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Electrical properties of heavily doped and partially compensated calcium germanium substituted yttrium iron garnet films

Yuan, Sui Hua, Ph.D.
The Ohio State University, 1988
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ELECTRICAL PROPERTIES OF HEAVILY DOPED AND PARTIALLY COMPENSATED CALCIUM GERMANIUM SUBSTITUTED YTTRIUM IRON GARNET FILMS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Sui Hua Yuan, B.Sc., M.S.

*****

The Ohio State University
1988

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Approved By
Advisor
Department of Physics
To

My Motherland

and

My Parents
ACKNOWLEDGMENTS

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CHAPTER I

Introduction

1.1 The problem

Germanium or Silicon substituted Yttrium Iron Garnet ($Y_3^{3+}Fe_{3-y}^{3+}Ge_y^{4+}O_{12}^{2-}$) epitaxial thin films have been an important material with controllable magnetic properties. This material has been used in magnetic memory devices and in microwave integrated circuits. To conquer the disadvantages of the low resistivity caused by $Ge^{4+}$ or $Si^{4+}$ donors, calcium ions $Ca^{2+}$ are used as the counter-dopant. Thus a widely used form of yttrium iron garnet (YIG) is one which has been counter-doped with $Ge^{4+}$ or $Si^{4+}$ and $Ca^{2+}$ ions ($Y_{3-x}^{3+}Ca_x^{2+}Fe_{3-x}^{3+}Fe_{x-y}^{3+}Ge_y^{4+}O_{12}^{2-}$). The impurity ions influence both the magnetic and the electric properties of YIG depending on their amount and location in the YIG lattice.

Pure yttrium iron garnet ($Y_3Fe_5O_{12}$) has a cubic crystallographic lattice structure with a lattice constant 12.37 $\text{Å}$. Each primitive cell of YIG contains 8 formula units. Among the forty $Fe^{3+}$ ions in the unit cell 24 have tetrahedral symmetry and 16 have octahedral symmetry. The magnetic moment of the pure YIG originates from the net 5/2 spins per formula unit of the $3d$ electrons attached on the iron ion at the excess tetrahedral site. This
net spin is the resultant of the oppositely directed spins of the 3d electrons attached respectively on the iron ions at the tetrahedral and the octahedral sites. The Y³⁺ ions are located at the centers of the 24 dodecahedrons. The O²⁻ ions are located at the vertices of the polyhedrons, however the existence of oxygen vacancies is allowed.³ All the tetrahedral, octahedral, and dodecahedral sites are distorted slightly along the [111] direction to form the cubic primitive cell.⁴ Consistent with their smaller size, the Ge⁴⁺ or Si⁴⁺ ions are located mainly at the tetrahedral sites, substituting for the Fe³⁺ ions. The presence of Ge⁴⁺ or Si⁴⁺ ions reduces directly the magnetic moment of YIG due to the reduction of the ratio of Fe³⁺ ions at the tetrahedral sites to that of Fe³⁺ ions at the octahedral sites.⁵ The large Ca²⁺ ions are located at the dodecahedral sites, substituting for the Y³⁺ ions.⁶ The presence of the uncompensated Ca²⁺ and/or oxygen vacancies produces a change in the crystal field, which in turn influences the line width of the ferromagnetic resonance (FMR) and the coercivity.⁷ On the other hand, the presence of all the impurity ions and the oxygen vacancies influence the electrical properties of YIG, acting as impurity dopants in a wide gap (2.86 ev) semiconductor.⁸ When the doping is highly uncompensated, the eddy currents due to free carriers provided by the dopants broadens the FMR line width.⁹ Efforts have been made to study if, in addition, there is any other magneto-electric coupling in YIG. In the high temperature range up to the Curie temperature, the fundamental parameters such as conductivity and magnetization have been investigated and no coupling was reported.¹⁰ But, in the lower temperature range (150 K to 4 K), it has been found in this laboratory
that there are anomalous magnetic and electric effects occurring in parallel in those samples having Ca$^{2+}$ in excess to the Ge$^{4+}$ in heavily doped garnets. Further investigations on the electrical properties at low temperatures have exposed unusual effects which constitute the subjects of this work. The effects observed are listed as following:

1) The activation energy of conductivity has two values, one at high temperatures (above 200 $K$) on the order of 0.40 $eV$ and the other at low temperatures (below 100 $K$) on the order of 0.01 $eV$.

2) In the temperature range above 200 $K$, the conductivity and its activation energy are dependent on the applied voltage across the sample.

3) The time constants of the transient current through the sample are dependent on the temperature of the sample.

4) There is a special $I - V$ characteristic of the samples in low electric fields ($\sim 10^2 V/cm$).

5) There is a metastable high conductivity state (HCS) in the samples at low temperatures. The conductivities in HCS are about 5 orders of magnitude higher than those in the normal state (NS) of the samples at the same temperatures. The samples remain in the HCS until they are thermally annealed by raising the temperature above some critical value.

A model of amorphous-like electronic band structure is proposed to explain the unusual electrical properties of the heavily doped and partially compensated YIG($Y_{3-a}Ca^{2+}_{a}Fe^{3+}_{5-a}Fe^{4+}_{2-a}Ge^{4+}_{2-a}O_{12}$). In this model, the density of states tails and the mobility edges of the conduction and the valence bands are assumed. The Fermi level is located in the tail of the valence band in the case that the concentration of acceptors is in excess of
that of donors. The compensated acceptor levels within $kT$ of the Fermi level act as the hole trap levels which lead to the temperature dependence of the transient current and the voltage dependence of the activation energy of the conductivity. The oxygen vacancies are assumed to function as repulsive electron traps. When electrons in the partially compensated acceptor levels are excited by light and trapped in these repulsive trap levels with the assistance of electric field at low temperatures, the Fermi level is lowered towards the mobility edge of the valence band. The sample is then in the HCS until the electrons are released from the repulsive traps by increasing temperature to some critical value. The released electrons compensate the acceptor levels again to raise the Fermi level to its original value and the sample restores its normal state (NS). By assuming recombination levels within the tail of the valence band a slow process of the excitation of the HCS from the NS is expected. The details of this model will be discussed in Chapter III (proposed model) and in Chapter V (results and discussion). In Chapter II, a new transient current spectroscopy method is proposed for the study of the hole trap effects and some other theories are reviewed for understanding the experimental techniques. Chapter IV describes the instrumentation, the experimental procedures, and the sample characterizations. Chapter VI gives the conclusions and some suggestions on the further research of this project.
1.2 The experimental techniques

The experimental techniques used in this work are the following:

1) D.C. conductivity measurements with the following parameters: temperature, voltage, time, and intensity and frequency of light (DCC).

2) Space charge limited current (SCL).

3) Transient space charge limited current spectroscopy (TSLCS).

4) Thermally stimulated current (TSC).

5) Thermopower measurements (TP).

6) Pulsed I-V measurements (PIV).

7) Optical absorption spectroscopy.

For the purpose of comparison, materials such as germanium substituted YIG, calcium substituted YIG, excess germanium over calcium substituted YIG and nominally pure YIG are also investigated using the same techniques when appropriate.
CHAPTER II

Background

In this chapter, theoretical background for developing the model proposed in Chapter III and for understanding the experimental techniques used in this work are given by reviewing some basic concepts in the literatures and by reviewing and/or developing the theories concerned in the experimental measurements.

2.1 Review of the band structure and the electrical properties of oxides

There are only a few reports on the properties of the heavily doped and partially compensated yttrium iron garnet found in the literature. He, Yuan and Wigen\textsuperscript{12} reported an anomalous behavior of the magnetization at temperatures below 100 $K$. He, et al. assumed a third sublattice composed of Fe\textsuperscript{4+} ions ordered antiparallel to the tetrahedral sublattice to explain the experimental results. Yuan and Wigen\textsuperscript{11} reported a hopping conduction effect below 100 $K$ and a photo-memory effect of the conductivity below 200 $K$. A band-trap model has been proposed to explain these effects.\textsuperscript{13} Han, He, Yuan and Wigen reported a change in the anisotropic energy due to the presence
of the Fe⁴⁺ ions. Yuan and Wigen also presented a report on the kinetics of the photo-memory effect.

This dissertation is based on the work of the electrical properties of the CaGe:YIG. Except for the reports described above, no references are available on the fundamental properties of the heavily doped and partially compensated YIG such as energy band structure, dielectric properties, electric transport properties and so on. However, it is considered that these properties would be similar for the CaGe:YIG and for the singly doped and/or nominally pure YIG. In this chapter a review of the literature is given for the electrical properties of the singly doped and/or nominally pure YIG to give some background for the model proposed to explain the observed phenomena in the CaGe:YIG. Also the theories of electrical contacts, space charge limited current, transient current spectroscopy, and thermopower are reviewed for the purpose of understanding the corresponding techniques used in this work.

Pure YIG and n- or p-type singly doped YIG are similar to the heavily counter-doped YIG in crystal structure. The electric properties of YIG were reviewed by R. Metselaar and P. K. Larsen and by A. Tucciarone and P. De Gasperis. In the review of R. Metselaar and P.K. Larsen the energy bands, the mechanisms of electric conduction, the activation energy and the mobility of the n- and p-type YIG doped with Si, Ge, or Ca are described.

The width of the energy gap effective in the transportation phenomena is measured as 2.86 eV by measuring the activation energy of the intrinsic conductivity of YIG. This value is in excellent agreement with the value 2.8 eV ~ 2.9 eV of the optical absorption spectral lines assigned to the charge
transfer transitions.\textsuperscript{17,18,19} Lightly doped Ca:YIG was used in these experiments to measure the energy gap at appropriately high temperatures and in the appropriate partial pressure of oxygen. The oxygen vacancies created in YIG completely compensate the Ca\textsuperscript{2+} acceptors and an intrinsic band conduction is realized. The singly doped Ge\textsuperscript{4+} or Ca\textsuperscript{2+} ions are considered to constitute the narrow impurity band in the energy gap.

By comparing the activation energy of the Seebeck coefficient to that of the D.C. conductivity, the conduction of the n- and p-type YIG is determined as band conduction at temperatures above 600 K. At temperatures around 300 K it is difficult to measure the Seebeck Coefficient because of the high resistivity (>10\textsuperscript{8} Ωcm) of the sample. The activation energy of the conductivity at this temperatures is measured as 0.3 eV for n-type YIG and 0.4 eV for p-type YIG. These values are very close to those measured above 600 K for the corresponding n- and p-type YIG. It is inferred then that the conduction is still of the band type for either n- or p-type YIG at temperatures around 300 K. At lower temperatures the activation energy changes and when the temperature approaches 120 K the activation energy approaches a value of a few tens of meV. It is believed that the mechanism of the conduction at low temperatures changes to a hopping of carriers in the impurity bands. As the impurity doped YIG is always partially compensated by the natural counter-dopants such as Pb\textsuperscript{2+} or Pb\textsuperscript{4+} and Pt\textsuperscript{4+} from the melt flux in the process of growth, the partial compensation of the impurity centers makes hopping of the carriers possible among these centers.

The Hall mobility of electrons in Si-doped YIG is found to be 0.1 ~ 0.4 cm\textsuperscript{2}/sec.V by the measurements of the Hall coefficient and conductivity.
above room temperature. No data on the Hall mobility for Si-doped YIG at low temperatures and for Ca-doped YIG is available. To explain the low value of the Hall mobility, the electrons are considered to be coupled by coulomb interaction with the ionic lattice of YIG to constitute electric polarons. A comparison of the activation energy of the Seebeck coefficient with that of the conductivity gives an activation energy of the mobility in the neighborhood of 0.10 eV. This suggests that the polaron is a large polaron with radius greater than a few lattice constants.

The magnetization and the conductivity of the n- and p-type YIG have also been studied at high temperatures covering the Curie temperature. It is found that the conductivity has a minimal change at the Curie temperature. R. Metselaar and P. K. Larsen pointed out that the uncompensated impurity charges are balanced by the cations Fe$^{2+}$ in n-type YIG or Fe$^{4+}$ in p-type YIG. The existence of the Fe$^{2+}$ or Fe$^{4+}$ ions is evidenced by the optical absorption spectral and the chemical analyses.\textsuperscript{20}

A Tucciarone and P. De Gasperis described the non-ohmic behaviour in the $I - V$ characteristic at low electric fields ($\sim 10^2$ V/cm) for both n- and p-type YIG films. The $I - V$ characteristic is ohmic at very low fields and follows a square law when the field is increased. Finally the $I - V$ characteristic becomes ohmic again when the field is increased further. A two layer model is used to explain the experimental results. The current is first determined by the space charge limited effect in the surface layer at low fields and then it is determined by the bulk resistance at the higher fields. The surface layer is composed of the absorbed foreign ions or atoms and of the mechanical defects of the surface in the case of n-type YIG films. For the
p-type YIG films, the surface layer is due to the reduction of the area just under the electrodes.

It is argued that the electron or the hole trap levels, basically due to impurity ions and/or defects, play an important role in the space charge limited current effect. The trapping of the injected electrons or holes near the electrode build up an internal electric field which prevents the flow of the current. The long time (from msec. to min.) transient current flowing through the sample when the applied voltage is changed is taken as evidence for the existence of trap levels.

A few other findings on the n- or p-type YIG are also reviewed by A Tucciarone and P. De. Gasperis. A negative resistance is found on Si-doped YIG at room temperature when the applied electric field is in excess of some threshold value ($10^5 \sim 10^6 \text{ V/cm}$). The mechanism has been identified as "self-heating" by fitting the data to a numerically calculated $I-V$ curve. Self-heating is caused in such a way that the Joule heating of the current raises the local temperature, the decreased local resistivity due to the increased local temperature enhances the current and finally the current will be confined in a filament with very high local temperature. The self-heating effect will be significant in the materials with high activation energies of conductivity, such as impurity doped YIG.

A second conductivity state has been reported in Si-doped YIG at room temperature. The sample can be switched to a high conductivity state by a high A.C. voltage and switched back to low conductivity state by a large current pulse. The mechanism of this effect is unknown. A non-uniform magnetic field-induced high conductivity effect has been found at room tem-
perature on Ca-doped YIG. The conductivity can be increased by about 20% in a few hours in the magnetic field gradient. The mechanism of this effect is also unknown.

A Tucciarone and P. De Gasperis pointed out that self-heating may be applied to “write in” a memory state in a magnetic memory device but that the low resistivity of the singly doped YIG is harmful to their applications in the microwave devices.

The heavily Ge and Ca counter-doped YIG thin films have controllable small magnetic moment, large coercivity and high resistivity ($10^6 \Omega cm - 10^7 \Omega cm$ are measured in this work at room temperature). This is an alternative substitute for the singly doped YIG films. The effects described above, such as the non-ohmic $I - V$ characteristic and the transient current, are also observed in this material. The corresponding theories will be reviewed and/or developed in the next sections of this chapter. A model will be developed in Chapter III to explain the most unusual HCS effect observed in this material. This model will be based upon the concepts on the conduction mechanism reviewed above and on the effects of electron trapping and high concentration of impurities which will be reviewed below.

As a transition metal oxide, like many other transition metal oxides, the electrical properties of YIG cannot be predicted well by using the energy band model based on the single electron Hartree calculation. The basic difficulty is that the unfilled band of $3d$ electrons predicts a metallic behavior while YIG and other transition metal oxides are good insulators with a resistivity greater than $10^{12} \ \Omega cm$ at room temperature. A modification of this model will be discussed in Chapter III. What would be pointed out here is that
YIG (pure or doped) may have some peculiar electrical properties just as the transition metal oxides usually have.

J.P. Zielinger, et al. reported a photo-memory effect in Cu$_2$O in the temperature range between room temperature and 130 K. Upon illumination with light, a conductivity one to two orders in magnitude higher than its original value in the dark is reached in a few hours. This high conductivity state is maintained after switching off the light and is removed only by heating the sample to a much higher temperature. There are two models to explain this effect: optical-chemical and physical models. By the optical-chemical model Cu$_2$O is decomposed partially to copper and oxygen atoms in the illumination of light. The copper and oxygen atoms are combined again into Cu$_2$O at higher temperature. In the physical model the electrons are excited by light from the acceptor levels and trapped in some electron trap levels. In this process the Fermi level is lowered towards the valence band. These trapped electrons are released to the acceptor levels again when the temperature is increased above some values and the Fermi level is then lifted to its original position. J. P. Zielinger, et al argued that the physical model is closer to the truth. In their model four electron trap levels, an acceptor band partially compensated by unknown donors and some recombination levels in the acceptor band are assumed. The origins of electron trap levels and the recombination levels are also unknown.

A similar phenomenon was reported in amorphous selenium by Kurrovoskii, et al. The special feature of this material is that its conductivity has a "color memory", i.e., the value of the photo-induced conductivity can be switched back and forth by light of different frequencies. The following
mechanism is proposed. The electrons are pumped by light from the valence band to the conduction band or to an impurity donor band and then penetrate into repulsive electron traps leaving holes in the valence band to give rise to the resulting conductivity. This increased conductivity state is a function of the frequency of the light applied to the sample because the capture cross-section of the electron trap is dependent of the frequency of the light.

According to the activated nature of the conductivity, the YIG films studied in this work may be classified as heavily doped and partially compensated semiconductors. B. L. Shklovskii and A. L. Efros have given an overall theoretical analyses on this subject. They have proven that the impurity levels may constitute a band and that this band may overlap with the host band to form the band tail. Below a threshold temperature which depends on the degree of compensation of the impurity bands, the conduction may be dominated by a hopping of carriers in the impurity bands (or band tails). They also pointed out that the band edges may be bent by the long range (longer than the lattice constant) potential fluctuations (PF) induced by the random distributions of the charged donors and acceptors. B. Pistoulet et al. assumed a Gaussian distribution of the PF and calculated the conductivity of the semiconductors. They concluded that the PF with the dimension of a few hundred Angstrons lead to an additional activation energy for the mobility of carriers in the conduction or valence band.
2.2 Contacts

The appropriate contacts of electrodes to the sample are important in any study of electrical properties of materials. A review is presented here of a few kinds of contacts concerned in this work. For simplicity, the electrodes are assumed to be in contact with a perfect crystal solid lightly doped with impurity to give the solid either n- or p-type conductivity. The application of these contact models to the heavily doped samples in this work will be discussed in the related sections with the appropriate modifications.

2.2.1 Neutral contacts.

When the work function of the electrode (usually made of metal) is the same as that of the sample, the electric contact of the electrode to the sample is neutral: neither electrons nor holes pile up inside the sample near the contacts. For a p-type sample the neutral contact is as shown in Fig. 2.1 (for definiteness, a p-type sample will be dealt with from now on). In this figure, $E_c$, $E_v$, and $E_f$ are the edges of the conduction and the valence bands and the Fermi level respectively, $E_{\text{vacuum}}$ is the energy of the electron in the vacuum and will not be marked in the following figures for simplicity. The electrical contact is ohmic, i.e. the forward and the backward $I - V$ characteristics of this contact are the same, until the voltage is so high that the current density reaches the limitation of the thermoionic emission of holes from metal to the sample

$$J_s = q \frac{(2kT)^{1/3}N_e \exp\left(-\frac{E_f - E_v}{kT}\right)}{m_h^{1/2}}$$

(2.1)
Figure 2.1: The energy band diagram of the neutral contact. The circles represent the holes in the valence band. Other symbols are as described in the text.
where $J_s$ is the maximum thermally emitted current density with the subscript $s$ referring to "the saturation value of the current density for the neutral contact", $q$ is the electronic charge, $k$ the Boltzman constant, $T$ the temperature in degrees Kelvin(K), $m_h^*$ the effective mass of hole in the valence band, and $N_v$ the density of states equivalent of the valence band, $N_v = 2(2\pi m_h^* kT/h^2)^{3/2}$ (see Ref. 29, also rederived in appendix B) with $h$ being the Plank constant. To have an idea about the value of $J_s$, assume $m_h^*$ is equal to the mass of a free electron, $T$ equal to 300 K, and $E_f - E_v$ equal to 0.4 ev, the result is a value of $J_s$ equal to 9.45 A/cm$^2$. This $J_s$ gives a total current $I_s$ of 0.189 A for a crosssection 0.02 cm$^2$ of the conduction channel as used in W samples in this work. The value of the voltage at which the current reaches $I_s$ depends on the width and the thickness of the conduction channel. If the mobility of the hole is 0.1 cm$^2$/v.sec and the width 100 microns and the thickness 10 microns are assumed the saturation voltage of 2000 V is obtained at room temperature. At voltages higher than this value the current will be saturated until breakdown occurs. No charge carriers can be injected into the sample through a neutral contact unless tunneling of carriers through the contact occurs under high voltages or the interface of the contact is irradiated by high energy beams such as light or high energy electron beams.

