ABSORPTION OF LIGHT IN THE WAVELENGTH
BAND FROM ONE TO TWENTY-FIVE MICRONS IN
GERMANIUM AS A FUNCTION OF TEMPERATURE

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INTRODUCTION

It was observed, probably first by Michael Faraday, that certain materials possessed electrical properties that were different from those of metals or insulators. By 1885 it was established that these materials, called semiconductors, all had at least four fundamental properties: (1) negative temperature coefficient of resistance, (2) rectification, (3) photoconductivity, and (4) photovoltaic effects.

When E. H. Hall discovered that electrons flowing in a metal could be deflected by a magnetic field perpendicular to the direction of current flow, a useful tool was added for the investigation of conduction processes.

When "Hall effect" measurements were made on these semiconductors very interesting results occurred. It was found that, instead of indicating that the carriers were negative charges or electrons, as in the case of metals, some of the semiconductors had Hall coefficients that indicated positive charge carriers. Measured mobilities ruled out the possibility that these were positive ions. Disregarding this problem for the moment researchers were able to show that the conductivity could be broken into its two components: (1) the density of carriers n and (2) their
mobility $\mu$ so $\sigma = ne\mu$ where $\sigma$ is the conductivity and $e$ is the charge on an electron. It was found that the mobility was a property of the crystal lattice and it decreased with increasing temperature of that lattice. The density of carriers was found to increase very rapidly with temperature. It was also found that $n$ varied considerably from specimen to specimen. This established the difference between metals and semiconductors. In metals the mobility was only slightly structure sensitive and it decreased with increasing temperature. The number of carriers stayed essentially the same as a function of temperature, whereas in semiconductors, the value of $n$ rose from a low value to a very high value as a function of temperature, thus overriding the change in mobility and making the negative temperature coefficient of resistance observable.

At high temperatures it was observed that the density of charge carriers was no longer structure sensitive but equal for all samples. In fact, the carrier concentration rose even more rapidly with temperature increase and followed a simple logarithmic function $n \sim e^{kT}$. An activation energy proportional to the slope of this curve turned out to be the same for every semiconductor and therefore was an intrinsic property of the solid. Many attempts were made to correlate the low temperature effects to the high temperature results but since the activation energy was structure sensitive and also temperature sensitive to some
degree, any correlation was difficult.

Further understanding of these problems were greatly enhanced by quantum mechanical interpretation of the behavior of electrons, atoms, and molecules influenced by a periodic potential. In 1931 A. H. Wilson presented a quantum mechanical model of a solid semiconductor which has become the basis of present understanding in this field. If one considers the electrons as waves throughout the crystal lattice, there will be certain frequencies at which there is interference between these waves and the regularity of the crystal lattice. At these frequencies, corresponding to a definite energy, \( E - \hbar \nu \) an electron cannot exist within the structure. This led to the now well known energy bands in solids.

At low temperatures the electrons in the lattice fill the lowest energy bands, two electrons with opposite spin to each level. When the band structure is such that the least bound or valence electrons completely fill their band, there is an energy gap \( E_g \) from the last filled band to the next possible allowed energy site. Now in order for conduction to occur, electrons being accelerated in a certain direction by an electric field, must have empty energy states for these electrons to go to or else the electrons can't progress in the direction of the field. If the valence band is filled, the only allowable place for
conduction to occur is for the electrons to jump to the next available energy level which means that it must cross this forbidden energy gap, $E_g$ into what is called the "conduction band".

At any finite temperature, however, there is some thermal excitation, causing some electrons to exist above the energy gap and leaving some vacant energy states below the gap. Fermi-Dirac statistics dictates the electron population in these regions. This explains very well the intrinsic conductivity observed at high temperatures. The electrons excited across the energy gap would be free to conduct and their density would depend on the temperature and the magnitude of $E_g$. There would, for each excited carrier, be a vacant spot in the valance band or a hole which should also be free to conduct. This means that for each excited electron there would be two carriers available for conduction. The activation energy described in the high temperature results would actually be only one-half of the energy gap $E_g$ since we now have twice as many carriers as before supposed. The reason the Hall coefficient is always negative for intrinsic conduction is interpreted as meaning that the mobility of the electrons is greater than that of the holes.

The low temperature structure sensitive information was explained by the supposition that the lattice is not exactly
perfect. Let us say that a tri-valent impurity atom exists within the structure. This atom is able to acquire an electron from the valence band with far less excitation energy than that needed to cross the forbidden region. This would leave a hole free in the valence band to assume conduction. This, in a sense, gives the electron a higher energy level to which it may be excited from the filled band. This is, however, a local state. These are called acceptor states.

If we have an impurity atom of valence 5, it can give up an electron if the electron is excited to a higher allowed band, where it may be free to conduct. These states, since they give up an electron are called donor states.

With this picture, although admittedly only a rough sketch of some of the properties of semiconductors, we may now at least be able to discuss, with some intelligence, the physical entities involved in optical transmission through germanium.

Optical absorption in germanium can be broken down into five fundamental effects;

(a) lattice absorption
(b) absorption due to the excitation of electrons or holes within their respective bands
(c) the absorption of free holes from one valence band to another
(d) absorption due to the excitation of electrons
across the forbidden band

(e) absorption by the impurity atoms.

In considering the absorption by excitation of electrons across the forbidden band we must come to the conclusion that as long as the energy of the incident quanta is greater than the energy gap $E_g$, this fundamental absorption process will occur, and when the energy of the quanta becomes so small that it is less than $E_g$ the process will not occur. This conclusion has been born out very well by numerous experiments and shows up very well on the transmission graphs shown on later pages of this thesis. This process is slightly temperature dependent in that as we increase the temperature of the specimen the forbidden energy gap also increases slightly. For germanium the gap is 0.65 ev. wide at 300° K.

