} d^3r$$

We rotate the coordinate system about the Z axis so that the new x axis will coincide with \bar{B}_2 and introduce polar coordinates with the new x axis as polar axis,

$$\begin{aligned} x &= -\frac{1}{2} x' - \frac{3}{2} y' & x' &= r \cos\vartheta \\ y &= -\frac{3}{2} x' - \frac{1}{2} y' & y' &= r \sin\vartheta \cos\varphi \\ z &= z' & z &= r \sin\vartheta \sin\varphi \end{aligned}$$

Making the substitutions and performing the integration over φ we obtain:

$$\beta = \frac{\pi N^2}{2k^4} \int (r \cos\vartheta - B) r^4 e^{-r} \sin^3\vartheta \frac{e^{-R}}{R} dr d\vartheta$$

Comparing this expression with (A.4) we obtain:

$$\beta = -\frac{1}{2} \alpha$$

APPENDIX 2

The technique employed in the evaluation of the integrals in Chapter 3 was to integrate the approximate expressions for the integrands near the corner of the Brillouin zone, and neglect the contribution of \bar{k} values farther away from the corners. It is necessary to substitute the squared matrix element

$$\left| \langle u_+ | \frac{\partial}{\partial x} | u_- \rangle \right|^2 = 2 \left[\cos\left(\frac{ak_x}{2} + \delta\right) - \cos\left(\frac{ak_x}{2} - \delta\right) \cos\left(\frac{ak_y}{2}\right) \right]^2 \quad (A.5)$$

with expressions readily integrable in the neighbourhood of the corners.

(a) $\delta(\bar{k})$ is defined by the expression:

$$e^{i\delta(\bar{k})} = \frac{H_{12}^*}{|H_{12}|} \quad \text{or} \quad \delta(\bar{k}) = \frac{\text{Im } H_{12}^*}{\text{Re } H_{12}^*}$$

Expansions of H_{12}^* about the corners yield:

$$\begin{aligned} \delta_1 &= \frac{\pi}{6} - \varphi & \delta_4 &= \frac{5\pi}{6} - \varphi \\ \delta_2 &= -\frac{\pi}{6} + \varphi & \delta_5 &= -\frac{\pi}{2} - \varphi \\ \delta_3 &= \frac{5\pi}{6} - \varphi & \delta_6 &= \frac{\pi}{6} + \varphi \end{aligned}$$

(δ_i denotes the expression representing $\delta(\bar{k})$ around corner i).

(b) The squared matrix element (A.5) is expressed

in polar coordinates, then expanded to first order in k . Using this technique we obtain for (A.5) in the vicinity of e.g. corner 2 $(0, \frac{4\pi}{3a})$:

$$\frac{9}{4} \sin^2 \varphi + \frac{3\sqrt{3}}{4} a \sin \varphi k$$

Similar expressions are obtained for the other corners.

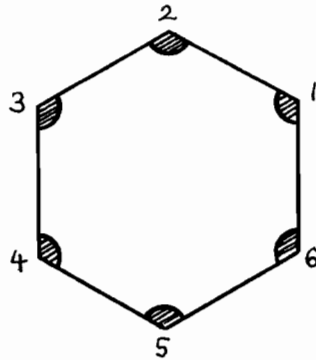
Suppose now that we want to integrate (A.5) in the shaded region depicted in the figure. We simply integrate the different approximate expressions between the angle limits appropriate to the corners (E.g. $\frac{7\pi}{12} < \varphi < \frac{11\pi}{12}$ at $(0, \frac{4\pi}{3a})$) and add the results.