2.2.2 Injecting contacts.

When the work function of the sample is smaller than that of the metal, the bands of the sample bend up towards the interface, as a result more holes pile up at the interface to form a reservoir of charge as shown in Fig. 2.2. The
Figure 2.2: The energy band diagram of the injecting contact. The bands bend up giving rise to a hole reservoir at the contact interface.
holes are ready to go into the sample once the electric field of appropriate polarity is applied to the sample. The contact is ohmic until the current approaches a value

$$J_s = q\left(\frac{3kT}{m^*_h}\right)^{1/2}N_e \exp\left(-\frac{\Delta}{kT}\right),$$  \hspace{1cm} (2.2)

where \(\Delta\) is the energy difference between the Fermi level and the edge of the valence band at the interface when the electrode is in equilibrium with the sample.

2.2.3 Blocking contacts.

In this case the band bends down towards the interface, as shown in Fig. 2.3. Only an extremely small current \(I_s\) can flow through the contact until the applied electric field is strong enough to cause a tunneling of holes through the potential barrier at the interface.

$$J_s = q\left(\frac{3kT}{m^*_h}\right)^{1/2}N_e \exp\left(-\frac{\Psi}{kT}\right),$$  \hspace{1cm} (2.3)

where \(\Psi\) is the energy difference of the Fermi level and the edge of the valence band at the interface when the electrode is in equilibrium with the sample.

2.2.4 The sharp edge effect of the electrodes on the contact properties.

When the electrodes consist of thin layers of metal deposited on the same surface of a thin film sample, as shown in Fig. 2.4 a, the sharp edges of the electrodes may result in an intense electric field at the interface of the contact edges. When the contact edges are of neutral or blocking type, this intense field may cause the injection of carriers into the sample from the electrode.
Figure 2.3: The energy band diagram of the blocking contact. The bands bend down giving rise to the lack of holes at the contact interface.
Figure 2.4: The sharp edge effect of the electrodes on the contact properties. The intense electric field at the sharp edge of the electrodes may cause the injection of carriers into the solid even when the contacts are neutral or blocking.
which is forward biased. If the other electrode is made of the same metal, it is then backward biased. The $I-V$ characteristic of this contact-sample system is determined by the reverse characteristic of the contact. From a simplified one dimensional analysis, this $I-V$ characteristic can be expressed as

$$J = B(T) \exp\left[q \frac{qE}{4\varepsilon_s} 1/2 / kT\right],$$  

(2.4)

where

$$E = 2q \left[ \frac{N_a - N_d}{\varepsilon_s} (V_r + V_{bi} - \frac{kT}{q}) \right]^{1/2},$$  

(2.5)

$E$ has the dimension of electric field, $V_r$ is the applied voltage across the backward biased contact, $qV_{bi}$ is the measure of the band bending ($V_{bi}=0$ for a neutral contact) as shown in Fig. 2.4 b, $B(T)$ is a function of temperature only and $\varepsilon_s$ is the static dielectric constant of the sample. It is possible that electrons are injected into the sample from one electrode and at the same time holes are injected from the other electrode. This is known as the double injection of the carriers and will be discussed in §2.3.3.

2.2.5 Ohmic contact of a metal to both n- and p-type conduction of the same material.

As has been pointed out by Albert Rose, the atoms of the metal used as electrodes can be embedded in the lattice at the surface of the sample substitutionally and interstitially. The substitutionally embedded atoms have lower energy while the interstitially embedded atoms have higher energy as shown in the energy band diagram Fig. 2.5. In this figure, diagram a shows the metal, a surface region of thickness $t$ in which metal atoms are embedded and the bulk of the sample in non-equilibrium with each other. Diagram b
Figure 2.5: The energy band diagram of the ohmic contact to both p- and n-type conduction of the host material.
shows the case where this system is in equilibrium. A hole reservoir is formed at the bulk side of the surface layer and results in the ohmic contact to the p-type material. The thickness of the surface layer is of the atomic size and thus is transparent to the holes. Diagram c and d show the cases of the metal atoms embedded interstitially in the surface lattice when the metal-surface-bulk system is in non-equilibrium and in equilibrium respectively. An electron reservoir is formed that results in the ohmic contact to the n-type material.

2.3 Space charge limited current effects (SCL)

2.3.1 The space charge limited currents.

In highly resistive solids, as in a vacuum, the flow of electric current is prevented by space charge consisting of the injected carriers themselves because of the lack of intrinsic free carriers to relax them. Unlike the vacuum case, the flow of current in the solids is further influenced by scattering of the carriers by the vibration of the lattice and/or by the defects in the solids. The defects also act as traps or recombination centers. In addition, the electric contacts (electrodes) influence the flow of the current significantly. As a simple start in discussing the space charge limited current, the solid is assumed to be trap free and p-type and the contacts are assumed to be ohmic (injecting, see §2.2.2) for holes in the temperature range concerned. The equations characterizing this problem, when neglecting the thermal equilibrium holes, are

\[ J = p q u_h \epsilon, \]  
(2.6)
and
\[ \frac{d\mathcal{E}}{dx} = \frac{4\pi q \rho}{\epsilon}, \quad (2.7) \]

with the boundary condition
\[ \mathcal{E}(x = 0) = 0, \quad (2.8) \]

where the anode is assumed to be located at \( x = 0 \), the cathode at \( x = L \); \( L \) is the width of the conduction channel, \( \mathcal{E} \) the electric field, \( J \) the current density, \( \epsilon \) the dielectric constant and \( \rho \) the concentration of holes injected in the valence band. \( J \) is independent of \( x \) if the solid is isotropic and homogeneous and eq. 2.6 and eq. 2.7 can be combined to yield
\[ \mathcal{E}d\mathcal{E} = \frac{4\pi J}{\mu_{hf} \epsilon} dx. \quad (2.9) \]

The solution satisfying eq. 2.8 and eq. 2.9 is
\[ \mathcal{E}(x) = \left( \frac{8\pi J}{\mu_{hf} \epsilon} \right)^{1/2} x^{1/2}. \quad (2.10) \]

To find the \( J - V \) characteristic, integrate both sides of eq. 2.10
\[ V = \int_0^L \mathcal{E}(x) dx = \left( \frac{8\pi J}{\mu_{hf} \epsilon} \right)^{1/2} \frac{2}{3} L^{3/2}, \quad (2.11) \]

or
\[ J = \frac{9}{32\pi \mu_{hf} \epsilon} \frac{V^2}{L^3}, \quad (2.12) \]

or written in practical units where \( J \) is in amperes/cm\(^2\), \( V \) in volts, \( L \) in cm, \( \epsilon \) in relative units and \( \mu_{hf} \) in cm\(^2\)/V. sec.,
\[ J = 10^{-13} \mu_{hf} \epsilon \frac{V^2}{L^3}. \quad (2.13) \]
This is the result for the sandwich-type contacts. When the electrodes are deposited on the same surface of the thin film of the sample (gap-type), it can be shown that the \( J' - V \) characteristic is

\[
J' = 10^{-13} \mu_{hf} e \frac{V^2}{L^2}, \tag{2.14}
\]

where \( J' \) is the linear density of current. If the effective thickness of the thin film for conduction is \( t \), it is assumed in this work that

\[
J' = tJ, \tag{2.15}
\]

then equation (2.13) may be re-derived as

\[
J = 10^{-13} \mu_{hf} e \frac{V^2}{t L^2}. \tag{2.16}
\]

If there are thermal equilibrium holes of concentration \( p_0 \), the conduction is ohmic at the applied voltages up to \( V_x \)

\[
J = p_0 \mu_{hf} q \frac{V}{L}, \quad V < V_x, \tag{2.17}
\]

where \( V_x \) satisfies the condition

\[
p_0 q \mu_{hf} \frac{V_x}{L} = 10^{-13} e \mu_{hf} \frac{V_x^2}{L^3}. \tag{2.18}
\]

\( p_0 \) and \( \mu_{hf} \) can thus be found as

\[
p_0 = 10^{-13} \frac{e V_x}{q L^2}, \quad \text{for sandwich-type},
\]

\[
= 10^{-13} \frac{e V_x}{q t L}, \quad \text{for gap-type}, \tag{2.19}
\]

and

\[
\mu_{hf} = \frac{I_x L}{p_0 q V_x W t}, \tag{2.20}
\]

(2.20)
where \( I_e \) is the current when \( V = V_a \), \( W \) is the total length of the conduction channel along the electrodes.

When the temperature is too low to support a sufficient thermal emission of the holes from the anode into the solid, the space charge limited current \( J \) is proportional to \( V^n \) with \( n \) less than 2.

### 2.3.2 The trap effects.

A trap is an energy level that originates from a defect and is located between the demarcation level and the band edge. The demarcation level is an imaginary level in the band gap, at which a carrier has the same probability to be excited to the band (conduction band for electron or valence band for hole) and to be recombined by the carrier of opposite charge sign. A trap level can become a recombination level when the demarcation level is closer to the band edge than the trap level.

Traps can be classified into majorities or minorities in terms of whether they can trap the majority or the minority carriers. Traps can also be classified into shallow or deep ones in terms of their locations being either above or below the equilibrium Fermi level. In the NS, since there are no minority carriers injected (see §2.2.2, §2.2.3), only the majority shallow trap levels are active in influencing the electric properties of the sample studied in this work.

Assume a single trap level \( E_{th} \) above the mobility edge of the valence band (the detail about the mobility edge will be discussed in Chapter III) with concentration \( N_{th} \) in equilibrium with the valence band. The concentration
of trapped holes is

\[ p_t = N_{th}(\exp\frac{E_f - E_{th}}{kT} + 1)^{-1} \approx N_{th}\exp(-\frac{E_f - E_{th}}{kT}), \quad (2.21) \]

when \(|E_f - E_{th}| \gg kT\). Here \(E_f\) is the quasi-Fermi level in the presence of the applied voltage across the sample. The total charge per unit area forced into the sample is

\[ Q = qL(p_t + p_f) \approx qLp_t, \quad if \quad p_t \gg p_f, \quad (2.22) \]

where

\[ p_f = N_{v\mu}\exp(-\frac{E_f - E_{v\mu}}{kT}) \quad (2.23) \]

is the concentration of free holes in the valence band. \(p_f\) can also be written as

\[ p_f = \frac{N_{v\mu}}{qLp_t} \exp(-\frac{E_{th} - E_{v\mu}}{kT}) \]

\[ \approx \frac{qVN_{v\mu}}{qLp_t N_{th}} \exp(-\frac{E_{th} - E_{v\mu}}{kT}) \]

\[ \approx \frac{4\pi qL^2 N_{th}}{qLp_t N_{th}} \exp(-\frac{E_{th} - E_{v\mu}}{kT}). \quad (2.24) \]

The current density is thus given as

\[ J = qp_f \mu_{hf} \frac{V}{L} = 10^{-13} \epsilon \mu_{hf} \theta \frac{V^2}{L^3}, \quad (2.25) \]

with

\[ \theta = \frac{N_{v\mu}}{N_{th}} \exp(-\frac{E_{th} - E_{v\mu}}{kT}). \quad (2.26) \]

This result can also be obtained by viewing all of the injected holes as still movable with a reduced mobility \(\theta \mu_{hf}\). From this viewpoint, the current in the case of gap-type electrodes can be immediately written as

\[ J' = 10^{-13} \epsilon \theta \mu_{hf} \frac{V^2}{L^2}. \quad (2.27) \]
Usually $\theta \ll 1$ and the effect of the shallow trap levels is thus to reduce the space charge limited current.

When the trap levels are exponentially distributed in the gap, it can be shown that\textsuperscript{34}

$$J \propto V(T'/T)^{+1},$$

(2.28)

where $T'/T$ is the characteristic temperature for the trap level distribution $N_{th}(E) = N_{th0} \exp(E - E/kT)$, $N_{th0}$ is a constant. The parameter $T'/T$ may be the same as the parameter $T_c$ characterizing the distribution of the acceptor levels. The validity will be discussed by fitting the models of the trap levels to the experimental data in Chapter V. In this case the holes are trapped near the Fermi level within a few $kT$.

2.3.3 Double injection.

1. Tunneling of electrons at cathode.

Double injection of holes and electrons into the solid from the anode and the cathode respectively and simultaneously may occur when the applied voltage is so high that electrons can tunnel through the barrier at the cathode. Fig. 2.6 shows the band bending in the sample when the electric field is applied. In this figure $V > 0$ is the applied voltage, $L$ the spacing between the electrodes, $L_1$ the place at which electrons in the conduction band have the same energy as those electrons in the cathode at $E_F$, and $\Delta$ is the barrier height in electron volts. For simplicity, single shallow traps are assumed, which does not result in any essential difference in the physics. Taking the energy of an electron at $x = 0$ as zero and using eq. 2.10, the
Figure 2.6: The tunneling of electron from the cathode to the conduction band of the sample. The symbols are defined as following: $L$ is the spacing between the electrodes, $L_1$ is the position at which electrons in the conduction band have the same energy as those electrons in the cathode at $\delta \, eV$ above $E_f$, $\Delta$ is the barrier height in electron volts and $qV$ is the band bending in electron volts.
energy of an electron in the conduction band can be expressed as

\[ E_{ce} = \Delta + q \int_0^x e(x) \, dx = \Delta + \frac{qV}{L^{3/2}} x^{3/2}. \]  \hspace{1cm} (2.29)

Then the transmission coefficient \( T_r \) of an electron from the cathode with energy \( qV + \delta \) tunneling into the conduction band of the sample is\(^{35}\)

\[ T_r = \exp\left[ -2 \int_{1 - \frac{\Delta - \delta}{qV}}^{L} \frac{2m^*}{h^2} \left( \Delta - \delta - qV(1 - \frac{x^{3/2}}{L^{3/2}}) \right)^{1/2} \, dx \right]. \]  \hspace{1cm} (2.30)

For small \( L \) and large \( V \), \( T_r \) may be significant. In particular, if \( \Delta \sim 2 - 3 \) eV, the irradiation of visible light on the cathode may be able to make the tunneling possible even at relatively low electric fields by raising the electron’s energy \( \delta \).

2. Current-controlled negative resistance.

In the case of double carrier injection, the hole trap levels discussed previously may also act as recombination levels. Assume that the hole capture cross-section \( \sigma_h \) of these centers is larger than their electron capture cross-section \( \sigma_n \), since these centers are acceptor-like and filled with electrons (compensated) in the equilibrium state. At low injection levels of the current, only a few holes are injected and almost all the recombination centers are still filled with electrons. The life time of the injected holes is

\[ \tau_{h,low} = \frac{1}{N_R < v \sigma_h >}, \]  \hspace{1cm} (2.31)

where \( N_R \) is the concentration of the recombination centers (\( N_R \) may equal \( N_d \)), \( v \) the thermal velocity of the holes and \( < v \sigma_h > \) represents the average
of $\nu \sigma$ over the distribution of the velocity. The average drift time of holes across the distance between the electrodes is

$$\tau_{h,d} = \frac{L^2}{\mu_h f V} > \tau_{h,\text{low}}.$$  \hspace{1cm} (2.32)

Equation 2.32 can also be considered as the definition of a "low injection level". In this case, most holes are trapped and only a very small current can flow. For the convenience of description, it is said that there is a "recombination barrier" to the flow of the holes. When the applied voltage is increased to such a value, $V_{th}$, that $\tau_{h,d} \approx \tau_{h,\text{low}}$, the situation is drastically changed. Since $\sigma_h > \sigma_n$, the recombination centers preferentially capture holes and will therefore be filled up with holes. This in turn, will cause the hole life time to increase. Since both electrons and holes are injected into the body of the sample, it will be largely neutral. At high injection levels, where the injected electron and hole concentrations exceed $N_R$, they are necessarily free and approximately equal. With $n \simeq p$, the steady state requires that $\tau_{n,\text{high}} \simeq \tau_{h,\text{high}}$, where $\tau_{n,\text{high}} (= 1/N_R < \nu \sigma_n >)$ and $\tau_{h,\text{high}}$ are the respective life times of electrons and holes at high injection levels. Thus between low and high injection levels, the hole life time increases by $< \nu \sigma_h > / < \nu \sigma_n >$, a factor which may easily be many powers of ten. An increase in $\tau_h$ may result in $t_{h,d} < \tau_{h,\text{high}}$. In that event the "recombination barrier" disappears. Then the voltage required decreases as the current increases. This is the negative resistance feature which may lead to a current oscillation. This negative resistance is current-controlled, i.e. it will not appear until the current is large enough even when the applied voltage is very high. In the region of the negative resistance, the electrons are transferred from the recombina-
tion centers (compensated acceptors) to the conduction band via the double injection mechanism.

3. The $I - V$ characteristic of double injection.

The detailed discussion of this subject is very lengthy because of its complexities. Hence only the physical background and the mathematical results are discussed here. Detailed derivations can be found in the book written by M.A. Lampert and P. Mark.\textsuperscript{36}

In the presence of thermal equilibrium carriers, e.g. $p_0$ for p-type sample, the current is linear in the voltage when the injection is low,

$$J = p_0 q \mu_f \frac{V}{L}. \quad (2.33)$$

In the region of higher injection levels, the electrons and holes may neutralize each other and the recombination of the electrons with the holes, instead of the space charge, limit the current

$$- \frac{dJ_n}{dx} = \frac{dJ_p}{dx} = r - g, \quad (2.34)$$

where $J_n = n q \mu_f \varepsilon$ and $J_p = p q \mu_f \varepsilon$, $r$ and $g$ are the recombination and generation rates of carriers respectively. The $J - V$ characteristic has a square law dependence

$$J = 10^{-15} \frac{\tau_{n,\text{low}}}{\tau_{p,\Omega}} \varepsilon \mu_f \frac{V^2}{L^3}, \quad (2.35)$$

where $\tau_{n,\text{low}} = 1/p_R < v \sigma_n$ is the life time of electrons at low injection levels with $p_R$ the empty recombination centers, $\tau_{p,\Omega} = \varepsilon / q p_0 \mu_f$ is the ohmic relaxation time due to $p_0$, the concentration of thermal equilibrium holes.
At a higher injection level with the voltage approaching $V_{th}$, the $J - V$ characteristic enters the negative resistance region. In this region electrons in the recombination centers are drawn largely to the conduction band until $n, p \gg N_R$ when the current will be limited by the direct recombination of electrons with holes and the resistance becomes positive again. Then the $J - V$ characteristic obeys a square law

$$J = \frac{9}{8} q(n_0 - p_0)\mu_{n_f}\mu_{h_f}\tau \frac{V^2}{L^2},$$

(2.36)

where $\tau$ is the life time averaged over electrons and holes, $n_0$ and $p_0$ the concentrations of thermal equilibrium electrons and holes respectively.

If the concentrations of the injected electrons and holes are much greater than the equilibrium values, the double injection of carriers, after passing the negative resistance region, results in a plasma in the sample. The $J - V$ characteristic of this plasma is a cubic relation

$$J = 10^{-13} \frac{125}{18} \epsilon \tau \mu_{h_f} \mu_{n_f} \frac{V^3}{L^2}.$$  

(2.37)

This $J - V$ characteristic of double injection is shown schematically in Fig. 2.7, where $V_m$ represents the voltage at which the negative resistance region terminates and the semiconductor or insulator plasma region starts. $V_m$ is determined by

$$t_{h,d} = \frac{L^2}{\mu_{h_f} V_m} \sim \tau_{h,\text{high}} = \frac{1}{N_R < v\sigma_n>}.$$  

(2.38)

### 2.4 The transient SCL currents.

The transient SCL currents have been measured in this work using a double box car technique to determine the position of the hole trap levels and
Figure 2.7: A sketch for double injection $J - V$ characteristic showing the linear and quadratic dependence, the region of negative resistance and return to the power law dependence at high currents. $V_{th}$ and $V_m$ are the threshold voltages for the start and end of the negative resistance region respectively.
to estimate the concentration of the trapped holes. The traditional deep level transient spectroscopy (DLTS) method is not applicable due to the high resistivity of the sample. The transient SCL current spectroscopy (TSLCS) method is then developed for this work.