The present problem now is the absorption behavior beyond the fundamental absorption edge. The fundamental absorption edge is where the absorption by electrons crossing the forbidden gap is just stopped due to insufficient energy.

These other processes of absorption must certainly be fundamental in the absorption at longer wave lengths. These processes occur, of course, at quanta energies greater than $E_g$ but are masked by the fundamental "quantum jump", absorption process.

The aim of this project is to gather additional know-
ledge about these processes by observing the transmission of infrared radiation through several germanium samples of different impurities as a function of temperature. Also an exploratory investigation of the absorption properties of germanium samples bombarded with 12.5 Mev. protons as a function of temperature will also be presented here in an effort to add a little more information to the still somewhat obscure mechanisms involved in optical transmission through such structures.
THEORY

In considering the present theoretical aspects of optical transmission through germanium, a section will be devoted to each of the processes involved with the absorption of light in the wavelength region under consideration. The first of which will be lattice absorption.

In order to understand the fundamental aspects of present day lattice absorption theory, it is imperative that one have a moderate understanding of lattice vibrations, both natural and induced, and also be familiar with the phonon concept.

The nuclei in a crystal can be set into oscillation about their equilibrium positions by the application of heat, by optical excitation, and by other means. Since atoms in a crystal are joined by strong bonds, a nuclear vibration will generally influence all the nuclei in that crystal. Any vibration of the nuclear assembly is called a lattice vibration because the nuclear arrangements form the lattice.

Since almost any periodic function can be analyzed into its harmonic components, the lattice vibration can be resolved into a number of normal modes of vibration. Each normal mode describes a possible type of vibration. The total number of normal modes of vibration is equal to
the total number of degrees of freedom of the nuclei in the crystal. It will suffice to say that in germanium there are six normal modes of vibration.

Each normal mode of vibration is essentially an elastic wave. It can thus be classified according to its frequency, its wavelength, and its direction of propagation. If the nuclei all vibrate in the same direction the polarization can also be established.

We may assign for each mode a reduced wave vector $q$, which gives the direction of propagation of the mode and also its wavelength, since $\lambda = \frac{2\pi}{q}$ this reduced wave vector is obviously restricted to a set of values in which nuclear directional vibrations are allowed.

The long wavelength modes belonging to the three lowest branches of the vibrational spectrum of any crystal correspond to sound waves and are called the acoustical branches. In the long wavelength region the frequency is directly proportional to $q$ for each direction of propagation, i.e. $\nu = \text{constant}$. This means the phase velocity is a constant for the long wavelength modes of the acoustical branches. This is a characteristic of sound waves.

We may consider a crystal with $N^3$ unit cells and $A$ nuclei per cell, where $N$ is an arbitrary large integer used in defining a cyclic crystal. The cyclic crystal may be defined as the portion of an infinite crystal enclosed by a parallelopiped with concurrent edges $Na_1$, $Na_2$, and $Na_3$. 
where \( a_1, a_2, \text{ and } a_3 \) are vectors defining the lattice direction. Since each nucleus has 3 degrees of freedom, there are \( 3AN^3 \) vibrational degrees of freedom. Since germanium has two nuclei per unit cell there are six vibrational modes. Three of these are the acoustical modes and the remaining ones are called optical branches. A crystal with \( A \) nuclei will have \( 3A-3 \) optical branches. In germanium we have 3 optical branches.

For each mode belonging to the long wavelength region of an acoustical branch, all of the nuclei in the unit cell vibrate in the same direction. However, in the long wavelength optical modes, the nuclei within a crystal often vibrate in different directions, and in germanium they vibrate in opposite directions. If the direction of vibration is parallel to the direction of propagation the branch is called a longitudinal branch and if the vibrational direction is perpendicular to the propagational direction it is called a transverse branch.

By comparison with many other vibrating systems we may anticipate that there are only certain discrete values of energy that the lattice may assume. It has been shown that these allowed energy values behave such that \( E = (n + \frac{1}{2})hv \) where \( n = 0, 1, 2, 3---K \) and \( \nu \) is the frequency of the particular vibrational mode in question. When a crystal is in thermal equilibrium the total energy is distributed among the various modes such that the average value for \( n \)
under these conditions is \( \overline{n} = \frac{e^{\frac{\hbar \nu}{2RT}} - 1}{e^{\frac{\hbar \nu}{RT}} - 1} \) (Planck's Law). The average vibrational energy would then be \( \overline{E} = (\overline{n} + \frac{1}{2}) \hbar \nu \). The total vibrational energy will be the sum of \( \overline{E} \) over all the normal modes.

At absolute zero \( \overline{n} = 0 \) for all the modes. At very low temperatures, only the normal modes with low frequencies are excited to any extent. These modes are of the long wavelength acoustical branch. At intermediate temperatures the acoustical modes are excited and some of the optical modes begin to show activity. However, the optical modes do not become significantly excited until quite high temperatures are reached.

The vibrational amplitude associated with a normal mode is directly proportional to the square root of the energy supplied to the system. As the temperature is raised the nuclei vibrate more violently thus increasing in amplitude. This amplitude or displacement is considerably smaller, however, than the inter-nuclei spacing.

It has become popular, and quite useful, to describe the vibrational state of excitation of a mode in terms of the phonon concept. A phonon represents a unit quantum excitation of a normal mode of vibration. The magnitude of excitation of a given mode may be expressed in the number of phonons, or unit quanta, present. If a normal mode is excited by a unit amount, a phonon is created, if the mode loses vibrational energy by a unit amount, a phonon is
destroyed.