If the integration of (A.5) is performed only over φ we obtain:

$$Ak + Bk^2$$

where

$$A = \frac{9}{2} \left(\pi - \frac{3\sqrt{3}}{8} \right), \quad B = -\frac{27}{4} a.$$



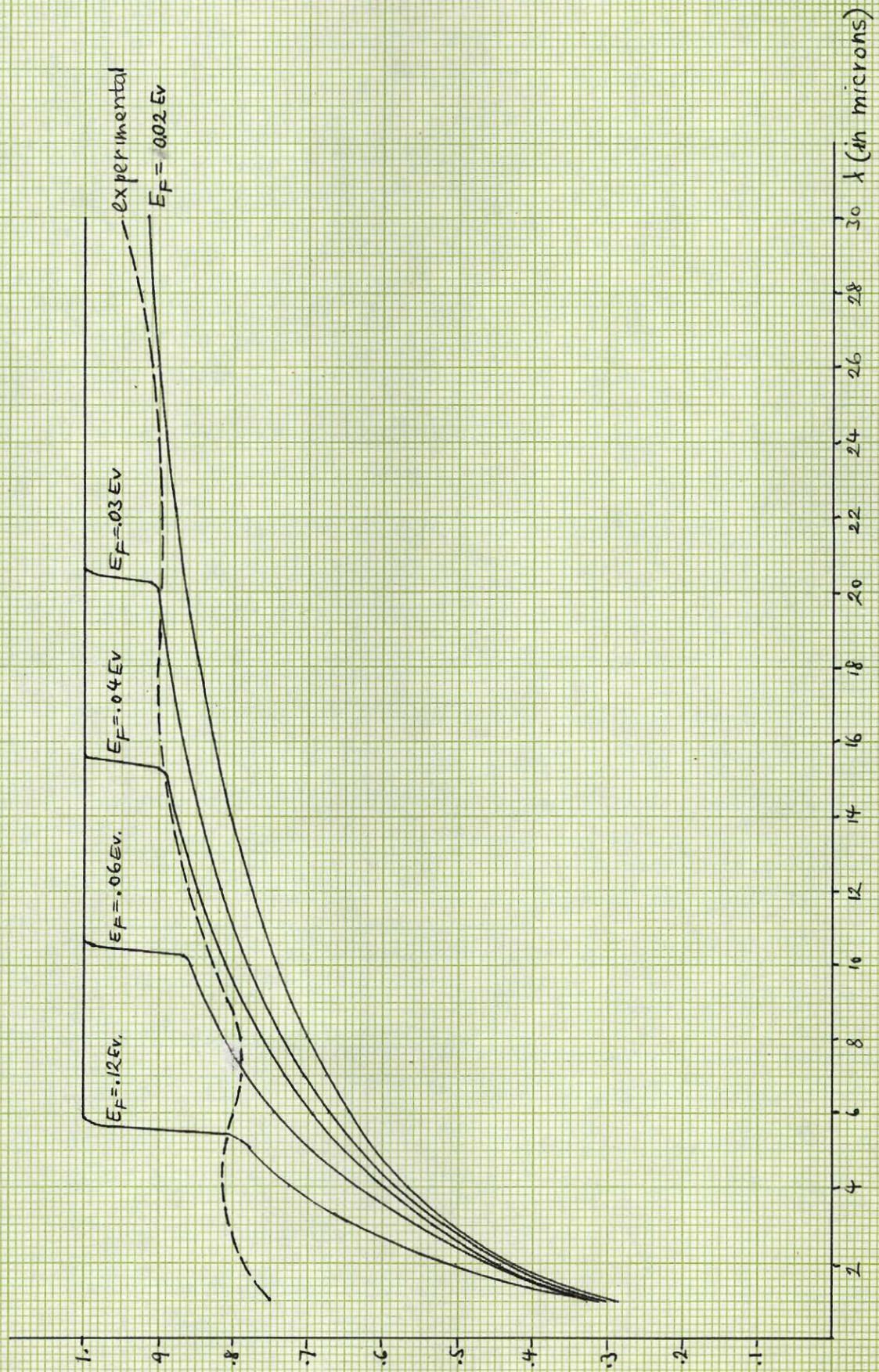


Figure 3.