2.4.1 The deep level transient spectroscopy (DLTS) method.

The DLTS method, introduced first by Lane\textsuperscript{37,38} in semiconductor research, is based on measuring the transient variation of the phase shift $\phi$ of the circuit, shown in Fig. 2.8, as a function of temperature using a double boxcar technique. The variation of the phase shift is caused by the variation of the junction space capacitance $C$. The change in $C$ is induced by the thermal emission of carriers from the traps in the depletion region of the junction in the semiconductor after a carrier injection pulse of voltage is switched off. In semiconductors, the bulk resistance $R$, which is in series with the capacitance $C$, is small. In semi-insulators or in insulators, $R$ is very large: $\geq 10^6 \Omega$ at room temperature. This large bulk resistance prevents the DLTS method from being directly applicable to semi-insulators or insulators. This can be shown as follows. The change in the phase shift is given by

$$\frac{d\tan \phi}{dC} = \frac{L' - 2R^2 C}{RC^2 \omega L'} + 2\frac{\omega^2 (CL' - R^2 C^2) - 1}{\omega^3 RL'C^3}, \quad (2.39)$$

where $L'$ is the induction externally set in the circuit and $\omega$ the frequency of the A.C. current applied to measure the phase shift. In the extreme case that $R$ approaches infinity, $d(\tan \phi)/dC$ approaches zero. Hence this method cannot be applied to the highly resistive materials even though a good junction space capacitance can be made in these materials. In fact, the
Figure 2.8: Block diagram representing the equivalent circuit for the DLTS measurements on semiconductors.
capacitance between the electrodes (not shown in Fig 2.8) will shunt the space capacitance when $R$ is very large.

2.4.2 The transient space charge limited current spectroscopy (TSLCS) method.

On the other hand, the transient current in the highly resistive solids is significant when a pulsed voltage is applied because there are few intrinsic carriers to relax the injected carriers. The time constant of the discharge transient current is related to the thermal emission rate of the carriers from the traps. Applying the double box car technique to measure this transient time constant as a function of temperature may give information about the position and concentration of the trap levels. When the electrodes are injecting for majority carriers, only the majority trap levels can be measured when the amplitude of the pulsed voltage is small. In the presence of double injection when the voltage is high, both majority and minority trap levels may be active in the transient current process. In this case the data analysis would be very complicated. In this work transient current measurements are made only in the low voltage range and only the majority trap effects are discussed. For simplicity this measurement will be called TSLCS from now on.

1. The position of the trap levels.

Assume there is a single trap level or a set of distributed trap levels of which only those within $kT$ of the Fermi level are active. Neglecting re-
trapping, the decay equation of the concentration of the trapped holes, upon switching off the voltage, may be expressed as

\[ \frac{dp_t}{dt} = -e_l p_t, \tag{2.40} \]

where \( e_l = N_{v_{hh}} < \nu \sigma_h > e^{(E_{v_{hh}} - E_{hh}/kT)} \) is the thermal emission rate of holes from the trap levels (in the case of distributed trap levels, \( E_{th} \) may be replaced with \( E_f \)). The solution to this equation is

\[ p_t(t) = p_t(0)e^{(-e_l t)}, \tag{2.41} \]

where \( p_t(0) \approx N_{th}e^{(E_{th} - E_f/kT)} \) is the concentration of trapped holes when the voltage \( V \) is switched off. In the case of distributed trap levels, \( p_t(0) \) is approximately equal to \( Q_t/L \) with \( Q_t \) being defined by

\[ Q_t \approx \frac{Ve}{4\pi L} \approx qL \int_{E_f0-\Delta E}^{E_f0} N_{th0}e^{(-\frac{E - E_{vuh}}{kT_e})}dE, \tag{2.42} \]

where \( Q_t \) is the area density of the trapped charge, \( E_{f0} \) the equilibrium Fermi level, \( \Delta E \sim \text{a few } kT \) the shift of the Fermi level when voltage is applied. If the time constant of the circuit consisting of the sample, the sampling resistance \( R_s \) and the stray capacitance \( C_0 \) (see Fig. 2.9, a) is much shorter than the time constant of the thermal emission, the discharge current \( I \) can be expressed as

\[ I \approx -\frac{dQ(t)}{dt} = qV e_l p_t(0)e^{(-e_l t)} = I_0e^{(-e_l t)}, \tag{2.43} \]

where \( Q(t) \) represents the trapped charge in the sample and \( V \) the volume of the sample. The current \( I \) flows through \( R_s \) and results in a voltage \( V_s \) varying with time.
Figure 2.9: The transient current due to hole trap effects. a) The equivalent circuit; b) The signal fed to the double box car integrator.
\[ V_\tau = I R_\tau = V_{\text{so}} \exp(-e_\tau t), \] (2.44)

where \( V_{\text{so}} = I_0 R_\tau = q \overline{N} e_t p_t(0) \). It is seen that the transient current of discharge due to thermal emission of holes is an exponential function of time.

The decay time constant of the transient current can be measured by measuring the time constant of the signal voltage \( V_\tau \) using the double box car technique as shown in Fig. 2.9 b. The output of the double box car is the difference of the amplitudes of \( V_\tau \) at different times \( t_A \) and \( t_B \). If the scanning rate of window A is chosen as half of that of window B, the output may be written as

\[ f(t) = V_{\text{so}} [\exp(-\frac{e_\tau t}{2}) - \exp(-e_\tau t)]. \] (2.45)

At a time \( t_m \), \( f(t) \) reaches its maximum, and \( e_\tau \) can be expressed by \( t_m \) as

\[ e_\tau = \frac{\ln 4}{t_m}. \] (2.46)

If \( e_\tau \) is measured in this way at various temperatures, it follows that

\[ \ln e_\tau = \ln N_{v\mu} < v\sigma_h > - \frac{E_{th} - E_{v\mu}}{kT}, \] (2.47)

for single trap level; or

\[ \ln e_\tau = \ln N_{v\mu} < v\sigma_h > - \frac{E_f - E_{v\mu}}{kT}, \] (2.48)

for distributed trap levels. The first term in eq. 2.47 or eq. 2.48 varies slowly with temperature. The plot \( \ln e_\tau \) vs. \( 1/kT \) thus gives \( E_{th} - E_{v\mu} \) (or \( E_f - E_{v\mu} \)) as its slope.
2. The estimation of the concentration of trapped holes.

From eq. 2.43, \( I_0 \) is given by the relation

\[
I_0 = qV e_t p_t(0). \tag{2.49}
\]

On the other hand, \( I_0 \) can be expressed using eq. 2.44 and eq. 2.45 as

\[
I_0 = \frac{V_{s0}}{R_s} = \frac{f_{\text{max}}}{R_s} \left[ \exp \left( \frac{-e_t t_m}{2} \right) - \exp \left( -e_t t_m \right) \right]^{-1} = \frac{4f_{\text{max}}}{R_s}, \tag{2.50}
\]

where \( f_{\text{max}} \) is the maximum value of \( f(t) \) when \( t = t_m \). The combination of eq. 2.49 and eq. 2.50 gives

\[
p_t(0) = \frac{4f_{\text{max}}}{qR_s e_t V} = \frac{4f_{\text{max}} t_m}{qR_s V \ln 4}. \tag{2.51}
\]

In the case of a single trap level, the total concentration of the traps may be estimated as

\[
N_{\text{th}} = p_t(0) \exp \left( \frac{E_f - E_t}{kT} \right), \tag{2.52}
\]

if \( E_f \) is known.

2.5 Thermopower studies.

Thermopower is the electric motive force produced by the accumulation of the carriers moving from the place of higher temperature to the place of lower temperature. If the carriers are electrons, the hot end of the solid will be positively charged relative to the cold end and there will be a positive electrical potential difference between the hot and the cold ends. If the carriers are holes, the electrical potential difference between the hot and the cold ends will be negative, as shown in Fig. 2.10. The value of the
Figure 2.10: Thermopower is a measure of voltage due to carriers moving from the hot end toward the cold end building up an internal electric field.
thermopower $| V_{AB} |$ is

$$| V_{AB} | = \alpha \Delta T,$$

(2.53)

where $\alpha$ is the thermopower coefficient which is a function of temperature and the nature of the solid. $\alpha$ can be found approximately as follows. Assume the cold end of the solid is at zero temperature, the hot end is at temperature $T$. The kinetic energy and the chemical potential of a carrier (say, electron) are considered as zero at zero temperature. The energy loss of one carrier when it reaches the cold end is $\bar{e} - \mu$, where $\bar{e}$ and $\mu$ are the average kinetic energy and the chemical potential of the carrier respectively at temperature $T$. From the conservation of energy, this is just the energy gain of this carrier in building up the internal electric field

$$q | V_{AB} | = q \alpha T = \bar{e} - \mu.$$  

(2.54)

The thermopower coefficient is thus

$$\alpha = \frac{\bar{e} - \mu}{qT}.$$  

(2.55)

In a semiconductor, eq. 2.55 can be rewritten as

$$\alpha q/k = A_+ + \frac{E_f - E_V}{kT},$$  

(2.56)

where $A_+$ is a constant. Since the conductivity $\sigma$ of a semiconductor equals to the product of the mobility of the carrier and the carrier's concentration which depends exponentially on the location of the Fermi level $E_f$, the plots $\alpha q/k$ and $\ln \sigma$ vs. $1/kT$ will give straight lines with equal slopes if the sample has the band conduction in which the mobility is weakly dependent on temperature.
For p-type samples, it is expected that the thermopower voltage $V_{AB}$ is negative in the NS. For n-type samples, $V_{AB}$ is expected to be positive in the NS.
CHAPTER III

Proposed model

In this chapter the physical model used to explain the effects observed in this work are discussed. This model is developed from the combination of the basic concepts from the relevant references and the modifications required by the experimental data.

3.1 The energy band model for the electric conduction of the heavily doped partially compensated yttrium iron garnet

3.1.1 The tails in the density of states due to impurities.

The energy band model based on the single electron Hartree calculation is usually not applicable to the transition metal oxides. The basic difficulty is that the transition metal oxides are predicated by this simple band model, in terms of their less than fully-filled 3d band, to be metal-like substances but they are usually good insulators. Yttrium iron garnet is a transition metal oxide. Nevertheless, experimental work on optical absorption\textsuperscript{41} and photoconductivity\textsuperscript{42} show that this single electron energy band model could be
applicable with some modifications. The $3d$ electrons are found to be localized in the crystal fields at the tetrahedral and octahedral sites respectively. These localized states are considered to be in the energy gap with the $3d$ band left empty. As reviewed in §2.1, R. Metselaar and P. K. Larsen found the energy gap to be $2.86\, eV$. The simple band model for pure YIG adapted in this work is: the $2p - 4s - 3d$ hybrid valence band are located $2.86\, eV$ below the $3d$ conduction band with the localized tetrahedral and the octahedral states of the $3d$ electrons in the band gap as shown in Fig. 3.1.\textsuperscript{41}

When pure YIG is doped substitutively with impurity ions some levels are split out from either the conduction or the valence band depending on the valence difference between the impurity ions and the host ions to be substituted. These split levels, called impurity levels, are located in the gap close to the band from which they are split off. When the concentration of the impurities is high these impurity levels may interact with each other to form an impurity band. This band may overlap either the conduction or the valence band to form a tail at the energy band edge of the host. For impurity concentration is $> 10^{20}/cm^3$, the Fermi level will enter the host band.\textsuperscript{43} In the samples used in this work the concentration of the dopants(Ca,Ge) is of the order of $4.0 \times 10^{21}/cm^3$ and can be considered as being very heavily doped and compensated. B. I. Shklovskii and A. L. Efros\textsuperscript{44} predicted an exponential distribution of the density of states of the tails measured from the corresponding band edges of the heavily doped semiconductors.

The impurity ions would distribute randomly in the host lattice. The presence of the Ca ions prefers the presence of the oxygen vacancies at the nearby lattice sites. The high concentration of the Ca and Ge ions(on the
Figure 3.1: Energy band model for pure YIG, cited from Ref. 41. Band states are shown to the left, and localized states to the right. The superscripts on the bands refer to the number of states per formula unit.
order of \(8.0 \times 10^{21}/cm^3\) and the oxygen vacancies may thus cause an amorphous-like structure seen by the electrons and/or holes which are introduced by the dopant ions and the oxygen vacancies. This may be understood in the following way. In the case of high impurity concentrations the impurity ions act essentially as one of the host components of the crystal. The bands are caused by the host and the impurity ions with comparable weights. But, due to Anderson localization\(^4\), any disorder in the lattice will result in the localization of some states. These localized states are at the band edges (where the energy is lower). If the disorder of the crystal potential is of the Gaussian type, these localized states will extend into the band gap to form the tails of the density of states.

N. F. Mott and E. A. Davis\(^4\) pointed out in their book that few exact calculations of the density of states are available for amorphous materials. The heavily doped semiconductors have been treated theoretically as amorphous by a few authors.\(^47,48,49\) The basic forms of the density of states tails obtained are in the hierarchy of the exponential functions. Although the results are in agreement with the optical and photo-emission studies, they are not very successful in predicting the electrical effects.

Since this work is the first study on the electrical properties of Ca in excess of Ge doped YIG, no theoretical study for the band structure of this material is available. Thus a density of states having decay tails which exponentially from the band edges (defined in the pure YIG or in the lightly doped YIG) into the gap is assumed in accordance with the previous review. Two mobility edges\(^5\), \(E_{\text{v}}\) and \(E_{\text{c}}\), are defined as the levels in the conduction and valence band respectively at which an electron or a hole is free to move.
carrying the electric currents. Since acceptors (Ca$^{2+}$ ions) are in excess of the donors (Ge$^{4+}$ ions) the valence band tail is partially filled with electrons while the conduction band tail is empty at room and low temperatures. The Fermi level is thus located in the valence band tail. These details are shown graphically in Fig. 3.2. The optical absorption edge is shifted to lower energy in this case than for that in pure YIG. This amorphous-like band model is found to be suitable for explaining the experimental results in this work and will be discussed in detail.

As described earlier, the concentration of the acceptor Ca ions is in excess to those of the donor Ge ions. The acceptor levels are thus mostly occupied at room and low temperatures by the electrons from the donor levels. The Fermi level is thus located in the valence band tail. Based on this model the following mathematical manipulations will give the expressions of the Fermi level and other parameters concerned.

According to the model the density of states in the band tail can be expressed as

$$A(E) = {A_0} \exp\left(-\frac{E - E_{V\mu}}{kT_c}\right),$$

(3.1)

where $T_c$ is the characteristic temperature of the density of states distribution in the tail, $T_c$ is found to be on the order of 1000 $K$ from a iteration calculation; $E_{V\mu}$ is the mobility edge of the valence band, and $A_0$ is a constant related to the density of the impurity levels. $A_0$ can be determined from the following

$$N_a = A_0 \int_{E_{V\mu}}^{\infty} \exp\left(-\frac{E - E_{V\mu}}{kT_c}\right) dE$$

$$= A_0 kT_c,$$

(3.2)
Figure 3.2: The amorphous-like energy band model of CaGe:YIG showing an exponential distribution of the density of states tail having a characteristic temperature $T_c$. Repulsive electron trap levels $E_{te}$ near the mobility edge of the conduction band $E_{c\mu}$ and recombination levels $E_R$ near the mobility edge of the valence band $E_{v\mu}$ are assumed. For the p-type material the Fermi level $E_f$ is located in the valence band tail. The compensated acceptor levels within $kT$ of the Fermi level act as the hole trap levels $E_{th}$. 
The concentration of the acceptors occupied by electrons is

\[ n_a = A_0 \int_{E_{\text{v}}}^{\infty} \left\{ \exp(-\frac{E - E_{\text{v}}}{kT_c}) \left[ 1 + \exp\left(\frac{E - E_{f_0}}{kT}\right)\right]^{-1} \right\} dE. \tag{3.4} \]

The condition for charge neutrality is

\[ N_d = n_a - p_0 \approx n_a, \tag{3.5} \]

when the temperature is not so high such that \( n_a \gg p_0 \), where \( p_0 \) is the equilibrium hole concentration in the valence band. From eq. 3.4 and eq. 3.5 the equilibrium Fermi level \( E_{f_0} \) can be determined. When \( T \ll T_c \) approximations are made in the following calculations to make analytical results available for practical applications.

\[ n_a \approx A_0 \int_{E_{\text{v}}}^{E_{f_0}-kT} \exp(-\frac{E - E_{\text{v}}}{kT_c}) dE \]

\[ + A_0 \int_{E_{f_0}+kT}^{\infty} \exp(-\frac{E - E_{\text{v}}}{kT_c}) \exp(-\frac{E - E_{f_0}}{kT}) dE \]

\[ + A_0 \int_{E_{f_0}-kT}^{E_{f_0}+kT} \left\{ \exp(-\frac{E - E_{\text{v}}}{kT_c}) \left[ 1 + \exp\left(\frac{E - E_{f_0}}{kT}\right)\right]^{-1} \right\} dE. \tag{3.6} \]

When \( E_{f_0} \gg kT \) the third term can be ignored and this condition will be verified by the experimental data. It then follows that

\[ n_a = A_0 kT_c \left\{ 1 - \exp\left(\frac{E_{f_0} - E_{\text{v}}}{kT_c}\right) \left[ \exp\left(\frac{T}{T_c}\right) - \frac{T}{T + T_c} \exp\left(-\frac{T + T_c}{T_c}\right) \right] \right\}. \tag{3.7} \]
The combination of eq. 3.5 and eq. 3.7 gives

\[ E_{f0} = E_{\nu\mu} - kT_c \ln(1 - \frac{N_d}{N_a}) + kT_c \ln[\exp \frac{T}{T_c} - \frac{T}{T + T_c} \exp\left(\frac{-T + T_c}{T_c}\right)], \quad (3.8) \]

where \( A_0 \) has been replaced by \( N_a/kT_c \). When \( T_c \gg T \)

\[ E_{f0} = E_{\nu\mu} - kT_c \ln(1 - \frac{N_d}{N_a}). \quad (3.9) \]

It can be seen that the Fermi level is "pinned" in the acceptor tail if the temperature is not very high \((T \ll T_c)\), just like the usual case in semiconductors. \(^{51}\) These details are included in the energy bands model as shown in Fig. 3.2.

In this figure a few additional features of the band model are also included for future use. They include the hole trap levels \( E_{th} \) which may be identified with the acceptor levels within \( kT \) of the Fermi level; the recombination levels \( E_r \) whose origin is unknown and the repulsive electron trap levels \( E_{te} \) which may originate from the oxygen vacancies.

The concentration of the free holes in the valence band can be calculated from \( p_0 = N_{\nu\mu} \exp\left(\frac{E_{f0} - E_{\nu\mu}}{kT}\right) \), where \( N_{\nu\mu} \) is the density of states equivalent at the mobility edge of the valence band. The expression for \( N_{\nu\mu} \) may be different from that based on the effective mass parabola band model without the band tail. However, the following discussion shows the application of the parabolic model to the valence band is valid independent of the details of the tail in the band. In eq. 3.8, the difference \( E_{f0} - E_{\nu\mu} \) is taken as the measured activation energy of the D.C. conductivity in the band conduction range within an error of about 0.1 eV which is on the order of the activation energy of the mobility. \(^{40}\) \( T_c \) is then calculated by iteration of \( T_c \) in eq. 3.8 with the temperature given in the range for the D.C. conductivity measurements.
The value of $T_c$ given by this analysis is nearly constant over the temperature range of the experiments. This result can be taken as the credence for the validity of the proposed model. While the value of $E_{f0} - E_{v\mu}$ is changed from 0.3 eV to 0.4 eV, $T_c$ changes from 1400 K to 1800 K. This result is not very far from the temperature of 1323 K at which the growth of the CaGe:YIG thin films took place. If the energy of the mobility edge of the valence band is taken as zero and energy is measured into the valence band, the parabolic density of states for the valence band is $4\pi(2m_h^*/h^2)^{3/2}E^{1/2}$. An extrapolation of the tail into the valence band is $(N_a/kT_c)\exp(E/kT_c)$. Using the mass of free electron for $m^*$, which is the lower limit of the effective mass of hole in the material studied, and substituting the values for $N_a$ and $T_c$, the intersection of these two curves of the density of states has been found by a graphical method to be $8.0 \times 10^{-35}$ eV. The missing states, when a discontinuity is allowed at $E_{v\mu}$ between these two curves of the density of states, is less than $2.8 \times 10^{-11}$. Therefore it has been shown that there is no need to worry about the details of the connection of the tail to the band. Of course it is possible that some of the impurity states are in the parabolic distributions or even that the host band is distorted so much that the parabolic model is not applicable at all, but this is beyond the scope of this experimental study. Nevertheless, the details of the density of states distribution does not qualitatively affect the physical argument needed in this work that the observed phenomena are due mainly to the reduction of the degree of compensation of the acceptor levels. This has been confirmed by assuming a uniform distribution of the impurity density of states instead of the exponential one. The concentration of the thermal equilibrium holes
in the valence band can be expressed as

\[ p_0 = N_{v\mu} \exp\left(-\frac{E_{f0} - E_{v\mu}}{kT}\right) \]

\[ = N_{v\mu}(1 - \frac{N_d}{N_a})^{\frac{T_c}{T}}/[\exp\frac{T}{T_c} - (\frac{T}{T + T_c})^{\frac{T_c}{T}}]^{\frac{3}{2}}, \]  

(3.10)

where \( N_{v\mu} = 4.74 \times 10^{15} (m_h^*/m_e)^{3/2} T^{3/2} \text{cm}^{328} \) with \( m_h^* \) being the effective mass of the hole, and eq. 3.8 has been used to substitute for \( E_{f0} - E_{v\mu} \). It can be seen that both the concentration and the activation energy of the free holes can be changed by changing the degree of compensation \( N_d/N_a \).