We may analyze a lattice vibration in this way. The possible vibrations of the nuclei in a crystal are given by the normal modes of vibration. The normal mode frequencies form a spectrum, the lattice vibrational spectrum. The energy of each normal mode is quantized and is given by the number of phonons in the mode itself. Thus, in this way, we find a way of expressing these events which can be correlated and integrated into a pattern in which we can understand the natural interaction of these modes with other physical events.

It will be shown later that, by considering simple onedimensional lattice vibration theory, very good correlation between theory and experiment is found. Consider a line of similar atoms of mass \( M \) spaced with lattice constant \( a \), and let \( u_n \) be the displacement from equilibrium of the \( n \)th atom.

If we consider nearest neighbor interactions alone, the force \( F_n \) acting on the \( n \)th atom may be written as

\[
F_n = \xi \left[ (u_n - u_{n-1}) - (u_n - u_{n+1}) \right],
\]

the first term in parentheses on the right being the increase in length of the bond between atoms \( n \) and \( n+1 \), the second term being the increase in bond length between atoms \( n \) and \( n-1 \). \( \xi \) is a force constant.
If we propagate an electromagnetic wave through this lattice arrangement we may expect the motion of the \( n \)th atom to be given by \( \ddot{u}_n = \beta (u_{n+1} + u_{n-1} - 2u_n) \) and we may expect solutions such that \( u_n = \beta e^{i(wt + kna)} \) where \( a \) is the nearest neighbor distance and \( n \) is a running index.

The wave vector in this case is \( k \).

\[
\begin{align*}
\dot{u}_n &= i \omega e^{i(wt + kna)}; \quad \ddot{u}_n = -\beta \omega^2 e^{i(wt + kna)} \\
-M\dot{\omega}^2 e^{i(wt + kna)} &= \beta \left[ e^{i(wt + kna)} \left( e^{ika} + e^{-ika} \right) \right] \\
-M\omega^2 &= \beta \left( e^{ika} + e^{-ika} \right) = \beta \left( e^{ika} - e^{-ika} \right)^2 \\
&= -4\beta \sin^2 \left( ka_2 \right) \quad \omega = \pm \left( \frac{\gamma \beta}{\omega^2} \right)^{1/2} \sin \left( ka_2 \right)
\end{align*}
\]

For two different types of atoms with \( \beta \) and \( ka \) close to the same value we may expect a relation such that

\[
\frac{\omega_1}{\omega_2} = \left( \frac{M_2}{M_1} \right)^{1/2} \quad \text{or} \quad \frac{\lambda_1}{\lambda_2} = \left( \frac{M_2}{M_1} \right)^{1/2}
\]

for resonant frequencies.

Lattice absorption theory has been hard pressed to explain some of the experimental results that have been observed in the past few years. One major problem has been to explain the broad absorption bands found in lattice absorption of germanium and other crystals when, at first glance, we might expect a sharp resonance type absorption band. A theory put forth by M. Lax and E. Burstein (17, pag. 39) regarding lattice absorption has definite merit.

In order for a lattice to interact with electromagnetic radiation it must have an associated electric field to couple with the oscillating electromagnetic field. In
the case of ionic crystals where we have a ready made charge displacement it is easy to see that a first order electric dipole moment will be induced when the system is set in oscillation. If some deformation of the electronic structure occurs during the oscillation, second order electric moments will be induced with a modification of the dipole moment also induced.

In nonionic homopolar crystals of diamond structure we have no inherent charge displacement. The diamond structure consists of two identical interpenetrating face centered cubic lattices with one of these lattices displaced relative to the other one-quarter of the distance up the main body diagonal. Because of the crystal symmetry, the displacement of one sublattice relative to another will not result in an electric moment. Thus, we should expect no first order electric moments in the diamond type structure. However, it has been observed that lattice absorption bands do exist in these structures. We can visualize the mechanism for absorption involving second order terms in the electric moment by considering the effects of several modes on a homopolar lattice. A compressional mode will produce a shift in the electronic charge distribution but will induce no moment. If in addition an optical vibration is present, a second order contribution to the electric moment will be made by the vibration of the charge increments. This contribution is proportional
to the product of the amplitudes of both the acoustic and optical modes, and results in absorption at the sum and difference of these two frequencies. This electric moment allows coupling to the radiation field. Since a long wavelength acoustical or optical mode does not alter the effective charges of the atoms on the two equivalent lattices, we expect that such long wavelength modes will be ineffective in producing second order moments. On the other hand, short wavelength modes introduce asymmetric displacements within the two sublattices and therefore produce charge deformations. Thus we may expect that the absorption will be produced primarily by a pair of short wavelength phonons.

Calculations for this two phonon process in diamond have been carried out by Helen Smith. F. Herman and J. Calloway also have made a corresponding analysis for germanium. Such analyses lead in general to a great number of possible absorption lines because there are six vibrational branches which may combine in pairs at many different propagation constants. Some of the intrinsic absorption lines have been interpreted as possible three phonon processes.

Fan and Collins have published some interesting results on lattice absorption by considering the temperature effects. The results on the temperature dependence give an important clue for the understanding of the absorption. According to the symmetry of the diamond lattice, optical vibrations
should be infrared inactive. There is also no theory predicting that combination modes should be present. On the other hand, experiments indicate that the absorption is not sensitive to lattice imperfections, either those arising from chemical impurities or those arising from the disorder produced by nucleon bombardment. The observed temperature dependence seems to indicate that the absorption is made possible by the thermal vibrations of the atoms. One might assume that the moment induced by a vibrational mode is to the first approximation proportional to the root-mean-square thermal displacement \((\bar{r}^2)^{1/2}\). The absorption should then be proportional to \(\bar{r}^2\). Lonsdale has shown that \(\bar{r} = \frac{\lambda \hbar}{2 \sqrt{\theta}} \left\{ \frac{\phi(x)}{\theta} + \frac{1}{\gamma} \right\} \), where \(\theta\) is the Debye temperature, \(\lambda\) is the atomic weight, \(\phi = \frac{\varepsilon^2}{r} \) and \(\phi = \frac{1}{\theta} \int_0^\theta \frac{L dL}{e^L - 1} \).