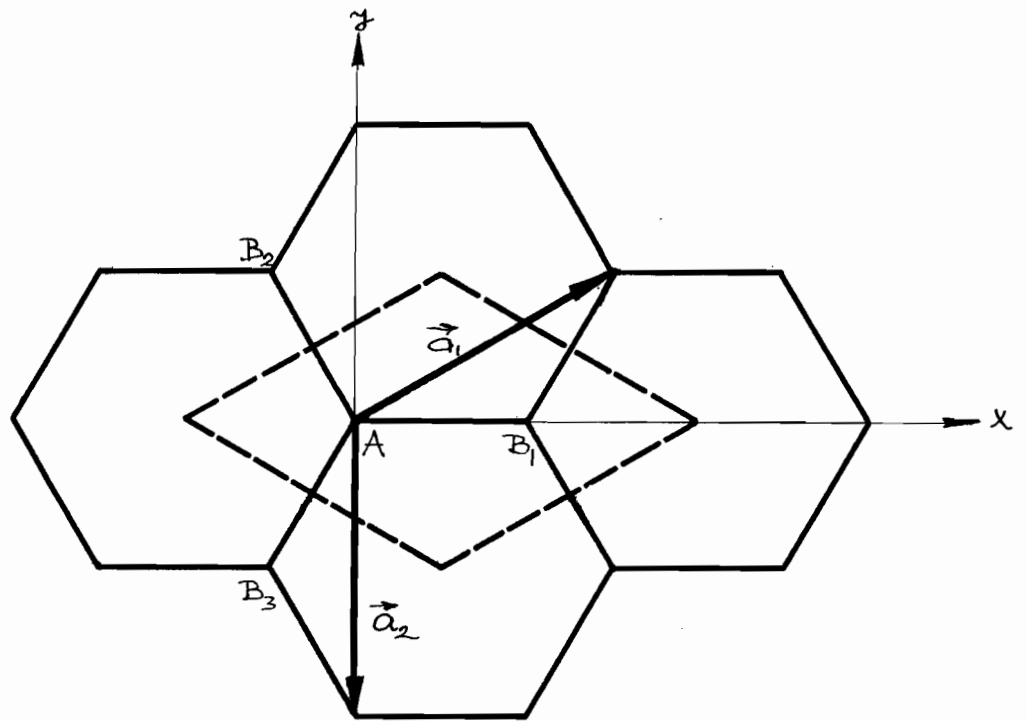


Figure 1.

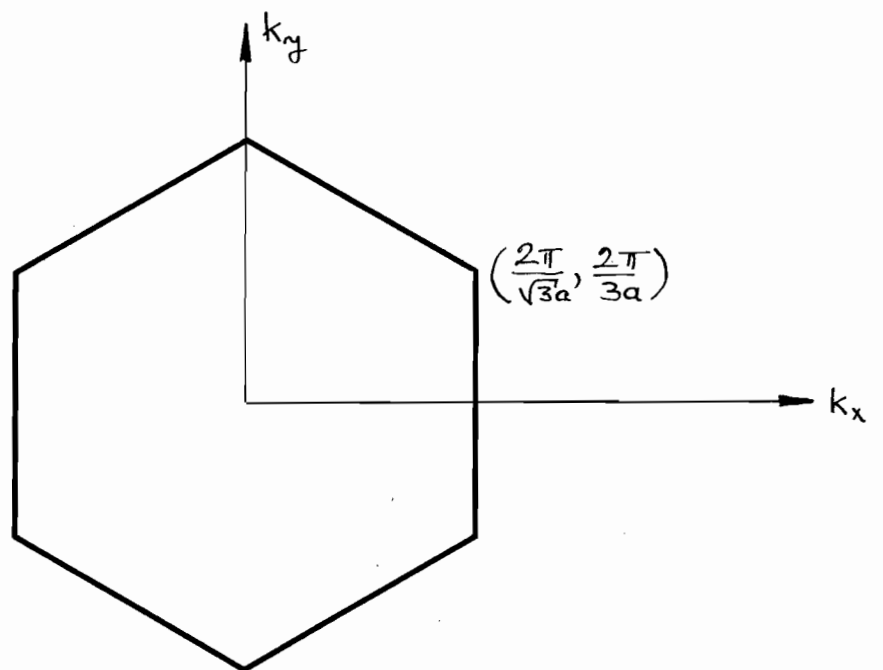


Figure 2.

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