3.1.2 D.C. and transient electrical properties in the NS at high temperatures.

High temperatures here mean temperatures at which band conduction dominates over hopping conduction. In the band conduction the mobility of the hole may have an activated process, given by

\[ \mu_{fh} = \mu_{fh0} \exp\left(-\frac{E_{sh} + E_m + E_{pf}}{kT}\right) \]

\[ = \mu_{fh0} \exp\left(-\frac{E_{\mu}}{kT}\right), \]  

(3.11)

where

\[ E_{\mu} = E_{sh} + E_m + E_{pf}, \]  

(3.12)

and \( \mu_{fh} \) is the mobility of holes in the valence band, \( E_{sh}, E_m \) and \( E_{pf} \) are respectively the barrier heights due to the short range fluctuations of the crystal potential\textsuperscript{25}, the magnetic structure of the lattice\textsuperscript{55} and the long range potential fluctuations of the compensated impurity centers\textsuperscript{26}. \( E_m \) vanishes when there is no magnetic disorder or when the holes are transported in
the same magnetic sublattice. \( \mu_{fh0} \) is a constant depending on the material parameters, e.g., the degree of the compensation of the impurities. The conductivity measured in the ohmic range of the \( I - V \) characteristic is given by

\[
\sigma = \rho_0 q \mu_{fh}
= q \mu_{fh0} N_{eA}(1 - \frac{N_d}{N_a}) T_e/T \exp\left(-\frac{E_\mu}{kT}\right),
\]  

(3.13)

when \( T \ll T_e \).

A noticeable feature of the conductivity is indicated here. It can be shown by further analysis that both the degree of compensation \( N_d/N_a \) and the mobility barrier height \( E_\mu \) can be reduced when the applied voltage is increased, i.e. the apparent conductivity and its activation energy are voltage dependent.

When the injected holes are trapped the quasi-Fermi level will be lowered because of the depopulation of the electrons from the hole traps which may be the compensated acceptor levels within \( kT \) of the Fermi level. Let the quasi-Fermi level be \( E_f \) when the concentration of the trapped holes is \( p_t \). It follows from eq. 2.21 and eq. 2.22 that

\[
\frac{eV}{4\pi q L^2} \simeq N_{th} \exp\left(-\frac{E_f - E_{th}}{kT}\right), 
\]  

(3.14)

and

\[
\frac{V_2}{V_1} \simeq \exp\left(\frac{E_{f2} - E_{f1}}{kT}\right). \]  

(3.15)

The apparent activation energies of the conductivities measured at two different applied voltages differ, within an error due to the activation energy of
the mobility, by

\[ |E_{f2} - E_{f1}| \approx kT \ln \frac{V_2}{V_1}. \tag{3.16} \]

The non-uniformly distributed compensated acceptors and donors produce fluctuations of the band edge.\textsuperscript{23,24} These potential fluctuations of width \( r \) affect neither the density of states of the band nor produce bound levels if the energy \( (E = (h/r)^2/2m^*_h) \) of the lower level above the bottom of the potential well is small.\textsuperscript{56} This condition is largely satisfied for \( r > 100 \text{ A.} \textsuperscript{24} \) These potential fluctuations also leave unchanged the local mobility of the carrier, if \( r \) is larger than the mean free path of the carriers. However, they may change the apparent mobility of the carrier by adding an additional activation energy to the motion of the carrier moving in the fluctuated band as shown in Fig. 3.3. There \( E_{pf} \) is the average height of the fluctuation barrier, \( l \) the dimension of the barrier and the open circles represent holes in the valence band. The mobility of the holes can be expressed as

\[ \mu_{hf} = \mu_0 e^P \left( -\frac{E_s + E_M + E_{PF}}{kT} \right), \tag{3.17} \]

where \( E_s, E_M \) are the contributions to the activation energy of the mobility from the short range lattice fluctuations and from the magnetic structure of the lattice respectively,\textsuperscript{24,54} \( \mu_{hf_0} \) depends on the type of scattering and on the polaronic nature of the hole. Applying an electric field may lower the potential barrier height by \( qVl/L \). The activation energy of conductivity under the applied voltage \( V \) is

\[ E_a = E_f - E_{\mu\mu} + E_{\mu f} - \frac{qVl}{L}, \tag{3.18} \]

where \( E_{\mu f} = E_s + E_M + E_{PF} \). Using eq. (3.14) to solve for \( E_f \) and substituting
Figure 3.3: The band bending due to the long range potential fluctuations (PF). The symbols are explained in the text. The potential fluctuations produce additional potential barriers to the motion of the holes in the valence band.
$E_f$ into eq. (3.18) yields

$$E_a + kT \ln V = E_{th} - E_{v\mu} + E_{\mu_f} - kT \ln \frac{e}{4\pi q N_t L^2} - \frac{qVl}{L}. \quad (3.19)$$

If $E_a$ is measured for various $V$, the slope of the plot $E_a + kT \ln V$ vs. $V$ gives $l$.

The hole trap effect may also induce a transient current upon the change of the applied voltage, of which the time constant depends exponentially on the position of the trap level and the reciprocal temperature. This effect may be studied using the TSLCS method given in §2.4.2.

3.1.3 D.C. and transient electrical properties in the NS at low temperatures.

If the activation energy of the conductivity is high (a few tenths of an $eV$), all the holes may be frozen in the acceptor tail of the valence band at low temperatures. The conductivity is then due to hopping of the holes near the Fermi level located in the tail. The hopping mobility of the hole can be expressed as\(^{87}\)

$$\mu_{hh} = \frac{\mu_{hh0}}{kT} \exp(-2\alpha R - \frac{W}{kT}), \quad (3.20)$$

where $\mu_{hh0}$ is a constant depending on the material parameters only, $R$ the range of hopping, $1/2\alpha$ is the decay range of the wave function of the localized hole, and $W$ is the activation energy of hopping which may consist of the terms $E_{sh}$ and $E_m$. According to the short range characteristic of hopping, the long range potential fluctuations have no effect on the hopping activation energy. At not very low temperatures that $W/kT < 2\alpha R$, the second term
in the exponent of eq. 3.20 dominates. It follows that

\[ \mu_{hh} \propto \frac{1}{kT} \exp\left(\frac{-W}{kT}\right). \]  

(3.21)

When \( T \) is so low that \( W/kT > 2\alpha R \), the mobility obeys the following law:

\[ \mu_{hh} \propto \frac{1}{kT} \exp\left(-\frac{B_3}{T^4}\right) \quad \text{for 3 - dimension,} \]  

(3.22)

\[ \propto \frac{1}{kT} \exp\left(-\frac{B_2}{T^3}\right) \quad \text{for 2 - dimension,} \]  

(3.23)

where \( B_3 \) and \( B_2 \) are constants.

The conductivity of hopping is expressed as

\[ \sigma = kTA(E_{f0})q\mu_{hh} \]

\[ = qN_a(1 - \frac{N_d}{N_a})\mu_{hh0} \exp\left[-(2\alpha R + \frac{W}{kT})\right]. \]  

(3.24)

It should be noted here that the details of hopping conduction are more complicated in the sense that the appropriate choice of the mathematical expression of the conductivity requires rigorous quantum mechanical calculations on \( \alpha \) and \( W \), as well as detailed quantum field analysis on the electric polaron nature of holes to find the details of \( \mu_{hh0} \). However the simplified model adopted gives a reasonable fit to the experimental data in this work.

At low temperatures, the transient current due to the hole trap effects will have a long time constant which may be beyond the range of measurements of the apparatus.

3.1.4 The effects of the polaron nature of the hole on the mobility.

Holes, either moving in the band or localized in the band tail, interact with the ionic lattice ions to form electric polarons. Polarons are classified as
small or large according to their radii being smaller or larger than the lattice constant. In n- and p- type YIG the polarons are identified as large ones\cite{39}. It is difficult to calculate the mobility of the polaron and different authors usually give different expressions. Feynman et al\cite{25} gave for large polarons

\[
\mu = \left\{ \frac{3q}{4m_\omega \omega \eta} \frac{kT}{h\omega} \right\}^2 \frac{kT}{\hbar} \exp \left\{ \frac{\omega^2 - w^2}{\omega^2 v} \exp \frac{h\omega}{kT} \right\},
\]

(3.25)

for large coupling constant \( \eta \) and low temperature \( \hbar \omega < kT \), where \( \hbar \) is the Plank constant, \( \omega \) is the frequency of the optical phonon. \( \eta \) is expressed as\cite{60}

\[
\eta = \frac{q^2}{\hbar} \left( \frac{m^*}{2\hbar\omega} \right)^{1/2} (\varepsilon_\infty^{-1} - \varepsilon_s^{-1}),
\]

(3.26)

where \( m_e \) and \( m_h^* \) are respectively the masses of a free electron and a hole in the valence band, \( \varepsilon_\infty \) and \( \varepsilon_s \) the optical and static dielectric constants, and \( \omega = 2\pi \nu \). When \( \eta \) is moderately small, \( \nu \sim \omega, w = 3 \) and

\[
\nu \simeq 3 + 2.22 \frac{\eta}{10} + 1.97 \left( \frac{\eta}{10} \right)^2 + \ldots.
\]

(3.27)

Platzman\cite{61}, on the other hand, found that for small \( \eta \) and low \( T \)

\[
\mu \simeq \mu_0 \frac{3 kT}{4 \eta \hbar \omega} \exp \frac{\hbar \omega}{kT},
\]

(3.28)

where \( \mu_0 \) is a constant; and for large \( \eta \)

\[
\mu \propto \eta^{-7} \exp(\eta^2).
\]

(3.29)

As can be seen, at low temperatures where more and more holes become localized, the positive exponent \( \hbar \omega/kT \) may lower the activation energy of
the mobility. $\hbar \omega$ is in the range from a few to tens of mev depending on the value of $\omega$. For pure YIG, $\hbar \omega$ is of the order of 40mev. Further effects of the polaron characteristic of holes on the mobility will be discussed in the next section.

3.2 Reduction of the degree of compensation; Anomalous high conductivity states (HCS)

According to eq. 3.13, an anomalous high conductivity state can be established if the degree of compensation of the acceptors can be reduced in some way and the reduced degree of compensation can be kept at least metastablelly. Two methods were developed in this work to establish the HCS: pumping the electrons away from the compensated acceptors by light in the presence of an electric field and by double injection of carriers using high electric field. In either process the electrons are transferred to the conduction band or the band tail and then trapped in the repulsive electron traps with the assistance of the electric field. The HCS can be eliminated by some extrinsic methods, e.g. thermally releasing or optically bleaching the trapped electrons to restore the degree of compensation of the acceptor centers. The repulsive electron trap model, the D.C. and transient electrical properties in the HCS, and the excitation and de-excitation processes of the HCS will be discussed in this section.
3.2.1 The model of the repulsive electronic trap levels.

The experimental fact that the HCS can be realized only in the presence of the electric field indicates that the electronic traps are of a repulsive nature to electrons. The electron overcomes the potential barrier surrounding the trap and gets trapped in the trap when it acquires sufficient kinetic energy in the electric field. The origin of this trap is discussed in the following.

1. Defects due to valence variation of ions and deformation of lattice.

In transition metal oxides, e.g. YIG, there is usually a deviation of the composition from stoichiometry. The presence of oxygen vacancies is a typical stoichiometric deviation. The deviation and/or the presence of foreign ions may lead to the presence of defects due to the valence variation of the ions. Defects may also be introduced by the deformation of the lattice. Defects may act as donors, acceptors, traps, recombination centers, etc. Oxygen vacancies lead to defects due both to the valence variation of ions and the deformation of the lattice. The presence of oxygen vacancies in YIG has been identified by many authors and are found to act as donors.\(^6\)\(^2\) The presence of oxygen vacancies is facilitated by the presence of the divalent ions in the crystal and suppressed by the presence of the tetravalent ions. The following qualitative discussion may show that the oxygen vacancies compensated by the divalent ions constitute the electronic repulsive traps.

In Fig. 3.4, diagram a shows an oxygen ion and its surrounding cations, the positive charges of the cations associated with this oxygen ion add up to \(2^+\). There is no excess local charge. Diagram b shows an oxygen vacancy
Figure 3.4: Oxygen ion and oxygen vacancy as repulsive trap. a) Oxygen ion and its surrounding cations; b) Oxygen vacancy and its surroundings.
and its surroundings. There are 2+ excess charges at the vacancy.

Assuming that the complex of the oxygen ion and its surrounding cations has an energy \(-U(U>0)\), the crystal will gain energy \(U\) in the formation of the oxygen vacancy. To minimize this energy gain the complex of the oxygen vacancy and its surroundings must polarize the lattice at their neighborhood. It can thus be assumed that an oxygen vacancy consists of a positively charged sphere surrounded by a negatively charged spherical shell. The energy diagram of such an oxygen vacancy is as shown in Fig. 3.5. In this form it will act as a repulsive trap to electrons.

In general, an oxygen vacancy may be in either one of three states: neutral\((V_o)\); single positively charged\((V^+_o)\); or double positively charged\((V^{2+}_o)\). In the presence of divalent ions, the oxygen vacancy is more likely to be in the state \(V^{2+}_o\) or \(V^+_o\).

2. The escape and the capture cross section of the repulsive electron traps.

Because of the special structure of the repulsive trap, its cross section for thermally releasing an electron from the trap and for capturing an electron from the conduction band may be different. As shown in Fig. 3.6, the trap is assumed to be in quasi-equilibrium with the conduction band and the quasi-Fermi level for the electron \(E_{fe}\) is assumed to be close to the trap level \(E_{RP}\), \(E_{fe} \approx E_{RP}\)(this will be reasonable when the concentration of electrons in the conduction band is much less than that in the traps). According to the principle of detailed balance, the rate of releasing and capturing electrons
Figure 3.5: The schematic energy diagram of an oxygen vacancy as a repulsive electronic trap.
Figure 3.6: The capture and release of electron by the repulsive trap. $E_{RP}$ and $E_b$ are the location and the barrier height of the trap respectively, $E_{fe}$ is the quasi-Fermi level of the electrons.
by the trap should be the same

\[ N_{cu}S_{te} e^{\left( -\frac{E_{cu} - E_{RP} - E_b}{kT} \right) } = nS_{tc}v = S_{tc}v N_{cu} e^{\left( -\frac{E_{cu} - E_{te}}{kT} \right) } \]

(3.30)

or

\[ S_{te} = S_{tc} e^{\frac{E_b}{kT}} \]

(3.31)

where \( S_{te}, S_{tc} \) are the cross sections of the trap for releasing and capturing electrons respectively, and \( E_b \) is the height of the potential barrier: \( E_{te} = E_{RP} + E_b, v \) the velocity of electron and \( E_{te} \) the quasi-Fermi level of electron.

It is assumed that the electron has to be over the top of the barrier when it is to be released from the trap. If tunneling of electrons through the barrier dominates, it can be proved that

\[ S_{te} = S_{tc} e^{\left( \frac{E_1}{kT} + \frac{\alpha}{E_1^{1/2}} \right) } \]

(3.32)

with \( \alpha = (2\pi^2 q^2/\varepsilon h)(2m^*_e)^{1/2} \); where \( \varepsilon \) is the relative dielectric constant, \( E_1 \) is determined by minimizing the exponent \( (E_1/kT + \alpha/E_1^{1/2}) \). At any rate, \( S_{te} \) may be many orders in magnitudes smaller than \( S_{tc} \).

3.2.2 D.C. and transient electrical properties of the sample in the HCS.

Assuming the concentration of electrons trapped by the electron traps is \( n_t \), the condition of neutrality now will be

\[ N_d - n_t = n_a - p + n \simeq n_a, \]

(3.33)
where $p$ and $n$ are respectively the concentration of free holes and free electrons in the HCS. The condition $n \ll n_a$ is guaranteed by the location of the Fermi level close to the valence band mobility edge and by the low temperature. The condition $p \ll n_a$ can be checked by experimental measurements on $N_d$ and $p$. For instance, $N_d \simeq 4.0 \times 10^{21}/cm^3$, $p \simeq 10^{15}/cm^3$, $p \ll n_a$ will hold until $N_d - n_t \simeq 4.3 \times 10^{-7}N_d$. Combining eq. 3.7 and eq. 3.34 gives the quasi-Fermi level in the HCS

$$E_f = E_{\nu \mu} - kTc \ln(1 - \frac{N_d - n_t}{N_a}), \quad (3.34)$$

at temperatures $T \ll T_c$. The Fermi level is lowered toward the valence band. Then four predictions can be made.

First, the sample in the HCS should have a p-type conductivity.

Second, the concentration of holes in the valence band can be computed

$$p = N_{\nu \mu}(1 - \frac{N_d - n_t}{N_a})T_c/T. \quad (3.35)$$

The conductivity can be expressed as

$$\sigma_{HCS} = N_{\nu \mu}(1 - \frac{N_d - n_t}{N_a})T_c/T q\mu_0(\eta_H)\exp(-\frac{E_{\mu_H}}{kT}). \quad (3.36)$$

The ratio of the resistivity in the NS to that in the HCS is

$$\frac{\rho_{NS}}{\rho_{HCS}} = \frac{\sigma_{HCS}}{\sigma_{NS}} = \frac{N_{\nu \mu H} \mu_0(\eta_H)}{N_{\nu \mu N} \mu_0(\eta_N)} \left(\frac{1}{1 - \frac{N_d - n_t}{N_a}}\right)\frac{T_c}{T} \exp\left(-\frac{E_{\mu_H} - E_{\mu_N}}{kT}\right), \quad (3.37)$$

where the subscripts $H$ and $N$ indicate that the corresponding parameters are measured in the HCS and in the NS respectively; $\mu_0$ represents the dependence of the mobility on the polaron nature of the holes as described
in equations 3.26 to 3.30. A significant characteristic of this ratio is that \( \ln(\rho_{NS}/\rho_{HCS}) \) is a linear function of \( 1/T \)

\[
\ln \frac{\rho_{NS}}{\rho_{HCS}} = \frac{C}{T} + B,
\]

(3.38)

where \( C \) and \( B \) are independent of temperature.

Further attention may be paid to the effect of the polaron nature of holes on this resistivity ratio. The reduction of compensation also reduces the polar nature of the sample by neutralizing the charged centers. \( \epsilon_e \) is thus reduced towards \( \epsilon_\infty \) but \( \epsilon_\infty \) is not affected (\( \epsilon_\infty \) depends on the electron configurations "inside" the ions). As a result, the reduction of \( \eta \) (from \( \eta_N \) to \( \eta_H \)) may lead to a \( \mu_0(\eta_H) \) much smaller than \( \mu_0(\eta_N) \) according to equations 3.26 and 3.28 or 3.30.

At low temperatures, the holes in the HCS will also be frozen in the valence band tail. However, this can occur only at much lower temperatures than those occurring in the NS because the position of the Fermi level in the HCS lies closer to the mobility edge of the valence band. The resistivity ratio at temperatures below but near the threshold temperature for hopping in the NS is the ratio of hopping resistivity in the NS to band resistivity in the HCS.

Holes in the valence band tail are neutral centers while electrons in this tail are negatively charged centers. Hopping of holes in the tail is equivalent to hopping of electrons within \( kT \) of the Fermi level. The hole hopping thus acquires the nature of polaron motion. Including this effect in the calculations, the hopping conductivity in the NS can be written as (see eq.
where $\nu_{ph}$ is the frequency of the longitudinal phonon and $T \ll T_c$. It is obvious that the resistivity ratio

$$\frac{\rho_{hN}}{\rho_{HCS}} = \frac{\sigma_{HCS}}{\sigma_{hN}} = \left\{ \frac{N_{\mu H} \mu_0(\eta_H)}{2q^2 R^2 \nu_{ph} \mu_0(\eta_{N})} \frac{(1 - \frac{N_e - n_i}{N_a})^{T_e/T}}{1 - \frac{N_d}{N_a}} \right\} \exp[-(E_{\mu H} + 2\alpha R + \frac{W}{kT})]$$

has a totally different functional form from that at higher temperatures.