Experimental evidence seems to bear out that the absorption is proportional to the mean-square thermal displacement of the atoms, indicating that it is made possible by the disturbance of the lattice symmetry.

It is very possible that impurity absorption may play a significant part in optical absorption. It has, however, been observed that most of the lattice absorption bands in germanium are there in every sample tested regardless of impurity concentration or type of impurities, thus indicating that impurity absorption cannot be a panacea for all the present problems in this field.

If impurities are introduced into a lattice there will
be a modification of the electronic structure in its neighborhood. This is because the impurity distorts the periodicity of the perfect lattice in its local region. This distortion will cause linear electric moments to appear where they were previously forbidden by selection rules. This dipole moment will, in vibration, permit coupling with a radiation field. Also, especially in germanium at room temperatures, most of the impurity atoms have given up their valence electrons to the conduction band leaving an ionized atom bound in the impurity level. The oscillation of this ion about its bound position will cause a coupling field to occur. It should be noted, however, that experiments seem to indicate that impurity absorption is probably quite small compared to the intrinsic lattice absorption.

There is, also, conclusive experimental evidence that the free electron carriers in germanium contribute to the absorption of light. The classical Drude-Zener theory has been used to try and explain this phenomenon. The equation of motion of a free electron is given by

\[ \gamma = -\frac{eE}{\sqrt{n^2m^2(-\nu^2+i\gamma)}} \]

which yields

\[ \alpha = -\frac{Ne^2}{4n^2m} \left( \frac{1}{\nu^2 + \gamma^2} \right) \]

\[ n^2 = 1 + \nu n \alpha \]

\[ n^2 = 1 - \frac{Ne^2}{4n^m} \left( \frac{1}{\nu^2 + \gamma^2} \right) \]

we should expect an optical absorption band when

\[ \gamma = \frac{Ne^2}{4n^m} \left( \frac{1}{\nu^2 + \gamma^2} \right) = 1, \text{ for } \gamma > 1 \text{ there would be total reflection} \]

for \( \gamma < 1 \) there would be transmission.
The absorption at wavelengths beyond the fundamental optical absorption region at 1.8 microns varies with the conductivity of the specimen and seems to depend on the concentration of conduction carriers. This means that the absorption seems to be a free electron effect. It is known that an electron cannot absorb a photon if it is perfectly free since conservation laws cannot be obeyed. These conditions can be fulfilled through the electron interaction with the lattice. The absorption then depends on the electron-lattice collision frequency, which also determines the conduction properties of the crystal.

The absorption coefficient is related to the conductivity by \( \alpha' = \frac{4\pi \sigma}{mc} \) where \( n \) is the index of refraction.

\[
\alpha' = \frac{N e^2}{\sqrt{\pi m^*} \gamma} \frac{1}{\gamma + \frac{1}{\gamma}} \quad \alpha' = \frac{2N e^2 \gamma}{mc \left( \gamma^2 + \frac{1}{\gamma^2} \right)} \]  

\( \gamma = \frac{1}{\tau} \) is the mean time between collisions. This which introduces the electron lattice interaction was taken into account by Drude's theory. This, essentially, introduced a damping factor which predicts a resonance absorption band at a frequency other than \( \omega = 0 \).

The introduction of a constant damping factor for the different transition processes of all electrons cannot be a satisfactory approximation. If \( \hbar \nu \) is much smaller than the thermal energy of the electrons, the electron-lattice collision frequency can be taken as a function of the initial electron energy only. However, \( \hbar \nu \) in the infrared region is comparable or larger than the average electron
energy of \( (kT) \), in semiconductors. We must, then, consider
more carefully the electron lattice interaction. This in-
teraction arises from disturbances in the periodic potential
field of the crystal due to lattice vibrations and impur-
ities or defects in the lattice.

Whenever a collision between an electron and the
lattice occurs, energy will be transferred from the electron
to the lattice or from the lattice to the electron. In
this transfer the lattice may be excited or deexcited by
unit phonon amounts.

Consider an electron initially in a state \( \frac{\mathbf{k}}{4} \) where
\[ \mathbf{k} = \frac{2\pi}{a} \]
Let us assume that the electron interacts with
the normal mode \( \omega \) and that the collision causes the elec-
tron to make a transition to a state \( \frac{\mathbf{k}'}{4} \) which was initially
unoccupied. In any collision energy and momentum must be
conserved. In quantum mechanics, these conservation require-
ments limit the possible transition between states.

These rules governing the transition are called selection
rules. The momentum conservation rule is \( \mathbf{k}' = \mathbf{k} + \mathbf{q} + \mathbf{h} \),
where \( \mathbf{h} \) is a reciprocal lattice vector. Any of these quan-
tities times \( \mathbf{k} \) is momentum. The reciprocal lattice vector
\( \mathbf{h} \) appears in the momentum equation to guarantee that \( \mathbf{k}, \mathbf{k}' \)
and \( \mathbf{q} \) all lie in the reduced zone. Since the propagation
vector of the electron is changed as a result of the colli-
sion, the electron is deflected, or scattered, by its inter-
action with the normal mode.

The second selection rule is an energy conservation condition, \( E_{\eta'}(k') = E_\eta(k) \pm \hbar \nu \). If the normal mode is excited by a unit amount the minus sign is correct, and if it gives up energy the plus sign is correct. The interaction between a normal mode and an electron leading to the creation or destruction of a phonon is commonly called an electron-phonon collision.

In a homopolar crystal, the phonons most likely to be involved in electron-phonon collisions are the long wavelength acoustical phonons. When an electron collides with such a phonon, it will gain or lose a small amount of energy and be deflected only slightly. Hence, the electron will make a transition from its initial state to an adjacent final state.

If we consider a crystal like germanium in which there are a number of nondegenerate minima within the conduction band, the electrons can collide with both the short and long wavelength acoustical phonons under suitable conditions. If an electron collides with a long wavelength acoustical phonon, it will make a transition between two states both of which lie near the bottom of the same conduction band minimum. If an electron collides with a short wavelength acoustical phonon, it can make a transition between two states which lie near the bottoms of different conduction band minima. In this case the electron will be strongly
deflected since the short wavelength phonon has more energy and a large wave vector $q$.

At very low temperatures, the collision with long wavelength acoustical phonons will account for nearly all the collisions. At moderate and high temperatures, both types of collisions will occur. At high temperatures, collisions with long and short wavelength optical phonons will also occur. This is rather obvious when one considers the phonon population at the different temperatures. A temperature dependent probability function for phonon collisions could probably be devised.

The probability per unit time of an electron making a collision is $\frac{T}{\tau}$, where $\tau$ is called the collision time. The collision time for an electron will depend upon its dynamical characteristics, such as its energy, its effective mass, and its direction of propagation. These in turn depend upon the state it occupies prior to the collision. The collision time will usually exhibit a marked temperature dependence. In general, the collision time will decrease as the temperature is increased.

This free electron interaction involves three things, the creation or destruction of a photon, the transition of an electron from some initial to some final state, and the creation or the destruction of a phonon. Of course, the electron must make a transition into an unoccupied state with the conservation laws being obeyed. The momentum
conservation condition would be \( \hbar^* = \hbar + \nu_{\text{phonon}} + \hbar \cdot q_{\text{photon}} \) is omitted because it is so very small in the infrared region.

\( \hbar \) appears to insure that \( k, k', \) and \( q_{\text{phonon}} \) all lie in or on the boundaries of the reduced zone, that is, the central unit cell of the germanium lattice. An electronic transition involving the creation or the destruction of a phonon is called nonvertical transition because the wave vector of the electron changes as a result of such a transition.

The energy conservation conditions for the four possible types of nonvertical electronic transitions may be written as follows, \( E_{\beta'} (k') = E_{\beta} (k) \pm \hbar \nu_{\text{phonon}} \pm \hbar \nu_{\text{photon}}, \) where the minus sign refers to creation and the plus sign to destruction.

At absolute zero temperature, there are no phonons present, and the absorption or emission of a photon can occur only if a phonon is created, since there are none there otherwise. As we increase the temperature and thus increase the phonon population, interaction with photons should become more likely, especially since the collision time \( J \) is decreased. These two events enhance photoelectric absorption by the free electrons since they can more easily obey the conservation laws under these conditions.

The photon energy required for an electron to cross the forbidden energy gap is \( \hbar \nu_{\text{photon}} = E_{\text{gap}} \pm \hbar \nu_{\text{phonon}} \) depending on whether a phonon was created or destroyed. The width of the gap will decrease with increasing energy. The funda-
mental absorption edge has been found to depend on the phonon population which in turn depends on the temperature.

Experiments have shown that the Drude-Zener theory just does not account for all the absorption observed. However, Bardeen has proposed a modification of the Drude-Zener theory which predicts a higher absorption cross-section. He points out that the optical modes of vibration may contribute to the scattering of the excited carriers whereas these modes have only a small influence on the scattering of unexcited carriers. Thus the mean free time between collisions would be much smaller for the excited carriers than that estimated from the mobility of the thermal carriers and a larger cross-section for the capture of a photon would be expected.

The absorption by free holes will not be discussed since it is very similar to the free electron type of argument.

It is of importance to discuss the electron population in the electronic quantum states. The occupancy of each quantum state \( \epsilon, \mathbf{k} \) is strictly limited by the Pauli Exclusion Principle. According to this principle, no more than two electrons can occupy a given quantum state \( \epsilon, \mathbf{k} \). If two electrons do occupy the same state they must have opposite spins. In order to really know an electronic state we must also know the spin orientation. Two electrons occupying the same quantum state have the same energy \( E_\epsilon(\mathbf{k}) \) and the same
The Bloch function $\psi_k (kr)$ appears as a solution of Schrödinger's wave equation $\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$

where the Bloch function is $\psi = \psi(r) e^{i\mathbf{k} \cdot \mathbf{r}}$ where $\psi$ is the modulating function. The solution of this equation gives the allowed and forbidden energy states for an electron in such a periodic structure.

The distribution of the electrons among the various quantum states under conditions of thermal equilibrium is governed by Fermi-Dirac statistics. These statistics take into account the restriction on the occupancy of states imposed by the Pauli exclusion principle. According to Fermi-Dirac statistics, the probability that a quantum state with energy $E$ is occupied by an electron of either spin orientation is

$$f = \frac{1}{e^{(E - E_F)/kT} + 1}$$

where $E_F$ is the Fermi energy and $k$ is the Boltzmann constant.

For semiconductors since $E - E_F \gg kT$ the Fermi-Dirac distribution function reduces to

$$f \approx \frac{1}{e^{(E - E_F)/kT}}$$

This probability times the number of energy states between $E$ and $E + dE$, $g(E) dE = \frac{1}{2\pi^2} \frac{2m}{\hbar^2} (E - E_F)^{3/2} dE$ where $E_g$ is the width of forbidden gap, is simply the number of electrons per unit volume in the conduction band $N_e = \frac{1}{2\pi^2} \frac{2m}{\hbar^2} (E - E_F)^{3/2} e^{(E - E_F)/kT}$

The function $g(E) dE$ gives us the distribution of energy states. The Fermi-Dirac theory maintains that most of the states are at the high energy end. This is also predicted by the solution of the Schrödinger wave equation for periodic structures. As energy increases the number of states tend
toward a continuous distribution or an infinite number of discrete states, where at lower energies, there are discrete states with finite energy gaps between each allowable energy site. The number of holes may be calculated for an intrinsic specimen since \( f_h \approx f_e \). The same general procedure may be followed as was used to find the number of electrons in the conduction band.