The third prediction is that the hole trap effect would disappear when the sample is in the HCS because most of the hole traps have been converted to recombination centers due to the lowering of the quasi-Fermi level. The equations 2.19 and 2.20 may be applied to approximately determine the concentration and the mobility of the holes in the HCS if the thickness of the HCS layer is known.

The fourth prediction, since the Fermi level in the HCS is lowered toward the valence band mobility edge it is expected that the TSLCS signal will disappear in the temperature range in which this effect was observed in the NS. This occurs if the Fermi level moves a few $kT$ below the (original) single hole trap level or if the Fermi level is shifted to a position very close to the mobility edge of the valence band in the case of distributed hole trap levels.
3.2.3 Kinetics of the excitation process of the HCS.

1. The general kinetic equations.

Assuming only one kind of electron trap of concentration $N_{te}$ is involved, the following kinetic equations are used to describe the relaxation process when light and electric field are applied to the sample,

$$\frac{d(n + n_t)}{dt} = \alpha \beta I_l - \frac{n}{\tau_r}, \quad (3.41)$$

and

$$\frac{dn_t}{dt} = -\gamma_{te} N_{eu} n_t \exp\left(\frac{E_{te} - E_{eu}}{kT}\right) + \frac{n}{\tau_t}, \quad (3.42)$$

where $\alpha$ is the optical absorption coefficient, $\beta$ the quantum yield, $I_l$ the intensity of light, $\gamma_{te}$ the escape coefficient of electron from the electron trap, $\tau_r$ and $\tau_t$ the life times of electrons in respectively the recombination and the trapping processes, $E_{te}$ the electron trap level, and $N_{eu} = 4.83 \times 10^{15} \left(\frac{m_e^*}{m_a}\right)^{3/2} T^{3/2} / \text{cm}^3$ the is density of states equivalent of the conduction band when a parabolic band is assumed. Generally $N_{eu}$ should also include the contribution to the number of states from the conduction band tail. However, the exponential factor will make the first term on the right hand side of eq. 3.43 vanish when $kT \ll E_{eu} - E_{te}$. Therefore no special attention needs to be paid to the fine structure of $N_{eu}$ at sufficient low temperatures.

2. The kinetics of the excitation process of the HCS.

If the temperature is sufficiently low in the process of excitation, thermal
release of the electrons from the electron traps may be neglected and eq. 3.43 becomes
\[ \frac{d n_t}{d t} = \frac{n}{\tau_t}. \]

Eliminating \( n \) from eq. 3.42 and eq. 3.43 leads to
\[ \alpha \beta I_t = (1 + \frac{\tau_t}{\tau_{r}}) \frac{d n_t}{d t} + \tau_t \frac{d^2 n_t}{d t^2}. \]

At a time sufficiently beyond the initial interval in which \( n_t \) may vary quickly with time, the Fermi level approaches the region of the recombination levels (see Fig. 3.1) so that \( \tau_r \ll \tau_t \), \( \frac{d^2 n_t}{d t^2} < \frac{d n_t}{d t} \) and eq. 3.44 is simplified to
\[ \alpha \beta I_t \approx \frac{\tau_t}{\tau_r} \frac{d n_t}{d t}. \]

At times not close to the end of the excitation process, \( \tau_t \) can be expressed as
\[ \tau_t \approx \frac{1}{\gamma_{te} N_{te}}, \]
where \( \gamma_{te} \) is the capture coefficient of the electron traps of which the concentration is \( N_{te} \), while \( 1/\tau_r \) is in reciprocal proportion to the concentration of the empty recombination centers.
where \( \tau_{r0} \) is a constant and \( T \ll T_c \) is assumed. Substituting eq. 3.47 and eq. 3.46 into eq. 3.45 and integrating eq. 3.45 lead to

\[
\alpha \beta I_1 t \simeq \frac{A_0}{\gamma \tau_0 N_e \tau_{r0}} \left\{ n_t \left[ kT_c \left( 1 - \frac{N_d}{N_a} \right) - \exp \left( \frac{-E_{r2} - E_{\mu\mu}}{kT_c} \right) \right] \right. \\
+ \frac{kT_t n_t^2}{2 N_a} - \frac{kT^2 N_a}{T_c} \exp \left( \frac{-E_{r2} - E_{\mu\mu}}{kT} \right) \\
\left. \left( 1 - \frac{N_d}{N_a} \right)^{1} \right\}. (3.48)
\]

When \( T \ll T_c \) and \( n_t \ll N_a \), eq. 3.48 can be written as

\[
C t + \frac{N_a kT^2}{T_c} \exp \left( \frac{-E_{r2} - E_{\mu\mu}}{kT} \right) \left( 1 - \frac{N_d}{N_a} \right)^{1-rac{\gamma_k}{kT}} \simeq kT_c n_t, (3.49)
\]

where \( C = \alpha \beta \gamma \tau_0 / A_0 \) is independent of time. The derivative

\[
\frac{dn_t}{dt} = \frac{C}{[kT_c + \frac{kT^2}{T_c} \left( \frac{T_c}{T_c} - 1 \right) \exp \left( \frac{-E_{r2} - E_{\mu\mu}}{kT_c} \right) \left( 1 - \frac{N_d}{N_a} \right)^{1-rac{\gamma_k}{kT}}]} \\
\simeq \frac{C}{[kT_c + kT(1 - \frac{N_d}{N_a})^{2-\frac{\gamma_k}{kT}} \exp \left( \frac{-E_{r2} - E_{\mu\mu}}{kT} \right)]} (3.50)
\]

approaches a constant rate when \( T \ll T_c \) and \( n_t \) increases with time. Therefore, \( n_t \) may be proportional to \( t^{1+\delta} \) with \( \delta \ll 1 \).
When $T \ll T_c$ and $n_t \sim N_d$, eq. (3.48) can be written as

$$Ct + \frac{kT^2N_a}{T_c} \exp(-\frac{E_v2}{kT}) \simeq kT_cn_t + \frac{kT_c}{2N_a}n_t^2.$$  (3.51)

It is possible to solve for $n_t$

$$n_t \sim \frac{2N_a}{kT_c}[-kT_c + \sqrt{(kT_c)^2 + \frac{2kT_c}{N_a}(Ct + B)}],$$  (3.52)

where

$$B = \frac{kT^2}{T_c}N_a\exp(-\frac{E_v2}{kT}).$$  (3.53)

From the above discussions it can be seen that the rate of excitation of the HCS is very slow in time beyond the initial interval in which the excitation is started. In the calculations above, the recombination levels are assumed to have the same distribution as the acceptor levels have. Alternatively, a uniform distribution of the recombination levels has been assumed and a similar low rate of excitation of the HCS has been obtained. As a matter of fact, once the Fermi level dips into the recombination level region the rate of the excitation is decreased regardless of the specific distribution of the recombination levels.

In the process of the excitation of the HCS, the compensated acceptor levels within $kT$ of the Fermi level may act as the hole trap levels. The injected holes will be trapped closer to the anode to reduce the electric field inside the sample as shown schematically in an energy diagram in Fig. 3.7. This effect competes with the trapping of electrons in the repulsive electron traps under the assistance of the strong electric field. The initiation of the excitation process may thus be chaotic in time.
Figure 3.7: Potential barrier to the flow of injected holes. a) Non-equilibrium: more holes located in region 1 than in region 2; b) Quasi-equilibrium: a "barrier" to the flow of holes appears at the joint of region 1 and region 2.
3.2.4 Double injection, impact ionization and self-heating as alternative way to excite the HCS.

As examined in §2.2.2, and §2.2.3, an injecting contact for holes is a blocking contact for electrons. However, this contact may also become injecting for electrons if the electric field at the electrode is strong enough or if irradiation of light is applied so that the following effect can occur: tunneling of electrons from electrode to the conduction band; internal photo-effect in the electrode, which lifts the electrons to a height over the contact potential barrier; photo-effect in the sample, which produces enough electrons in the conduction band at the vicinity of the electrode. The injection of both holes and electrons may result in two effects: first the differential negative resistance and second the transportation of the electrons from the compensated acceptors and hole traps to the conduction band. The free electrons may then be trapped by the repulsive traps under the assistance of the electric field, which leads to the HCS. This is the alternative way of realizing the HCS.

The excitation of the HCS is usually realized when both the electric field and the illumination of light are present. At low temperatures, the rate of generation of carriers by light may be much higher than that by heat. In the case where $\sigma_h \gg \sigma_n$ (capture cross-sections of holes and electrons, see §2.3.3), the concentration of free holes $p_0^l$ may be much less than that of free electrons $n_0^l$, where the superscript $l$ means "excited by light". Under low applied voltages, the tunneling of electron is impossible, the current is carried by $p_0^l$ and eq. 2.33 applies with $p_0$ replaced by $p_0^l$. When the voltage is increased, there are two possibilities. First, the double in-
jection becomes significant and eq. 2.35 applies with the only change that
\[ \tau_{n, \text{low}} = 1/p_R^I < v \sigma_n >, \]
where \( p_R^I \) is the empty recombination centers due to the illumination of light. Second, the double injection is still not significant in the initial range of the increased voltages. Then the space charge limited current dominates and eq. 2.25 applies. In either case, the \( J - V \) characteristic obeys the square law in the pre-negative resistance region. The significant feature of double injection in the excitation process of the HCS is that the negative resistance region may terminate at a voltage higher than \( V_m \) due to the large increase of the thermal holes resulted in by the lowering of the Fermi level toward the valence band when electrons are removed from the acceptors (recombination centers) and are trapped in the repulsive electron traps which become active in the strong electric field and the high local temperature produced by the un-avoidable current filament in the negative resistance region. Once the sample has been in the HCS, its \( J - V \) characteristic may follow a different trace which is characterized by a much higher concentration of the thermal equilibrium holes \( p_0 \) and a much lower concentration of the recombination centers (compensated acceptors) \( N_R \).

At the same time when the double injection occurs or even before it occurs, another mechanism, the impact ionization of electrons from the valence band to the neutral acceptors and the self-heating which is always a concomitant and an enhancer to the current avalanche, may also lead to the HCS. In this case it is expected, in terms of the local high temperature raised by self-heating, that deeper electron traps will be involved in the process of exciting the HCS than the electron traps involved in the excitation of the HCS by light pumping at the same operating temperature.
At low temperatures where holes are almost localized at the acceptor centers, the initial band holes and electrons generated by light are accelerated by the applied electric field to gain enough kinetic energy in their motion over a number of mean free paths to ionize the electrons in the valence band. The recombination of the photo electrons in the conduction band with the holes in the valence band may also eject the electrons in the valence band to the acceptor centers by an Auger process. The current avalanche induces the Joule heat which in turn enhances the avalanche rapidly because of the large activation energy of the band holes. The avalanche current, which has a characteristic of differential negative resistance, prefers to be confined in filaments and the local temperatures in the filaments may be so high that a significant number of electrons can be excited to the conduction band. For example, taking \( N_{\text{eSR}} = 4.83 \times 10^{15} T^{3/2} / \text{cm}^3 \), \( T = 3000 \) K (indicated by the evaporation of the Au electrodes in the current filaments formed in the double injection experiments) and the energy band gap \( E_g = 2.86 \) eV, the thermally generated concentration of electrons in the conduction band will be \( 3.2 \times 10^{18} / \text{cm}^3 \). Some of these electrons will be trapped in the repulsive electron traps in the presence of the high temperature and the electric field. After reducing the electric field (this is realized automatically in practice because of the constant load resistance and voltage source) and the lowering of the local temperature to the operating temperature (this is realized together with the reduction of the electric field), the trapped electrons will stay in the traps, the degree of compensation of the acceptors is reduced and the HCS is realized. It is also possible that a large pulse current can quench the HCS by thermally releasing the trapped electrons.
The competition between the impact ionization of the electrons from the valence band and the recombination of the electrons in the filled acceptors with the holes in the valence band may result in a current oscillation prior to the presence of the HCS. This current oscillation is also enhanced or modulated by the concomitant self-heating and thus has a low frequency relaxation-type characteristic. This is the key point to distinguish this current oscillation from the current oscillations due to other mechanisms such as high electric field domain (Gunn effect) and piezoelectric effect.

The self-heating effect was investigated by many authors experimentally and theoretically on various materials among which one is Si doped YIG. The basic idea of the analysis is the same as described above while the detailed calculation needs the use of a numerical method. The interested reader may refer to the references. Here a simple model on the impact ionization effect will be discussed.

Assume the system is in quasi-equilibrium when the ionization of electrons from the valence band is initiated, i.e., the rate of gain of energy from the electric field is equal to the rate of loss of energy to the lattice

\[ qE \nu_d = q \mu_e E^2 = \frac{m^*_h \nu_d^2}{\tau M} \left(1 - \frac{4kT}{m^*_h \nu_d^2}\right), \tag{3.54} \]

where \( E \) is the intensity of the electric field, \( \nu_d \) the drift velocity of holes in the valence band, \( 1/\tau \) the frequency of collision, and \( M \) the mass of the lattice ion. Considering the distribution of the velocity, the ionization may happen when the average kinetic energy is somewhat less than the required ionization energy \( I \),

\[ \frac{m^*_h \nu_d^2}{2} = \gamma I, \tag{3.55} \]
where $\gamma$ is a constant less than unity and is dependent of the mechanism of scattering. In eq. 3.54, the first term on the right hand side represents the energy transferred from the hole to the ion in the collision. This can be proven by the elementary kinetics when $m_h^* \ll M$. The second term represents the energy transferred from the lattice to the hole due to the longitudinal and shear phonons. Using $\mu_{hf} = qr/m_h^*$, the combination of eq. 3.54 and eq. 3.55 gives the critical electric field for the impact ionization of electrons from the valence band

$$\varepsilon_c = \frac{1}{\mu_{hf}} \left[ \frac{2\gamma I}{M} \left( 1 - \frac{2kT}{\gamma I} \right) \right]^{1/2}.$$  

(3.56)

It can be shown that the mass associated with lattice vibration is given by $M = kT/c^2$, where $c$ is the longitudinal velocity of sound. Equation 3.56 can be written as

$$\varepsilon_c = \frac{2c}{\mu_{hf}} \left( \frac{\gamma I}{2kT} - 1 \right)^{1/2},$$  

(3.57)

with the following conditions to be satisfied:

$$\frac{v_d}{c} = \left( \frac{2\gamma I}{m_h^*} \right)^{1/2}/c \gg 1,$$  

(3.58)

and

$$\frac{M}{m_h^*} = \frac{kT}{c^2 m_h^*} \gg 1.$$  

(3.59)

At last it may be noted that the measured critical field may be lower than expected by eq. 3.56 when the impact ionization is induced by the Auger process of the photo electrons in their recombination since the recoil electron may acquire energy more than $2 \text{eV} (\sim$ the band gap). It is also expected that the excitation of the HCS by the combination of double injection, impact ionization and self-heating will be a rapid process in contrast to the slow
nature of the excitation process when caused by light pumping, because of the critical nature of the former three effects.

3.2.5 Kinetics of the de-excitation process of the HCS.

The de-excitation of the HCS to the NS may be brought about by heating the sample in the dark with no or just low electric field (for the sake of measuring conductivity) to thermally release the electrons from the electron traps. The recombination of these electrons with the emptied acceptors raises the Fermi level and thus brings back the NS. In the following analysis on the kinetics of the de-excitation process, re-trapping of the released electrons is neglected according to the repulsive nature of the electron traps. In the simplest case, the rate of emitting electrons from traps is constant. The concentration of trapped electrons varies with time as

$$n_t(t) = n_{t0} \exp(-e_t t),$$  
(3.60)

where $n_{t0}$ is the concentration of trapped electrons before releasing. However, since $e_t = N_{ct} \gamma_{te} \exp[-(E_{ct} - E_{te})/(kT)]$ is a function of temperature, when the temperature is scanned in time eq. 3.60 should be generalized to

$$n_t(t) = n_{t0} \exp[- \int_0^t N_{ct} \gamma_{te} \exp(-E_{ct} - E_{te}) dt].$$  
(3.61)

The rate equation of the de-excitation process is then

$$\frac{dn_t}{dt} = -n_{t0} N_{ct} \gamma_{te} \exp[-E_{ct} - E_{te} / kT] - \int_0^t N_{ct} \gamma_{te} \exp(-E_{ct} - E_{te} / kT) dt],$$  
(3.62)

or

$$\frac{d n_t}{dT} = -n_{t0} N_{ct} \gamma_{te} \exp[-E_{ct} - E_{te} / kT] - \int_{T_0}^T N_{ct} \gamma_{te} \exp(-E_{ct} - E_{te} / kT) dT].$$  
(3.63)
where $T_m$ is the temperature at which the releasing of the electrons is initiated, and $b$ is the rate of increasing temperature: $dT = bdt$. A solution to eq. 3.63 gives the evolution of the HCS to the NS with increasing temperature. Unfortunately, this equation cannot be integrated in a closed form.

Alternatively, an approximation can be used to find the conductivity in the de-excitation process as a function of temperature to determine the electron trap levels $E_{c_m} - E_{t_e}$. The concentration of the electrons in the conduction band can be expressed as

$$n = n_{t_0}N_{c_m}\gamma_{t_e}T_{re} \exp\left[-\int_0^t N_{c_m}\gamma_{t_e}T_{re} \exp\left(-\frac{E_{c_m} - E_{t_e}}{kT}\right)dt - \frac{E_{c_m} - E_{t_e}}{kT}\right],$$

(3.64)

where $T_{re}$ is the recombination life time of the electron with the acceptor.

In the ordinary thermally stimulated current problem, it is these electrons that give rise to the extra current in excess to the normal current in the case of no electron trap effect. However, in the case of this work, these electrons recombine with the holes at acceptors almost immediately to raise the Fermi level. $n$ is thus small and the rise of the Fermi level results in a large reduction of the concentration of holes in the valence band. This effect minimizes the current when the applied voltage is constant. Assuming all of the released electrons recombine immediately with holes at acceptor levels, the variations of the concentrations of carriers in the de-excitation process can be shown schematically in Fig. 3.8. In this figure, $P_{HCS}$, $P_{NS}$, and $P_{DE}$ are the concentrations of holes in the HCS, in the NS and in the de-excitation process respectively; $n_t$ is the concentration of the trapped electrons. With the increase of temperature, the decrease in $P_{DE}$ is
Figure 3.8: Schematic diagram of the concentration of the various holes and the trapped electrons ($n_t$) as functions of temperature in the de-excitation process of the HCS. $P_{HCS}$, $P_{DE}$ and $P_{NS}$ are the concentrations of the holes in the valence band in the HCS, in the de-excitation process and in the NS respectively.
The first two terms have positive sign while the third term has a negative sign. Assuming the mobility is nearly constant when \( T \) is a little higher than \( T_m \), \( \Delta P_{DE} \) is determined to be negative by the observed change of conductivity in experiments when \( T \) is scanning across \( T_m \). The first two terms can thus be ignored in the practical applications. This is equivalent to the condition that \( E_{ci} - E_{te} > -kT_c \ln(1 - \frac{N_d - n_t}{N_a}) \). When \( T \) is close to \( T_m \) and \( b \) is not too small (\( \geq 2K/min. \)), \( \Delta P_{DE} \) is determined mainly by the exponential factor \( \exp[-(E_{cu} - E_{te})/kT] \). Equation (3.57) can be re-written, multiplying both sides by \( q\mu_hf \), to give

\[
|\Delta \sigma| = B \exp\left(-\frac{E_{cu} - E_{te}}{kT}\right),
\]

where \( \Delta \sigma \) is the measured difference of the conductivity when temperature is changed from \( T_m \) to \( T \), while \( B \) varies with temperature slowly. The slope of the plot \( \ln |\Delta \sigma| \) vs. \( 1/kT \) gives \( E_{cu} - E_{te} \). The larger value of \( b \), i.e. faster increase of temperature, is preferred to reduce the error in experimental measurements. Of course a compromise should be made between the requirements on the fast change of temperature and on the thermal equilibrium of the system.