In the case of impurities we may also calculate in a very similar way the number of electrons elevated to the conduction band. \( N_e = N_0 \frac{1}{2} \left( \frac{2\pi m k T}{\hbar^2} \right)^{\frac{3}{2}} e^{-E_1/2kT} \), where \( N_0 \) is the number of impurity atoms per unit volume, \( E_1 \) is the energy gap between the impurity level and the conduction band.

At low temperatures, due to the fact that \( E_1 < E_g \) most of the conduction electrons will probably be due to the impurities. As the temperature is raised however, the intrinsic conduction, due to many more available electrons, will soon dominate the picture. A graph for a normal germanium sample may look like this

![Graph](image)

The electrical properties of diamond lattice semiconductors are extremely sensitive to lattice disordering ef-
fects which result from bombardment with high energy particles. Lattice defects by high energy nucleons introduce localized energy states into the forbidden energy band of germanium. This is due to the disturbing effects on the periodic structure from this bombardment.

James and Lark-Horovitz have proposed a model for the energy levels associated with Frenkel defects, which we should expect to be the result of bombardment. This model has been quite effective in explaining the results obtained by bombardment of several different types of semiconductors.

Earlier ideas concerning energy levels associated with lattice defects were based on single ionization of lattice vacancies and interstitial atoms. Hence a vacancy was expected to behave as an acceptor or an electron trap whereas an interstitial atom was expected to behave as a donor or a hole trap. However, examination of the conductivity versus neutron bombardment time curves for n-type germanium revealed that extrapolation of the initial linear slope to zero conductivity gave a value of exposure which is only about one-half of that required to produce the conductivity minimum or intrinsic behavior. This behavior would seem to indicate the presence of two electron trapping centers, of which one is rather shallow. It was on the basis of this observation that James and Lark-Horovitz considered the possibility of multiple ionization. It should be noted that proton bombardment should produce more ionization for the same bombardment be-
cause of the coulomb interaction effects. James and Lark-Horovitz found that, in a lattice with as high a dielectric constant as that of germanium, one might expect states corresponding to the first and second ionization energies of the interstitial atom to lie in the forbidden energy band. Similarly, the energy required to put as many as two electrons into a vacant site is expected to lie in the forbidden gap. When both the interstitial and vacancy are present simultaneously, the electrons arising from the interstitial atoms are redistributed among all of the localized states to positions of lowest energy. Hence, for germanium they find the following levels of localized states; (a) a shallow vacant level corresponding to the first ionization of the interstitial atom which is estimated to lie \( \sim 0.05 \) ev. below the bottom of the conduction band; (b) a vacant level below the middle of the conduction band which arises from either the second ionization of the interstitial or the second ionization of the vacancy; and (c) the two remaining levels, which are occupied and which lie near the top of the valence band. Because of the complex nature of the wave functions in the diamond lattice and because of large perturbing effects due to the defects, any more precise statements from theoretical considerations alone, cannot be made.

For n-type germanium, one shallow level of electron traps is partly effective in removing electrons and the deep level is completely effective in removing them. It is
assumed for the following considerations that all the chemical impurities are ionized and that the intrinsic electron contribution is negligible. The electron concentration is given by \( n^0 - N_s^- - N \), where \( n^0 \) is the initial electron concentration, \( N_s^- \) is the concentration of occupied shallow traps, and \( N \) is the concentration of deep traps. From the law of mass action it can be shown that \( N_s^- \) is given by \( N_s^- = \frac{n N K_s}{1 + n K_s} \), where the equilibrium constant for the shallow trapping process (trap + electron \( \rightarrow \) occupied trap) is given by \( K_s = \frac{\hbar^2 e^{\frac{e^2}{\sqrt{2m^*}}}}{(2\pi m^* \hbar^2)^{3/2}} \) in which \( \varepsilon_s \) is the depth of the shallow traps, \( m \) is the appropriate effective mass, and \( \gamma \) is the ratio of the statistical weights of the reactants to that of the product. For the case in question the shallow trap is identified with a singly ionized interstitial atom. Hence \( \varepsilon_s = \gamma \). By manipulation of the above equations one may solve for a quadratic in \( n \), which is

\[
\frac{d n}{d N} = \left( 1 + 2 K_s n^0 \right) / \left( 1 + K_s n^0 \right)
\]

Calculated temperature dependence of electron concentration reveals a condition in which all the shallow traps are occupied to one in which they are completely empty, with increasing temperature. Experimental evidence of electron concentration at room temperature, after standing for one month, reveals that the electron concentration decreased from \( 4.9 \times 10^{10} \) to \( 3.5 \times 10^{10} \). This is contrary to the normally expected event and has caused some confusion. However, it
appears that the James and Lark-Horvitz model works very well, in general, for n-type germanium irradiated at or near room temperature. It certainly does well to explain the tremendous loss of conduction electrons due to bombardment. Further experimental evidence will go a long way to resolve some of the difficulties now encountered, and it seems that the fundamental concepts considered are basically sound, with perhaps, only further refinements to clear up the situation.
The optical measurements were made on a Perkin-Elmer infrared spectrometer using three prisms in order to cover the desired wavelength range. A KBr prism was used from 1.6 microns to 2.5 \( \mu \). From 2.5 \( \mu \) to 15 \( \mu \) a NaCl prism was used and from 15 \( \mu \) to 30 \( \mu \) we used a CsBr prism.

In the spectrometer mechanism is a glow bar light source which emits strongly in the infrared. This light is reflected by a mirror through two openings, on the last of which is mounted the sample holder. From there the light goes through the prism and is reflected back through it several times in order to get good resolution. It passes through a slit and is by then, essentially monochromatic. A rotating chopper breaks the light up into finite pulses and the light is reflected to a thermopile which transfers it to electrical pulses. The chopper is used so that we may have an output that can be amplified by use of a linear amplifier. Then the pulse is fed into a Leeds-Northrop automatic potentiometer recorder.

The method used for measuring the percent transmission was the standard, sample in, sample out technique. After measuring the no signal recorder reading, a background run was taken with the sample out. This was done after about every five runs with the sample in the holder. These charts
were then compared and normalized in order to get the per-
cent transmission.

For the temperature measurements an a.c. power supply
was used with a variac and a variable resistance in series
to control the current passing through the crystal. This
resistance heating method stabilized very well around the
particular temperature at which readings were to be taken.
To read the temperature an iron-constantan thermocouple was
used which was calibrated using water from 0°C to 100°C and
the melting points of appropriate organic compounds after
that. One lead was kept in ice water and the other was
pushed close between an insulator and the sample in order to
assure fairly accurate readings.

In order to get sufficient transmission and in order to
assume the reflectivity of all the samples were the same,
both sides of each sample were optically polished. This was
done by grinding the surfaces with different grades of
abrasives on a bees-wax lap. The final abrasive used was
cerium oxide.

The resistivity of the samples were measured, after
many unsuccessful techniques and trials, by mounting the
samples in a paraffin block with only the ends uncovered
and dropping them into two partitioned mercury baths, then
sticking an electrode in each bath. The faces were cleaned
with Ethyl acetate in order to assure good contact. This
seemed to be very important in obtaining consistant results.
The resistance was measured in two ways. One was simply by using a Simpson ohm-meter and the other was by using a resistance box, galvanometer, and battery in a typical wheatstone bridge type circuit. The dimensions of the sample were measured with a micrometer.

The sample holder was simply a small piece of plywood with a rectangular hole in the center just a millimeter smaller than the sample itself. Mounted on each of the long ends of the hole is a silver electrode with enough spring to allow some adjustment until they hold the sample firmly in place. To the other ends of the electrodes were soldered leads running to the power supply. The thermocouple is wedged in between the sample and an insulating guard along the length of the hole.

In measuring the transmission of the bombarded samples, it was necessary to test the annealing effects on a similar sample with the same bombardment time. This was accomplished by allowing the sample to remain at each temperature used in the transmission measurements for about one hour. After this time the resistivity of the sample was measured again in order to detect if there was any change due to annealing. This was done with the same method previously described.

For the 12.5 Mev proton bombardment of the germanium samples, the 60 inch Berkeley cyclotron was used. The samples were bombarded with a flux of one microampere for
one hour.
RESULTS AND CONCLUSIONS

In all uniradiated samples tested there are several outstanding features inherent in all of them that deserve comment.

The general shape of the transmission versus wavelength curves, at least at room temperature and at 56°C, are quite compatible with observations of other workers. That is, a jump from zero to 40% transmission at the wavelength threshold, a plateau with slight irregularities out to approximately 15 microns, and then a general decrease in transmission until it is almost zero at 27 microns. At certain regular intervals in this spectrum there seems to be absorption peaks inherent in all the samples tested. It has been suggested that many of these absorption peaks are due to lattice absorption since they seem to be independent of the impurities present. If we consider only a one-dimensional lattice vibration theory such as was discussed on pages 12 and 13, we find that if the force constant and the sin (ka) are relatively the same degree of magnitude for two different materials, which is the case for germanium and silicon, we should expect a comparison between their resonant frequencies to be given by

\[ \frac{\lambda_1}{\lambda_2} = \left( \frac{m_2}{m_1} \right)^{\frac{1}{2}} \]

For germanium and silicon, the ratio of the absorption frequencies is \((\frac{72}{28})^{\frac{1}{2}} = 1.4\). From a transmission graph for germanium and silicon, copied from another worker,
(2, pp. 1327-1337), appearing on page 42 of this report, a comparison of the successive absorption peaks of the two curves show these results,
\[
\frac{18 \mu}{11.3 \mu} = 1.61, \quad \frac{15.5}{19} = 1.72, \quad \frac{13}{8.1} = 1.605, \quad \frac{16.5}{7.5} = 1.58
\]
By comparison, these results are very close to the value of 1.61 for the ratio of the resonant absorption frequencies as predicted by the one dimensional lattice vibration theory. This theory, of course, is at the very best, only a poor approximation of what is really the case and also predicts only one absorption peak instead of the several observed. The very close correlation of the results with this theory is, in spite of its simplicity, startlingly good and is at least a hint that these absorption peaks are, as supposed, really connected with the vibrational spectrum of the lattice. There are undoubtedly, absorption peaks due to impurity absorption but these can be resolved for what they are by making measurements with samples of relatively few impurities. The absorption peak at 7.5 microns may be due to hole absorption. The reason behind this statement will be further explained on later pages.

As we consider the change in transmission as a function of temperature several obvious changes occur. First we notice that as we increase the temperature, the transmission from one to 20 microns decreases as we increase the temperature. From 18 to 20 microns it seems to be independent of temperature, and from 20 to 30 microns the transmission
increases with temperature. Another effect noticed is that a large absorption band occurs at the higher temperatures around 7.5 microns. This, as was mentioned before, will be considered later.