Another method to decide \( E_{cu} - E_{te} \) is derived below. This method may be more accurate than that one derived above but needs more experimental work. This method may be used to check the results from the first method.
Using equations 3.13, 3.42, 3.43 with $I_t = 0$ and neglecting $n$, the temperature $T_m$ can be found as following

\[
\left( \frac{d\ln \sigma}{dt} \right)_m = \frac{-T_e}{T_m^2} + \frac{1}{N_a} \left( \frac{d n_t}{dT} \right)_m / \left( 1 - \frac{N_d - n_t}{N_a} \right) + \frac{1}{T_c + T_m} \\
+ \frac{3}{2T_m} + \left( \frac{d \ln \mu_{hf}}{dT} \right)_m
\]

\[= 0, \quad (3.67)\]

where

\[
\frac{d n_t}{dt} = -\frac{n_t \gamma_{te} N_{eu} }{b(1 + \tau_{ea} / \tau_t)} \exp\left( -\frac{E_{eu} - E_{te}}{kT} \right). \quad (3.68)
\]

Substituting eq. 3.68 into eq. 3.67 and neglecting the term $d \ln \mu_{hf} / dT$ in eq. 3.67, it follows that

\[
\ln b = -\frac{E_{eu} - E_{te}}{kT_m} + \ln \left\{ \frac{(\gamma_{te} N_{eu} n_t(T_m))}{N_a} \right\} \\
+ \frac{3}{2T_m} + \frac{1}{T_c + T_m - T_m} \\
\left( 1 + \frac{T_m}{T_c} \right) \left( 1 - \frac{N_d - n_t(T_m)}{N_a} \right) + \frac{1}{T_c} \}
\]

\[= 0 \quad (3.69)\]

In eq. 3.69 $n_t(T_m)$ can be assumed to change only slightly with $T_m$ because $n_t(T_m)$ is evaluated at the beginning of the de-excitation process and the second term changes very slowly with $T_m$ since $n_t(T_m)$, $T_m$ in the second term is in the logarithmic function. The plot $\ln b$ vs. $1/kT_m$ gives $E_{eu} - E_{te}$ again. The result obtained applying eq. 3.69 contains the same error arising from the activation energy of the mobility as applying eq. 3.65 but it contains less error arising from the activation energy of the valence band holes. The advantage of using eq. 3.65 is that $E_{eu} - E_{te}$ may be determined by running the de-excitation process only one time.
CHAPTER IV

Experimental procedure

In this chapter, the sample and electrode preparation and the instrumentation are described. Also described are the measured sample characteristic and the contact properties, which are the first step data in any electrical measurements on materials.

4.1 Sample preparation and electrode preparation

The experimental procedure used in this work is described in this chapter. The samples used are supplied by The Institute of Solid State Electronics Laboratory, CNR, Rome, Italy and by The Central Research Institute for Physics, Hungarian. The electrodes and the electrical measurements are deposited and made in The Ohio State University, U.S.A..

4.1.1 Sample preparation.

The films of Ca excess CaGe:YIG(Y_{3-y}Ca_{x}Fe_{5-y}Ge_{y}O_{12}, samples W5 and W7) used in this work were grown by the liquid phase epitaxy technique. The molar percent compositions of the melt for the growth of the W5 and W7 samples are 8.27 Fe_{2}O_{3}, 0.34 Y_{2}O_{3}, 1.79 GeO_{2}, 2.68 CaO, 80.98 PbO, 5.74 B_{2}O_{3} and 9.47 Fe_{2}O_{3}, 0.34 Y_{2}O_{3}, 1.89 GeO_{2}, 2.67 CaO, 79.66 PbO, 5.65
B\textsubscript{2}O\textsubscript{3}, respectively. Before each growth the melt was homogenized at 1050 °C by stirring at 300 rpm for 1 hour. The substrates used in the sample growth were single crystal plates of (111) oriented Gd\textsubscript{3}Ga\textsubscript{5}O\textsubscript{12} (GGG). The compositions of the films were determined by electron probe microanalysis (EMP) as \(x = 0.89, y = 0.81\) for W5 and \(x = 0.99, y = 0.90\) for W7.

The thickness of the films was measured using an optical interference technique.\textsuperscript{69} A Cary 14 spectrometer or a Beckman DU-8 spectrophotometer was used to transmit electromagnetic radiation normal to the film. As the wavelength was swept from 2000 nm to 200 nm, conditions for destructive and constructive interference alternated, resulting in a transmission spectrum consisting of a series of interference maxima and minima. The index of refraction of the CaGe:YIG\textsuperscript{70} was used to correct for the influence of the reflection on the transmission spectrum. The thickness of the film was calculated from the positions of the extrema. The accuracy of this method was limited by the fact that the index of refraction varies with composition. Nevertheless, the overall accuracy was estimated to be about 5%. When the film was too thin, a scan electron microscope was used to measure the thickness.

The Ca:YIG (\(Y_{3-x}Ca_xFe_5O_{12}\), sample 3CSS7), Ge:YIG (\(Y_3Fe_{5-y}Ge_yO_{12}\), sample 2SL15), Ge excess GeCa:YIG (\(Y_{3-x}Ca_xFe_{5-y}Ge_yO_{12}\), sample 160820) and the nominally pure YIG were grown in a similar fashion. The compositions and thicknesses were measured by the same methods applied for the CaGe:YIG samples. The results are listed in table 4.1.
Table 4.1. The characterization of the samples $Y_{3-x}Ca_xFe_{5-y}Ge_yO_{12}$

$E_a$: activation energy for the conductivity;

$t$: thickness; $\mu m$: micron; $\rho_{300}$: resistivity at 300 K.

<table>
<thead>
<tr>
<th>sample</th>
<th>composition</th>
<th>$t$</th>
<th>$\rho_{300}$</th>
<th>$E_a$</th>
<th>conduction type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(x)</td>
<td>(y)</td>
<td>(µm)</td>
<td>(Ω cm)</td>
<td>(eV)</td>
</tr>
<tr>
<td>W5A</td>
<td>0.89</td>
<td>0.81</td>
<td>15</td>
<td>$\sim 6.0 \times 10^6$</td>
<td>$\sim 0.40$</td>
</tr>
<tr>
<td>W5B</td>
<td>0.89</td>
<td>0.81</td>
<td>2</td>
<td>$\sim 4.0 \times 10^6$</td>
<td>$\sim 0.40$</td>
</tr>
<tr>
<td>W7</td>
<td>0.99</td>
<td>0.90</td>
<td>10</td>
<td>$\sim 4.0 \times 10^6$</td>
<td>$\sim 0.40$</td>
</tr>
<tr>
<td>3CSS7</td>
<td>0.08</td>
<td>-</td>
<td>2</td>
<td>$\sim 1.5 \times 10^9$</td>
<td>$\sim 0.67$</td>
</tr>
<tr>
<td>2SL15</td>
<td>-</td>
<td>0.10</td>
<td>8</td>
<td>$\sim 3.1 \times 10^5$</td>
<td>$\sim 0.34$</td>
</tr>
<tr>
<td>168021</td>
<td>0.7</td>
<td>0.72</td>
<td>12</td>
<td>$\sim 1.7 \times 10^{10}$</td>
<td>$\sim 0.70$</td>
</tr>
<tr>
<td>YIG</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>$\geq 10^{12}$</td>
<td>-</td>
</tr>
</tbody>
</table>

### 4.1.2 Electrode preparation.

Due to the high resistivity of the samples ($\sim 10^7 \Omega cm$, at 300 K), the standard four probe method for measuring the resistivity is not appropriate in this work, especially at low temperatures. Gold(Au) or Indium(In) was chosen as the material for the electrodes. A 2200 Å thick layer of Au or In was evaporated in a vacuum of $10^{-6}$ Torr onto the surface of the thin film sample. This metal layer was then etched into the pattern as shown in Fig. 4.1 by photo-lithography to give the greatest conduction area available in order to reduce the high resistance encountered when measuring the high resistive YIG films. This pattern of electrodes also had the advantage of minimizing the thermopower effect on the conductivity measurements. The
Figure 4.1: The special pattern of the electrodes.
average width of the conduction channel was measured by microscope and electron microscope to be in the range of 50 to 100 μm. Any residual tiny islands or horns of metal, which were inevitable due to the long length of the channel (~20 cm), were removed using a needle under the microscope and by re-etching. The etching agent was diluted HNO₃ for In and 19% I₂ plus 81% KI diluted solution of water for Au. A smooth, clean and dry surface of the sample film was required for obtaining the high qualities in the metal layer deposition and in the photo-lithography process. The samples were etched by H₃PO₄ at 100°C to remove about 100 Å surface layer of the garnet film before depositing the electrode metal layer. Since it was found that this procedure had no significant influence on the measurements in this work, the later measurements were on samples that had not been etched before the electrode deposition to save the sample material. However, the surface of the sample was usually degraded when the electrodes are prepared many times. This is one of the main sources producing some discrepancies in the experimental measurements. The samples that were deposited many times became inappropriate for measurements in the sense that it was harder to realize some of the effects, e.g. the HCS, in such samples as compared to a fresh sample. The straight line channel electrodes, which were easier to make, were also made when needed. Soft thin copper wires were stuck onto the metal electrodes by indium and pressure. These wires formed a good access to the external circuit in the temperature range from 350 K to 4.2 K.
4.2 Experimental procedures

4.2.1 Resistivity measurements.

The resistivity measurements were made by employing a two probe method with a constant voltage applied. This was realized in two ways.

The first method was to measure the current through the sample by measuring the voltage across a sampling resistor when the source voltage was applied to the sample and the sampling resistor in series with the sample. This method was relevant when a voltage higher than 100 V was required for experimental purpose. The block diagram of the apparatus is shown in Fig.4.2 with the switches set as following: $S_1$ in position 2, $S_2$, $S_4$ being on and $S_3$, $S_5$ off. All the switches, the associated resistors, and lead wires were enclosed in an aluminum box. This box and the D.C. voltage supply were in a static shielding screen cage. The insulation for all the circuit components in the box was made of teflon to minimize the leakage current. For the same purpose the electric adaptor to the heli-tran cold finger, on which the sample was kept, was insulated by a ceramic of the highest quality. The wire leads were insulated by teflon and electrically shielded. A resistor, $R$, ten times greater in value than the sampling resistor $R_s$ was in series with $R_s$ to suppress the pick up noise. The resistance of the sample was calculated by the relation

$$R_{sample} = \frac{V_{ap}}{I} = \frac{V - V_s}{V_s} R_s - R,$$

where $V_{ap}$ is the voltage across the sample, $I$ the current flowing through the sample, $V$ the total voltage across $R_{sample}$, $R_s$, and $R$. $V$ was adjusted to keep $V_{ap}$ constant in the measurements. The apparent resistivity of the
Figure 4.2: Block diagram of the apparatus for measuring D.C. resistivity, $I - V$ and $I - t$ characteristics and thermopower measurements.
sample was then calculated by
\[ \rho = \frac{R_{\text{sample}} W d}{L}, \] (4.2)

where \( d, W, L \) were the thickness of the sample, the length and the width of the conduction channel respectively. The value of \( \rho \) obtained in this way may need to be corrected by a geometric factor because of the non-uniform distribution of the current in the thin film when the gap type electrodes are applied. Nevertheless, it does serve the purpose since the relevant points in this work are the variations of the resistivity and of the activation energy of the resistivity with temperature, applied voltage and the degree of compensation of the acceptors.

The second method to measure the resistivity is more convenient. \( R_{\text{sample}} \) was measured by a K-617 multiple meter in the \( V/I \) mode in which \( V_{ap} \) was automatically kept constant. But the upper limit of the output voltage was only 100 V.

The sample was kept in vacuum on a heli-tran cold finger (APD model LT-3-110). The sample was tightly held by two teflon clamps to the holder which was screwed to the cold finger. A thin layer of the thermo-conducting grease was applied to the back surface of the sample to insure good thermal contact.

A GaAs diode was used to sense the temperature of the holder. Temperature was varied by varying the flux of the liquid helium in the cold finger and by heating the cold finger or the holder by electric current. Two heaters were available to provide the possibility of fast heating.

A hard glass window on the heli-tran allowed for the study of photo-
conductivity. A precaution was taken against the heating effect of light radiation on the sample. When the temperature of the holder was kept constant, a thermocouple across the surface of the bare sample and the holder monitored a maximum of $5 \, K$ rise in temperature with an illumination of 20 mw/cm$^2$ white light from a Bausch Halogen lamp.

It may be worth noting here that the resistivity and the activation energy of the highly resistive semiconductors were usually voltage dependent (see §3.1.2) and that a constant voltage was thus required in the measurements. Therefore, the four probe method, which uses a constant current source, was not appropriate in this sense, although it is usually used in the literature.

4.2.2 $I - V$ characteristic measurements.

In the range of voltage up to 100 V, the $I - V$ characteristics of the sample were measured using the K-617 meter in the $V/I$ mode with $V$ programed to scan. When the voltage range needed to be greater than 100 V, the apparatus arrangement was that shown in Fig. 4.2 with the following settings: $S_1$ on position 1, $S_3$, $S_4$, $S_5$ on and $S_2$ off. The maximum scan range was about 810 V. The rate of scan may be varied from less than 1 V/min. to greater than $10^3 \, V/sec.$ The sampling voltage $V_s$ (denoted as $Y$ in Fig. 4.2) as a measure of the current $I$ was subtracted from the source voltage (denoted as $X$ in Fig. 4.2) by an electronic subtractor to obtain the voltage $V_{op}$ (denoted as $X - Y$ in Fig. 4.2) across the sample. The temperature could be varied as in §4.2.1) when needed.
4.2.3 $I - t$ characteristic measurements.

The $I - t$ characteristic of the sample was measured by using the K-617 as an ammeter. The apparatus set-up is as shown in Fig. 4.2 with the settings: $S_1$ on position 1, $S_3$ on and $S_2, S_4, S_5$ off. The ramp generator could be adjusted to supply a ramp voltage which gave a constant voltage for a long time after the initial slow rise of the voltage. Different or varying temperatures and light of different colors and/or intensities could be applied as parameters in the measurements.

4.2.4 TSLCS measurements.

The TSLCS measurements were carried out using the circuit shown in Fig. 4.3. The variable capacitor was used to compensate for the stray capacitance in the circuit. The floating square wave voltage source was relevant for the capacitance compensation circuit. The signal voltage taken from the sampling resistor was transferred by a low gain (~10) amplifier to the limiter-amplifier for the purpose of having a good impedance match. The high amplitude leading edge of the signal was cut off by the limiter to allow for the correct operation of the double box car. This leading edge was originated from the residual stray capacitance and the pure geometrical component of the capacitance of the sample after having being compensated. The relevant part of the signal, produced by the thermally emitted current from the traps in the sample, was usually small and thus amplified by the amplifier. This resulting signal was compared on a dual trace oscilloscope with the original signal to make sure that the shape was not distorted during the limiting and
Figure 4.3: Block diagram of the apparatus for the TSLCS measurements.
amplifying process. The resulting signal was then fed to the double box car and the decay time constant was measured as a function of temperature.

4.2.5 Sign of thermopower measurements.

For measuring the sign of the thermopower, the conduction channel had to be in the shape of a straight line. The sample was mounted on a special sample holder with its conduction channel just above the gap between the two parts of the holder. One part of the holder was made of oxygen free copper and the other part was made of teflon. Those two parts were held together by three teflon posts and epoxy resin. Temperature differences were produced by cooling the copper part with liquid helium in the cold finger or by heating this copper block by two heaters, one of which was on the copper block and the other on the cold finger. The temperature difference, which could be as much as 100 K, was measured by a thermocouple. The temperature of the sample before the temperature difference was made was measured by the GaAs diode on the cold finger. The sample was kept in a vacuum of $10^{-6}$ r, and the thermopower was measured with a high impedance ($\geq 10^{14} \Omega$) K-617 electrometer in the V-mode.

In all measurements, data was recorded on an IBM PC-XT computer and/or on a H-P X-Y recorder.

4.2.6 Sample characterization and contact properties.

In growing magnetic bubble thin films, the Ca$^{2+}$ ion is chosen primarily to charge-compensate the tetravalent substitution ion Ge$^{4+}$ at the tetrahedral site. S. Geller$^{72}$ has shown that the Ca$^{2+}$ ion, having a radius almost twice
the size of the Fe$^{3+}$ ion, enters the dodecahedral site which is the largest one available in the YIG lattice. The charges of Ca$^{2+}$ ions are then compensated with the charges of Ge$^{4+}$ ions, singly and doubly positively charged oxygen vacancies (V$_0^-$ and V$_0^-$), and Fe$^{4+}$ ions which are preferentially located at the tetrahedral sites. The compensation gives rise to p-type conductivity when Ca$^{2+}$ ions are in excess of Ge$^{4+}$ ions or to n-type conductivity when Ge$^{4+}$ is in excess of Ca$^{2+}$. In Ca:YIG, Ca$^{2+}$ ions are compensated with V$_0^-$, V$_0^-$ and Fe$^{4+}$ ions to give rise to p-type conductivity. The nominally pure YIG contains Pb$^{2+}$, Pb$^{4+}$ ions as well as V$_0^-$, V$_0^-$ and has p-type conductivity. The samples studied in this work and their measured parameters are listed in Table 4.1.

The resistivities at room temperature and the activation energies in the temperature range from 300 K to 220 K were measured with a constant applied voltage in the ohmic range of the $I-V$ characteristic. The electrode pattern shown in Fig. 4.1 was used for each sample. The total length (denoted by $W$) of the conduction channel was 20 cm, the average width of the conduction channel (denoted by $L$) was in the range from 50 to 100 $\mu$m for various samples. The measured resistance of the conduction channel was denoted by $R_{\text{sample}}$, and the nominal resistivity of the sample was calculated by using eq. 4.2.

All the data in Table 4.1 were measured on fresh samples. When a sample aged, i.e., when the sample had experienced many cycles of chemical cleaning, thin metal film depositing, photolithographing, exposing in high vacuum for hundreds of hours at low and high temperatures (the local temperature in the sample may be as high as 2800 $^\circ$C due to self-heating), the
resistivity and the activation energy of the sample usually increased. This increase is probably the result of the reduction of the sample and roughing of the film surface, which causes bad electric contacts and may introduce more trap and/or recombination centers. However, when the samples (W5A and W7) had been annealed at temperatures from 453 K to 473 K for tens to hundred hours in order to de-excite the HCS, the resistivities of the samples increased by about one order of magnitude while the activation energies decreased by tens to hundreds of milli-electron volts. The reason is unknown. After the sample was aged in this way, it was hard to excite the HCS, especially when applying the light pumping method.

The experimental error was estimated to be less than 5% in the measurements on the sample in the NS in the temperature range from 300 K to 200 K and in the HCS at low temperatures down to 20 K. At temperatures below about 100 K, the error in the measurements on the samples in the NS was on the order of 100% when the samples had very high resistivity ($\geq 10^{13}\Omega\text{cm}$).

Au or In are recommended in the literature as the electrode materials which can make an ohmic contact to the n- or p-type YIG samples. The contact properties between Au or In and the samples used in this work were checked by measuring the $I-V$ characteristic of the electrodes-sample system at room temperature and low temperatures in the NS.

In the temperature range from 240 K to 300 K, the In contacts with the W samples have properties similar to those of the Au contacts. When the contacts are made to the fresh samples, the I-V characteristic curves show a S-shape in a range of electric fields of $10^4 V/cm$. The typical data is plotted
in Fig. 4.4 for W5A, and in Fig. 4.5 for W5B, where Au was applied as the electrode material.

If the $I - V$ curve is characterized by the relation $I \propto V^\alpha$, the value of $\alpha$ at low fields($< 10^2 V/cm$) is close to unity. It falls in the range 1.8 to 2.3 at intermediate fields($\sim 10^2 V/cm$), and approaches the range 1.3 to 1.4 at higher fields($10^3 \sim 10^4 V/cm$).

At temperatures below 240 $K$, the $I - V$ curves for the samples with electrodes of In show saturation. The $I - V$ curve at low fields($\mathcal{E} < 10^2 V/cm$) becomes convex, while it is concave around room temperature. With increasing electric fields($10^3 < \mathcal{E} < 10^4 V/cm$), the current tends to saturate. When the field is increased further($\mathcal{E} > 10^4 V/cm$), the current rises steeply. Typical data for W5A at 140 $K$ and W7A at 225 $K$ are plotted in Fig. 4.6. In the same figure an experimental $I - V$ curve and a theoretical $I - V$ curve based on eq. 2.4 and 2.5 for reverse biased Schottky contacts to silicon are also plotted for comparison. For ease of reading, these curves have been shifted up one order of magnitude. When the electrodes were made of Au, no saturation of the current was observed.

With aged samples, the $I - V$ characteristic, having Au electrodes, became simply ohmic at low electric fields($\mathcal{E} < 10^3 V/cm$) and quadratic at higher electric fields($\mathcal{E} \geq 10^3 V/cm$). Data for W5A at 120 $K$ and for W7 at 280 $K$ are plotted in Fig. 4.7, the lower curve has been moved up by one order of magnitude to have both curve in the same graph. Basically Au was chosen as the electrode material in this work for two reasons. One was its contact properties to the sample, the second was that the higher work function of Au reduced the probability of the emission of electrons between the electrodes.
Figure 4.4: $I - V$ characteristics for sample W5A at 300 $K$ (curve 1) and 290 $K$ (curve 2).
Figure 4.5: $I - V$ characteristic for sample W5B at 300 $K(x)$, 290 $K(\xi)$, 260 $K(\varpi)$, and 240 $K(\ddagger)$. 
Figure 4.6: $I - V$ characteristic for sample W5A at 140 $K(\bullet)$ and sample W7 at 225 $K(\dagger)$ with In electrodes. The experimental($\ddagger$) and theoretical (solid line) data resulting from a reverse biased Schottky junction in silicon are also plotted(Ref. 76).
Figure 4.7: $I - V$ characteristic for aged W samples at 280 $K(\ddagger)$ and at 120 $K(\ddagger)$. 
in high electric fields and high vacuum.

The $I - V$ characteristic of the W samples around room temperature may be explained using the double layer model described in §2.1 and §2.3.1. The fact that $\alpha$ approaches about 1.3 instead of unity when the curve has passed its quadratic regime may be due to the fact that the difference between the resistivities of the two layers is not significant.\textsuperscript{77,78} As the sample ages the reducing layer may nearly penetrate the entire depth of the thin film. This may be the main reason for the disappearance of the double layer effect when the sample is aged. There might also be other complicated reasons for the change of the $I - V$ characteristic as the sample aged, such as the introduction of recombination centers. However, it would not be relevant to discuss the details since the electric fields used in this work for observing the effects involved are basically greater than $10^3 \text{ V/cm}$.

The $I - V$ characteristics were also investigated on the samples 3CSS7, 2SL15 and 160021 with Au electrodes. The $I - V$ characteristics for 3CSS7 and 168021, at either room or low temperatures, follow the one layer space charge limited current law, i.e. ohmic at low fields and quadratic at higher fields. An S-shape for the $I - V$ curve was observed on the sample 2SL15 around room temperatures. This is explained in §2.1 by a double layer effect with the surface layer consisting of contamination from foreign ions and mechanical defects. No saturation effects of the currents were observed in any of the three samples. No investigation of the $I - V$ characteristic was made on the nominally pure YIG sample because of its high resistivity at all temperatures.

In conclusion, for the $I - V$ characteristics of all the samples measured,
contacts of Au or In to the samples are ohmic around room temperature and at low temperatures when the electrodes are made of Au. It is observed that Au (also In in some temperature range) is ohmic to both the n and p type YIG. The possible reason for this phenomenon was explained in §2.2.5.
CHAPTER V

Results and discussion

In a research on the electrical properties of materials, the general information such as the conduction type and the contact properties should be confirmed first and these have already been given in chapter IV. In chapter V, emphasis will be put on the experimental results that particularly fit our proposed model for the unusual phenomena observed in this work.

5.1 The optical data on the energy band model

The absorption spectrum of the samples and the photo-conductivity, measured in this work, can be used to support the proposed band model. The absorption spectrum of sample W5B is plotted in Fig. 5.1 together with that of a nominally pure YIG measured in this work as well as that cited from Ref. 79. The nominally pure YIG is the base material from which the doped samples used in this work are made when appropriate dopants are utilized. It can be seen that the “absorption edge” of the curve measured on pure YIG in this work is in coincidence with the cited one, while the curve “edge” of W5B is shifted toward the lower energy end by about 0.3 eV. Notice the same location of the peaks at about 2.08 eV for all the three spectra. This peak is assigned in Ref. 78 as the transition of electrons between the localized
Figure 5.1: Optical absorption spectra for a: CaGe:YIG, b: pure YIG(measured), and c: pure YIG(cited from Ref. 79).
$3d$ levels in the crystal fields. In this reference it is also pointed out that the oscillation strength of this crystal field transition is much lower than that of the band charge transfer transition. Also notice that the relative changes of the absorption coefficients between the $2.08 \text{ eV}$ peak and the “edge” for the W5B curve ($\sim 0.7$) is close to that measured in YIG ($\sim 1.0$). This may indicate that the shift of the spectrum is due to the formation of band tails rather than the further splitting of the localized $3d$ levels in the distorted crystal fields caused by the impurity ions. Further, according to Ref. 78 the charge transfer photoconduction occurs at the energy above $2.8 \text{ eV}$, but in the W samples, up to one order in magnitude increase of the photo-conductivity induced by red light ($1.9 \text{ eV}$) is observed at low temperatures. This charge transfer effect cannot come from the transitions among the localized $3d$ levels at all. It is thus assumed that the high concentration of the impurities in the W samples introduces band tails which result in the narrowing of the band gap.

5.2 Data on the electrical properties of the sample in the NS

The model proposed in this work has a few predictions on the electrical properties of the sample in the NS. They are the different values of the activation energy for the conductivity of the sample in the high and low temperature ranges, the voltage dependence of this activation energy, and the hole trap effect which results in the transient current spectroscopy. These predictions have been confirmed by the data collected and analyzed in this
section.

As already described, the activation energy for the conductivity of the W samples is about 0.4 eV (see §4.3) and that the characteristic temperature $T_c$ for the distribution of the density of states of the valence band tail is about 1400 - 1800 K (see §3.1.1), the conditions for the application of the formula developed in chapter III to the analyses of the experimental data, $E_f \gg kT$ and $T_c \gg T$, are justified for the temperature range ($T \leq 300$ K) involved in this work.

5.2.1 The activation energy for conductivity as a function of temperature and applied voltage.

The activation energy for conductivity was measured by taking the slope of the plot $\ln \sigma$ vs. $1/kT$. Typical results observed on sample W5A with various applied voltages are plotted in Fig. 5.2. The plots show different activation energies for the conductivity at temperatures above 200 K and at temperatures below 100 K. The activation energy in the higher temperature range is about 0.38 eV when the applied voltage is 200 V. As the temperature range is lowered the activation energy approaches about 20 meV for all of the applied voltages. The data at temperatures below 100 K was fit to eq. 3.21, eq. 3.22 and eq. 3.23. The best fit was found to be with eq. 3.21, i.e. the hopping of holes among the nearest available sites. This result fits to the model described in §3.1.2 and §3.1.3: in the higher temperature range, the conduction is due to the holes in the valence band with the activation energy being the difference between the Fermi level and the valence band mobility edge plus the activation energy of the band hole mobility; while in the lower
Figure 5.2: ln σ vs. 1000/T with \( V_{ap} = 0.061(x), 10(\star), 50(\alpha), 100(\dagger), 200(\bullet) \)

\( V \) for sample W5A.
temperature range, holes are frozen in the tail of the valence band and the conduction is due to hopping of holes at the Fermi level with the activation energy being the activation energy for the hopping mobility. The activation energy for the hopping conduction approaches approximately the same value because all of the electric fields applied are too small (< 2.5x10^4 V/cm) to influence the short range potential barriers to the hole hopping process.

The conductivity as a function of temperature was also observed on other samples. A typical result from sample 2SL15 is plotted in Fig. 5.3. A noticeable feature of this plot is that the “turning temperature”, at which the extrapolation of the band conduction curve intersects the extrapolation of the hopping conduction curve, is lower than that for the W samples by about 40 K, while the activation energy of the band conduction for 2SL15 is lower than that for the W samples by about 80 meV. These features support the assumed model of conduction at least qualitatively since carriers will be frozen in the impurity band at lower temperature when the Fermi level is closer to the band edges. As a further comparison, the conduction of n-type Ge transfers from band conduction to hopping of electrons in the impurity band at about 7 K when the ionization energy of the donor is 10 meV.\(^{80}\)

The activation energy for the band conduction was observed to decrease with increasing applied voltage as listed in Table 5.1 for the sample W5A and W5B. The differences between the activation energies with the 10 V applied and with 200 V applied are 0.129 eV and 0.125 eV for W5A and W5B respectively. If eq. 3.15 in §3.1.2 is used to calculate the difference
Figure 5.3: $\ln \sigma$ vs. $1000/T$ for 2SL15 with 10 V applied.
of the Fermi level at two different applied voltages, the lowering of the activation energy should only be about 0.068 eV when an average temperature of 260 K is used for the temperature range thermally scanned. The remainder of the measured change of the activation energy is thus attributed to the change in the activation energy of the mobility, which is considered in our model (§3.1.2) as the lowering of the long range potential fluctuation (PF) barrier by the applied electric field. According to eq. 3.19, the plots of $E_a + kT \ln V$ vs. $V$ should be straight lines as shown are in Fig. 5.4 for W5A and W5B. The first data points at 0.061 V do not fall on the straight lines followed approximately by the other data points. This is consistent with the
explanation in §4.3 that in an electric field of less than $10^2 \ V/cm$ only the properties of the thin layer immediately under the electrodes is measured.

The slopes of the plots give the dimensions of the PF as $233 \ A$ for W5A and $215 \ A$ for W5B, which are in the range given in the literature.$^{25}$

Adopting the value for the lowering of the Fermi level as that computed above and supported by the expected straight lines in Fig. 5.4, the characteristic temperature $T'_c$ should be around 260 K if a continuous distribution of the hole trap levels are assumed. This $T'_c$ is much smaller than the $T_c$ for the distribution of the energy levels in the acceptor band tail. The compensated acceptor levels may act as the hole trap levels, while no information is available to assume another origin of the hole trap levels. We therefore tend to assume that the compensated acceptors are the origin of the hole traps. Among these trap levels, only those within $kT$ of the Fermi level are active.

In the above treatment a single trap level model has been applied to these levels. This may not be a bad approximation since the Fermi level can move only in a narrow range when the applied voltage is not high, due to the large value of $T_c$ (see §3.1.1).

5.2.2 The TSLCS measurements for the hole trap effects in the NS.

The TSLCS results confirm the hole trap effects in the NS predicted by our model (see §3.1.2). As pointed out in Ref. 81 the transient current may be approximated as being exponential in time just after the very initial stage of the transient process even though multiple trap levels are present. The emission rate $e_t$ was measured according to eq. 2.46 at various temperatures
Figure 5.4: $E_a + kT \ln V$ vs. $V$ at $T = 260$ K. The symbols + and □ are for the samples W5A and W5B respectively.
and plotted against $1/kT$ according to eq. 2.47 or eq. 2.48 in Fig. 5.5(W5A) and Fig. 5.6(W7) to find the position of the trap levels. In the time domain of the double box car from 1 microsecond to 100 milliseconds, and in the temperature range from 300 $K$ to 220 $K$, only one hole trap level about 0.36 eV above the valence band mobility edge was observed in the W samples. At lower temperatures down to 170 $K$, the effect of this trap level was observed by taking an oscillogram of the transient current. As discussed in §5.1.2, the trap levels are identified as the compensated acceptor levels within $kT$ of the Fermi level. Equations 2.47 and 2.48 then have the same meaning. These trap levels were found for all the W samples to be located between 0.35 and 0.37 eV above the valence band mobility edge. Square wave voltages of different amplitudes ($E: 10^2 \sim 10^3 V/cm$) were used but no correlation between the voltage and the position of the trap levels has been observed. Within the error of $kT (\sim 26 meV$ at 300 $K$), the Fermi level may be identified as being 0.36 eV above the valence band mobility edge. The activation energy of the hole mobility may then be estimated as about 40 $meV$ for the fresh W samples, which is consistent with the estimation made in Ref. 39.

The concentration of the trapped holes may be estimated using eq. 2.51. The accuracy of the estimation depends on the accuracy in the determination of the volume in which holes are trapped. Unfortunately, in the case of gap-type electrodes on thin film samples the analysis is very difficult and there is no theoretical result available. As a very rough estimation the volume of the conduction channel is used. This may give a lower limit for the density of the trapped holes. The density of the trapped holes is obtained by dividing the concentration by $kT$. The typical values are in the range from $10^{14}/cm^3eV$ to
Figure 5.5: $\ln \varepsilon_t$ vs. $1/kT$ for W5A. Different symbols are for different square wave voltages: \(\square -11\,\text{V}, \star -22\,\text{V}, \triangledown -88\,\text{V}, \bullet -110\,\text{V}, \) and \(\times 2\,\text{V}\) respectively.
Figure 5.6: \( \ln \varepsilon_t \) vs. \( 1/kT \) for W7. Different symbols are for different square wave voltages: □ — 11V, ♦ — 50V, and × 1V respectively.
10^{10}/cm^3 eV depending on the amplitude of the square wave voltage applied.

5.3 Data on the electrical properties of the sample in the HCS

Several features of the excitation and de-excitation processes of the HCS and of the electrical properties of the sample in the HCS are predicted by our model in §3.2. Various data concerned in those processes are collected in this section and analyzed to confirm the predictions.

5.3.1 The excitation process of the high conduction state (HCS).

There are two ways to induce the HCS in experiments: transfer electrons from the valence band tail to the repulsive electron trap levels by light with the assistance of electric field or by double injection. Our model predicts a slow process of the excitation of the HCS when the HCS is induced by the first method. The second method manifests itself with its fast and critical nature.

1. The excitation process of the HCS by light with the assistance of the electric field.

Two ways of inducing the HCS are available: the excitation of the HCS by light at an intermediately strong electric field (≤ 6x10^4 V/cm) while cooling the sample from room temperature to low temperatures and the excitation of the HCS by light at an intermediately strong electric field and at a constant low temperature. In both cases, the excitation of the HCS is a slow process which develops in tens of minutes or even in hours. The excitation of the
HCS in these two ways has been observed in all of the W samples. However, only the details of the excitation process at constant temperature has been studied in sample W5B and will be discussed first. The samples W5A and W7 had been used many times and became aged in the previous study of the magnetic property project and in the development of the present work in which the HCS effect was found as well as the relevant apparatus were built up or purchased accordingly.

The basic parameter characterizing the excitation process of the HCS should be the variation of the conductivity of the sample as a function of the variables such as the temperature, the time, the electric field, the frequency and the intensity of the light. In experiments, only one parameter is changed in one time to observe the corresponding variation of the conductivity. Although conductivity data for all of the changing parameters are available, only those most directly related to our proposed model are discussed below for the sake of saving the pages of this thesis.

First, a typical variation of the conductivity of sample W5B with time is described. The temperature was decreased from 300 K to 140 K at a rate of about 2 K/min. in the dark with an applied electric field of 1.00x10^4 V/cm. Then the temperature was kept at 140 K. At this time red light (wave length ~ 640 nm) of intensity of 8 mw/cm^2 was switched on. The electric field was increased from 1.00x10^4 V/cm at a rate of about 1.73x10^3 V/cm/min. to an intermediate large value of 5.20x10^4 V/cm to meet the requirement on the intensity of the electric field, and to avoid the possible self-heating effect which might occur if the electric field was increased rapidly. Then the electric field was kept constant. The observed data of the conductivity as a function
of the time is shown in Fig. 5.7 by a semi-logarithmic plot. As can be seen, the HCS starts to develop rapidly at a time of about 7.5 hours but continues to increase for another several hours. The conductivity in the HCS is about 5 orders of magnitude higher than that in the NS. The initial rise of the conductivity has an exponential behavior with the time, the slower, long term increases the rate of the conductivity has a linear dependence on time and later approaches a square root dependence on time. This behavior is expected from the solution of eqs. 3.46 and 3.48. Details of the slower, long term increase in the conductivity during the excitation of the HCS is shown in Fig. 5.8. For this figure a portion of the data from Fig. 5.7 is plotted on a log-log scale. Note that the data points in Fig. 5.7 and 5.8 were taken at one minute intervals.

The time at which the excitation of the HCS starts varies from run to run but it is on the order of an hour. Generally, the time elapsed before the starting of the excitation process is less when the rate of increasing the electric field is larger. A rapidly increasing electric field results in a higher local temperature in the sample because of self-heating. This reduces the probability of the hole traps capturing the injected holes near the anode and thus leads to a more uniform distribution of holes and a larger electric field inside the sample. As pointed out in our model (see §3.2.3 2), the trapping of the holes near the anode is in competition with the excitation of the electrons from the valence band tail to the electronic repulsive traps inside the sample. This space charge trapping effect near the anode should result in a charging of the interface near the anode. On the other hand, the model predicts no charging of the sample in the excitation process of the HCS since no extra
Figure 5.7: \( \log \sigma \) vs. \( t \) for sample W5B at 140 K with red light of intensity 8 mw/cm\(^2\); the electric field is increased from \( 8.4 \times 10^3 \) to \( 5.2 \times 10^4 \) V/cm within 30 minutes and then kept constant.
Figure 5.8: The slow evolution of the conductivity following the initial rapid rise during the excitation process shown in Fig. 5.7. The slope 1 and 0.5 are predicted by eqs. 3.45 and 3.47.
charge has been injected into the sample in this process. This difference has been confirmed by the experimental measurements: the sample in the highly excited HCS is neutral with its $I - V$ curve symmetrical for the positive and the negative voltages, while the sample in the weakly excited HCS or in the NS with space charge trapped near the electrodes is charged and its $I - V$ curve is unsymmetrical for the positive and the negative voltages. The typical data on W5B are shown in Fig. 5.9 and Fig. 5.10, where the absolute values of the voltages are used for the log-log plots. In Fig. 5.10, the sample was charged and had a residual voltage $+63 \, V$. In addition, the sample with space charges trapped near the anode has been observed to discharge at some higher temperature and become neutral. This is shown in Fig. 5.11.

The effect of trapping space charges near the electrodes is unavoidable in the process of decreasing temperature with an electric field applied to measure the change of the conductivity in the dark for a long time period (usually 2 to 3 hours). When the light removes electrons from the occupied acceptor levels and these electrons are trapped by the repulsive electronic traps on their way to the anode in the electric field, the distribution of the electric charges inside the sample will be neutralized. This will enhance the electric field inside the sample and this in turn enhances the trapping of the electrons by the repulsive electronic traps. When this process becomes significant, the excitation of the HCS is initiated.

The process of exciting the HCS while cooling the sample from room temperature to low temperature has been examined for all of the W samples. A typical result from W5B is shown in Fig. 5.12. In this figure, the variation of the conductivity of the sample in the NS at low temperatures was not
Figure 5.9: The log-log plot of the $I - V$ characteristic for W5B in the HCS to show that the sample is not charged: The $I - V$ curves are the same for the positive and negative applied voltages.
Figure 5.10: The log-log plot of the $I-V$ characteristic for W5B in the NS to show that the sample is charged due to trapped holes near the anode: The $I-V$ curves are different for the positive(a) and negative(b) applied voltages.
Figure 5.11: The discharge of W5B in the NS as a function of temperature. The resistance of the sample was measured with an applied voltage of +10 V; the negative value of the measured resistance is due to the residual voltage developed by the interface charging of the sample.
Figure 5.12: The excitation of the HCS while cooling sample W5B in the presence of blue light of intensity 11 mw/cm². The arrow indicates the direction of the change of temperature.
well determined due to limited resolution of the recorder available at that time. Nevertheless, the data shows that the excitation of the HCS is a slow process (the rate of decreasing temperature is about 2 K/min.) and starts at a temperature higher than 140 K. It is believed that the electronic repulsive trap levels having a higher barrier is involved. As a matter of fact, the sample excited in this case can be annealed back into the NS only when the temperature is increased to about 400 K which is much higher than the temperature needed to anneal the sample excited at 140 K. However, the difference of the conductivity between the HCS and the NS is about the same as that obtained in the excitation process at 140 K (about four to five orders of magnitude). This is consistent with the inference of our model of a partially compensated band tail: only a certain number of electrons in the valence band tail are available to be removed and trapped no matter where they will be trapped, and the Fermi level is lowered to the same location if the same number of electrons are removed from the valence band tail no matter what method is used to remove these electrons and to trap them.