Now let us try to resolve from the theory already presented, how these observed results could be reasonably explained. First we notice that as we increase the temperature, the phonon population, especially the optical phonons, will be increased. This means that there should be an increase in absorption at all wavelength regions due to the larger interaction probability, but there should be no shift in the absorption spectrum with respect to wavelength. In the case of the free electron and so called free hole absorption mechanisms, however, we should expect, not only a general increase in absorption due to temperature at all wavelengths due to increased interaction with the lattice, but a shift in the spectrum toward the longer wavelengths. This is obvious when we consider how an increased value for $\gamma$ would affect the absorption using the Drude-Zener theory. The impurity absorption would be expected to increase with temperature due to increased amplitude of the coupling field but no wavelength shift is likely.

The results observed on figures 10, 24, and 17, can then be resolved if we consider the superposition of each absorption mechanism integrated to give one absorption pattern. The
lattice absorption with its localized peaks and the impurity absorption will, although fixed with respect to wavelength, have a sliding, free carrier type absorption whose shift is dependent on the temperature, superimposed on the lattice absorption. A shift toward the far infrared at increasing temperatures, for the free carriers, would then account for the increase in transmission as temperature is increased from 20 to 30 microns.

Figures 26 to 30, which show the transmission of all three impurity samples, no. 2 = 19.05 cm, no. one = 8.8 cm, and no. 4 = .8 cm, at fixed temperature with respect to wavelength, do not show any clear shift in transmission nor any change in the transmission for any sample from 25 to 30 microns. However at shorter wavelengths, the absorption seems to be greater for the purest samples. This is contrary to any theory now proposed and seems quite unreasonable. I suspect any comparison between samples may be in error because of possible differences in reflectivity at the surface. This is unfortunate since we could gain some insight on the relative contributions to the absorption due to each type of absorption process if we could compare, with some confidence, the data on transmission for several different impurity concentration samples.

Figures 10, 17, 24, show a possible shift in the transmission spectra with respect to temperature, but in the
wrong direction. Actually any remark along this line is senseless for two reasons. First, we do not know how much shift there should be and second, the data has not been carried out far enough into the long wavelengths, to properly investigate this possible shift. Lack of equipment limited the wavelength range. This shift could be calculated theoretically from the Drude-Zener theory and by making a calculation for the electron-lattice collision time $\tau$, however, lack of time limits further investigation along these lines.

The radiated sample showed some very interesting results due to the bombardment with 12.5 mev. protons for one hour at one microampere. The samples used were identical to the one sample used in previous results. Before bombardment the sample had a resistance of $86 \, \Omega$ and a resistivity of $8.8 \, \Omega \cdot \text{cm}$. After bombardment the resistance was $8.5 \, \Omega$. This may be explained in the following way. The bombardment produced many electron traps and interstitial atoms which absorbed electrons from the conduction band, thus decreasing the resistance. However, so many acceptor states were produced that they absorbed electrons from the valance band producing holes in this band. The results indicate that the hole conduction overrides the electron conduction in this case, thus causing a resistance ten times less than before bombardment. This could be checked by Hall effect measurements.
Transmission measurements were made only from 2 to 15 microns due to lack of time. The percent transmission was much lower than that of the sample before bombardment. This could be explained by supposing that the increased number of holes contributed enough to cause the extra absorption. However, the general shape of the curve does not seem to fit too well with those of the unirradiated sample. There is one interesting feature that seems to fit in with the other data. At about 7.5 microns there is an absorption peak just as there was for the unirradiated sample at high temperatures. The fact that we have this peak at only high temperatures in the unirradiated samples, where we start to get the same thing in the radiated sample at any temperature, seems to be a strong hint that this is caused by hole absorption. This is especially impressive when we observe that we have many holes in the radiated sample if our analysis of the conduction is correct.

In regard to the general decrease in transmission it is possible that some of the absorption was due to increased reflectivity since I was unable to get a good optical polish on one side of the sample.

Without any additional information, either experimental or theoretical, I hesitate to make any further comments on the transmission spectrum of this sample. The transmission versus temperature graphs are self-explanatory without
oration.

An accumulation of further experimental information such as running a more complete spectrum on the bombarded sample will probably make the absorption mechanism more apparent.
Thermocouple Calibration

Figure 3
Sample #2
Temp: ---- 33°C

Figure 5
Sample #2
Temp. --- 141°C

Figure 9
Sample #2

Red - 126°C
Green - 56°C
Blue - 141°C
Yellow - 92.5°C
Black - 33°C

Figure 16
Sample # 00
Temp. --- 141°C

Figure 16
Sample #010

Red — 126°C  
Green — 56°C  
Blue — 141°C  
Yellow — 97.5°C  
Black — 33°C

Figure 17
Sample #4
Temp. = 56°C

Figure 20
Sample #4
Temp. --- 97.5°C

Figure 21
Sample # 4
Temp. --- 126°C

Figure 22
Sample #4
Temp. ... 141°C

Figure 23
Sample #4

Red - 126 °C
Green - 56 °C
Blue - 141 °C
Yellow - 97.5 °C
Black - 33 °C

Figure 24.
Temp. = 33°C

Red -- #4
Green -- #10
Blue -- #2

Figure 26
Temp = 97.5°C

Red -- #4
Green -- #0010
Blue -- #2

Figure 28
Figure 30

Temp. = 141 °C
Red --- #4
Green --- #100
Blue --- #2
Radiated Sample
Temp. = 33°C

Figure 31
Figure 32

Temperature = 56°C
Radiated Sample
Radiated Sample
Temperature = 97.5°C

Figure 33
Figure 35

Radiated Sample
Temp. = 141 °C
Radiated Samples

Red  126°C
Green 56°C
Blue 141°C
Yellow 975°C
Black 32°C

Figure 36
BIBLIOGRAPHY


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