The electric field has an essential influence on the excitation of the HCS. The dependence of the rate of exciting the HCS on the electric field has been examined on sample W5B with other parameters kept constant. Typical data is shown in Fig. 5.13. As can be seen, the rate of exciting the HCS is reduced more than ten fold when the electric field is reduced by about a factor of two. Light of the same intensity and frequency has been used to illuminate all the W samples kept at 140 K for tens of hours without an electric field applied, and the conductivity has been observed to be the same before turning on and after turning off the light. When an electric
Figure 5.13: The dependence of the excitation rate on the electric field for sample W5B at 140 K with red light of intensity 8 mw/cm². The electric fields, in units of V/cm, are indicated at the curves.
field of the order of $10^4 \text{ V/cm}$ was applied with the light shining for tens of hours, a residual increase in the conductivity up to 100% was observed after turning off the light, although a photoconductivity ten times higher than the dark conductivity was observed. When the electric field is reduced to the order of $10^3 \text{ V/cm}$ no residual increase of the conductivity was observed after switching off the light. These experimental facts indicate that the electric field is a necessary condition for the excitation of the HCS. In combination with the low temperature (relative to the sintering temperature of YIG, $\sim 1400\text{ K}$) process of de-excitation of the sample from the HCS to the NS (which suggests a physical mechanism), the repulsive electronic trap levels due to the oxygen vacancies are assumed to explain the electric field dependence of the excitation of the HCS. The details of this assumption has been discussed in §3.2.1.

2. The excitation of the HCS by the double injection process.

The HCS has been induced by the double injection process in all of the samples listed in table 4.1 except for the Ge doped YIG. The emphasis here will again be put on the W samples. The results on other samples will be described briefly to give a proper basis for comparison. As will be clear through the arguments in the following texts our model is applicable as well in the HCS effects induced by the double injection process in which electrons are drawn from the compensated valence band tail and transferred through cathode to the conduction band and then trapped in the repulsive electron traps. The relaxation-type current oscillation before the excitation of the HCS can also be explained by the proposed model.

The double injection process is more easily realized when light of the
appropriate intensity is illuminated on the sample and higher temperatures are used. At lower temperatures, e.g. below 140 $K$, or in the dark, the HCS can also be realized by rapidly increasing the electric field to a high intensity, e.g. applying a high step voltage. The lowest temperature at which the excitation of the HCS has been tried was 30 $K$. In these cases, serious electrical-thermal etchings on the electrodes were observed as shown by the electronic-micrograph in Fig. 5.14. In the figure, a region of what may be a somewhat reduced area in the sample is noted. It may be due to the formation of a current filament of 30 microns average diameter when the sample was transformed to the negative resistance state by the high electric field(see §2.3.3 2, also see the theoretical paper by Ridely). This "shadow" may also remind people of "smoke" on the surface of the sample due to arcing between the electrodes. In a vacuum of $10^{-4}$ $τ$, the critical electric field for arcing is $5 \times 10^5$ $V/cm$ at a gap distance between the electrodes of 100 $\mu$m. In our case, the electric field used is of the order of $5 \times 10^4$ $V/cm$ while the vacuum is of the order of $10^{-6}$ $τ$ and the gap is 100 $\mu$m. In the worst case assuming the presence of arcing, the heating effect from the arc will have the same influence on the sample as that given by the current filaments described below.

If the current filaments are generated in the material, the temperature is estimated to be as high as 3000 $K$. This is estimated from the fact that the electrodes have been etched due to the evaporation of the gold. This high temperature certainly reduces YIG in a vacuum. Good repeatability is not expected in these processes. Further, the high temperature may induce intrinsic carriers in both bands. Among those carriers, trapping of electrons in
Figure 5.14: Electrical-thermal etchings on the electrode. a. magnification: 8000; b. magnification: 147.
the repulsive traps results in the HCS. This leads to confusion with the double injection effect. The measurements of the photo response of the current in the NS show that the ratio of the conductivity between the light and the dark is almost temperature independent at low temperatures. This indicates that it is hard at low temperatures to reach the current needed to initiate the negative resistance region in the double injection process without very rapid increase of the electric field. The double injection process inducing the HCS has therefore been studied in detail on the W samples at 140 $K$ with intense light and a reasonable rate of increasing the electric field.

The experiments to deal with the $I - V$ characteristic in the excitation process were carried out in two steps according to the apparatus available at the moment. First, an electronic subtractor was used to make it possible to use a x-y recorder to record simultaneously the voltage across the sample and the voltage across the sampling resistor, which is in proportion to the current through the sample. A typical result for sample W5A is shown in Fig. 5.15, where white light of 12 mw/cm$^2$ was applied and the rate of scanning the electric field was $1.87 \times 10^4$ V/cm/min. In this figure the information at low electric field was lost due to the low resolution of the subtractor and the recorder. Second, a high resolution ammeter was used to measure the current, the subtractor was used to measure the voltage across the sample, and data were recorded by a computer. A typical result is shown in Fig. 5.16, where white light of 16 mw/cm$^2$ was applied and the rate of scanning the electric field was reduced to $1.68 \times 10^2$ V/cm/min. to avoid the influence of the free space charge current on the current measurements. As can be seen in Fig. 5.16 and 5.15, the $I - V$ curve consists of an ohmic, a
Figure 5.15: $I - V$ curve for the double injection process for W5A.
Figure 5.16: $I - V$ curve in the double injection process in the low electric field range. White light of intensity 16 mw/cm² was incident on the sample.
quadratic, and a negative resistance regions as expected by the analysis in §2.3.3 3 for the double injection process. In the negative resistance region, the “working point” of the sample ran back and forth along the load line which was determined by a load resistor in series with the sample. At some point on this line a further instability occurred and the sample “jumped” into the HCS. Afterwards the sample became “quiet” with its resistance becoming positive. In the negative resistance region, the process of trapping the electrons available in the conduction band into the repulsive electronic traps may compete with the process of the recombination of these electrons with the holes in the emptied valence band tail and in the valence band. This competition may lead to further instability, but the details are not clear. Nevertheless, the final HCS of the sample has been confirmed to be due to the same band structure which is used to explain the HCS induced by “light pumping” with a medium electric field by the following measurements. First, the ratio of the conductivity between the HCS and the NS is also about 5 orders of magnitude. Second, one of the electronic trap levels was identified by a thermal annealing method to be the same as the one responsible for the HCS induced by the “light pumping” process in the same temperature range. The details of measuring the “positions” of the electronic trap levels will be discussed in §5.4.1.

A noticeable feature of the $I - V$ curve in the quadratic region, the irregular current oscillation, was usually observed and is discussed briefly here. The frequency of this oscillation was measured on the oscilloscope to be in the range from hundreds to thousands of Hz. This is at least 3 orders of magnitude lower than the frequency of the Gunn oscillation $^8$ and of the
piezoelectric oscillation which is possible in the magnetic garnet which has no center symmetry. This current oscillation is then considered to be due to the impact ionization of the holes from the valence band tail to the valence band and due to the self-heating effect of this ionized hole current as described in §3.2.4. Using reasonable values of the parameters for these materials, eq. 3.58 and eq. 3.59 are satisfied. Eq. 3.57 is then used to estimate the critical electric field. The following parameters are used: the velocity of sound in YIG at room temperature is $7.17 \times 10^5$ cm/sec, and the ionization energy, 0.3 eV, of the holes at the Fermi level (considering the lowering of the Fermi level by the applied voltage - see §3.1.2 and §5.1.2), and the electron mass equal to that of the free electron, and the temperature 140 K. No value of the hole mobility at 140 K is available. However, adopting the large polaron model, the mobility of the hole in the valence band varies slowly with temperature and has a theoretical value $\geq 0.7$ cm$^2$/secV at room temperature. At a temperature of 140 K, the coexistence of the holes in the valence band and in the valence band tail can be seen by inspecting the ln$\sigma$ vs. 1000/T curve (see Fig. 5.1). Substituting the parameters discussed above into eq. 3.57 and letting $\gamma$ be unity, the critical electric field for the impact ionization of the hole can be estimated as $5 \times 10^6$ V/cm which is about one order of magnitude higher than the average value observed in the experiments. The Young's modulus of YIG varies about 10% from 300 K to 100 K, so the approximate use of the room temperature value of the sound velocity in YIG would thus be justified. Considering the sharp (especially also the curved) edge effect of the electrodes on enhancing the local electric field and the effect of the light, which may raise the kinetic energy of holes, the real local electric field in the
sample would meet this calculated value. The light was found to reduce the critical field for the appearance of the negative resistance by a factor about 2 in a pulsed $I - V$ measurement. The sharp edge effect of the electrodes have been analyzed by simply assuming the planar circle rim of the electrodes. The coefficient of enhancement of the electric field is about 2 to 3 depending on the approximate radius of the curved portion of the electrodes. Owing to the complexity of the real electrodes, no exact analysis has been tried. The self-heating of the current enhances the current itself but lowers the voltage across the sample due to the presence of the load resistor and thus may stop the ionization process. This mechanism may give the current oscillations their low frequency and relaxation features.

Considering that the double injection process may induce the same HCS as induced by the "light pumping" process and that this process needs much less time in the experiments, the excitation of the HCS was examined on other samples by the double injection process for the purpose of comparison when discussing the mechanism. The conditions in the experiments are as follow: $T=140 \text{ K}$, white light of intensity $32 \text{ mw/cm}^2$, the electric field increased in abrupt steps from $10^4 \text{ V/cm}$ per step to $3\times10^6 \text{ V/cm}$ per step for different samples. The HCS was observed in Ca:YIG, Ge excess GeCa:YIG and in nominally pure YIG but not in Ge doped only YIG although a negative resistance was observed in this sample.
5.3.2 D.C. and transient electrical properties of the sample in the HCS.

As predicted by our model (see §3.2.2), the sample in the HCS should have a p-type conductivity with an activation energy much lower than that in the NS, the logarithm of the ratio of the resistivity between the NS and the HCS should be in proportion to the reciprocal temperature, and the TSLCS signal should disappear in the temperature range where the TSLCS signal measures the hole trap effects in the NS. These predictions have been confirmed by our experiments and will be discussed below.

1. The conduction type.

The sign of thermopower measured in the HCS show that all of the samples, except for the Ge excess GeCa:YIG, have a p-type conductivity. The thermopower of the Ge excess GeCa:YIG in the HCS was vanishingly small. A possible reason for this is the co-existence of filaments of the HCS imbedded in the NS background in this sample due to the excitation process of the HCS by the double injection method.

The sign of thermopower show that all of the W samples and the Ca:YIG sample have p-type conduction after they are thermally annealed back to the NS. The Ge excess GeCa:YIG sample has a n-type conduction after it is thermally annealed back to the NS, as it should be.

2. The disappearance of the hole trap effect in the HCS.

All the W samples in the HCS were checked at low temperatures and around room temperature (when possible) with the TSLCS technique and with the oscillogram to verify the disappearance of the hole trap effect. No
hole trap effect was found in the time scale in which this effect was significant in the NS. As an example, the photograph of the oscillogram of the current in the sample W5B, induced by a square wave voltage across the sample, in the NS and HCS is shown in Fig. 5.17. As can be seen, no transient current occurs when the sample is in the HCS. Indeed, even as the compensated acceptor levels at the Fermi level in the HCS work as the hole trap levels, the time constant of thermal emission of holes from these levels will be shorter than that in the NS because of the lowering of the Fermi level in the HCS towards the mobility edge of the valence band. The time constant predicted in the HCS will be 5 and 12 orders of magnitude shorter than that in the NS for the temperatures 300 $K$ and 140 $K$ respectively, due to the lowering of the Fermi level by 0.34 $eV$ from the NS to the HCS. The time constants of thermal emission of holes from the trap levels in the NS are in the order of 0.1 $msec.$ at 300 $K$ and 1 $sec.$ at 140 $K$ respectively. The corresponding time constants in the HCS are thus beyond the detection limits of the apparatus used in this work.

The TSLCS measurements were repeated on the W samples after they were thermally annealed back to the NS. The same hole trap level as that in the fresh W samples was found. Efforts have been made to check the TSLCS signal on W samples that were step wise annealed to see when the hole trap effect reappears in the process of lifting the location of the Fermi level. Unfortunately, in a few steps the Fermi level was not lifted sufficiently and in another step the Fermi level was lifted to its normal position in the NS. As this was a very time consuming experiment, it has not been re-tried. Nevertheless, the disappearance of the hole trap effect in the HCS confirms
Figure 5.17: The oscillogram of the current wave form for W5B in the NS(a) and in the HCS(b) at 170 K. The scales for both diagrams are: $X=20 \text{ ms/cm}; Y=5 \text{ mV/cm}$. The sample was in a HCS that was de-excited by thermal annealing at 373 K.
3. The conductivity and its activation energy of the sample in the HCS

The conductivity of the sample in the HCS was measured in the ohmic range of the $I - V$ curve to be 5 orders of magnitude higher than that of the sample in the NS at the same temperature. The activation energy of the conductivity in the HCS was measured by the slope of the plot $\ln \rho$ vs. $1000/T$ (the lower curve in Fig. 5.18, for sample W5B) to be about 20 $meV$ for all W samples. At this stage our model indicates that additional considerations than the new location of the Fermi level in the HCS are needed in explaining the measured 5 orders change of the conductivity. If the Fermi level in the NS is taken as 0.36 $eV$ above the mobility edge of the valence band (see §5.1.3), the Fermi level in the HCS has been lowered by about 0.34 $eV$ toward the valence band. If the mobility of the hole in the HCS is the same as in the NS and if the conductivity in the NS at 140 $K$ is mainly due to the conduction of holes in the valence band (this was verified by comparing the measured change of the conductivity between 300 $K$ and 140 $K$ in the NS with that calculated using 0.36 $eV$ as the activation energy, both are of 6 orders of magnitude), the conductivity should increase by 12 orders of magnitude when the sample is changed from the NS to the HCS in accordance with the change of the location of the Fermi level. However the measured change of the conductivity was up to 5 orders of magnitude. There may be two reasons to explain the huge discrepancy between the observed change of the conductivity and the change of the conductivity expected only by the change of the location of the Fermi level between the NS and the HCS.
Figure 5.18: \( \ln \rho \) vs. \( 1000/T \) for W5B in the NS(a) and in the HCS (b) respectively. The scatter in curve (a) at low temperatures is due to the limit of the apparatus.
First, the HCS may be excited in the layer whose depth may be on the magnitude of the absorption length of the light, for the red light the absorption length is about 1 micron evaluated from the measured absorption coefficient. If the conductivity is calculated in terms of the geometrical dimensions of the sample, an error of up to a factor of 10 may be introduced in the result as the thickness of the film is 10 micron. Further, the current filaments may also be formed even in the slow light pumping process by the following mechanism. The HCS may be initialized at some points next to the electrodes due to the high electric field there. Then the electric fields at these spots are reduced while the electric fields in front of these spots are enhanced. Thus the HCS may develop there and spreads into the sample in the form of filaments just like lightning in the air. This inhomogeneity would result in significant errors in the calculation of the conductivity in the HCS when a homogeneous change is assumed. But it is hard to estimate the order of the magnitude of the errors introduced in this case.

Second, the mobility of the holes in the HCS may be much smaller than that in the NS because of the reduction of the coupling constant of the electric polaron(hole). Both processes of removing electrons from the compensated acceptors and filling the positively charged oxygen vacancies with these electrons neutralize these electric charge centers. This makes the value of the static dielectric constant $\epsilon_s$ approach that of the high frequency dielectric constant $\epsilon_{\infty}$ since the static polarization is the sum for the polarization of the charged ions and the polarization of the electrons in the ions while the high frequency polarization is the polarization of the electrons in the ions only. According to eq. 3.26 this effect results in the reduction of the cou-
pling constant of the hole electric polaron which in turn, according to eq. 3.29 and eq. 3.28, reduces its mobility. As a very rough example, if the coupling constant $\eta$ is reduced from 5 to 1 (corresponding to moderately strong coupling and to weak coupling), the mobility will be reduced by 6 orders of magnitude. It is noticed here that although the two reasons described above seem reasonable qualitatively, the details of the mechanism for the variation of the pre-exponential factor of the conductivity in the excitation process of the HCS need more careful study.

A similar phenomenon was observed in the change of the conductivity induced by the light-created trap effect in the $\alpha$ Si:H, where the pre-exponential factor of the conductivity was found to be exponentially dependent on the activation energy of the conductivity. The reason for this is unclear. In fact, these kinds of phenomena have been found since 1938 and no satisfactory theoretical explanation has been achieved.

4. The ratio of the resistivity of the sample between the NS and the HCS.

The resistivity of the sample W5B in the NS, before an examination of the excitation of the HCS, was measured as a function of temperature with a voltage 10 V applied. The result is plotted together with the resistivity of the sample W5B in Fig. 5.18. The logarithm of the ratio of the resistivity of the sample between the NS and the HCS was plotted against $1000/T$ to confirm eq. 3.38 within the band conduction range of the sample in the NS. The typical data from W5B is shown in Fig. 5.19. As can be seen, the data lie on the straight line with a correlation coefficient 0.995.
Figure 5.19: Ln$\rho_{NS}/\rho_{HCS}$ vs. 1000/T for sample W5B.
In the Ca:YIG, Ge excess GeCa:YIG and nominally pure YIG samples, although the HCS were realized by the double injection process no comparison could be made between the resistivities in the NS and in the HCS because the resistivity in the NS at low temperature was too high to be measured accurately.

5.4 The de-excitation process of the HCS and the positions of the repulsive electron trap levels

Our model predicts that the trapped electrons can be thermally released at a temperature higher than the temperature at which they were trapped in the excitation process of the HCS. The sample “de-excited” in this way will return to the NS and have its original activation energy for the conductivity. When the sample is in a partially de-excited state, its activation energy for the conductivity should be greater than that in the HCS but smaller than that in the NS. All of these predictions have been confirmed by experiments and will be discussed below. In addition, the repulsive electron trap level can be determined from the de-excitation measurements. The results are collected and compared with the optical levels of the oxygen vacancies cited from literature.

5.4.1 The de-excitation process and the position of the electron trap levels.

A few methods such as ultraviolet quenching, infrared quenching and thermal annealing have been tried to de-excite the sample from the HCS back to
the NS. Only thermal annealing has been found to be effective in de-exciting the HCS. It is not understood why the optical techniques give a negative result. As described in §3.2.5, there are two ways to measure the positions of the repulsive electronic trap levels, represented by eq. 3.66 and eq. 3.69 respectively. In practice, the former equation was used for all the measurements with only one of the results checked by using the latter equation, in consideration of the extremely time consuming nature of the latter method.

In the following discussion, emphasis is put on the de-excitation process of the W samples while the corresponding results are also given for other samples for comparison.

The de-excitation processes of the W samples are similar in spite of the methods by which the samples were excited into the HCS. The conductivity of the sample starts to decrease when the temperature of the sample increases to some critical value. The conductivity continues to decrease with increasing temperature until all the electrons have been completely emptied from the repulsive traps at which point the conductivity reaches its original value in the NS. A typical result of the de-excitation process on W5B excited by the "light pumping" process is shown in Fig. 5.20 (also see the lower curve in Fig. 5.18). The plot of the ln of the change in the conductivity, |Δσ|, vs. 1000/T is shown in Fig. 5.21. In the region of decreasing conductivity with increase of temperature, applying eq. 3.66 gives the electronic trap level about 0.35 eV "below" the mobility edge of the conduction band. The measured "location" of the electronic trap level is indeed the summation of the real location of the level and the height of the potential barrier surrounding the trap (see §3.2.3). It is simply impossible to distinguish them in this work. This 0.35
Figure 5.20: The natural log of the conductivity during the de-excitation of the HCS (curve b) with increasing temperature for W5B. Curve a is the measurement for the NS.
Figure 5.21: $\ln |\Delta \sigma|$ vs. $1000/T$ for sample W5B.
$eV$ electronic trap level has been found in all the W samples when excited at $T \leq 140$ K either by "light pumping" or by double injection.

The method described above to measure the electronic trap levels was checked by applying eq. 3.69 to measure the de-excitation of the sample W5B which had been excited into the HCS by the "light pumping" process at 140 K. Two values of the rate of increasing the temperature, 2 K/min. and 10 K/min., were chosen in the two de-excitation processes of the sample. Two values of the temperature, 172 K and 160 K, at which the de-excitation process initializes were obtained. Substituting these parameters into eq. 3.69 gives the location of the involved electronic trap level as 0.32 eV "below" the mobility edge of the conduction band. This result is consistent with that obtained using the former method.

Multiple electronic trap levels were observed when the sample was excited by double injection at 30 K-40 K. A typical $\sigma$ vs. $T$ curve of the multiple de-excitation is shown in Fig. 5.22 for sample W5A. From this curve two electronic trap levels about 20 mev and 0.2 ev below the mobility edge of the conduction band are found. On the other hand, when the sample was excited at temperatures higher than 140 K either by double injection or by "light pumping" while cooling, an electronic trap level about 0.55 ev "below" the mobility edge of the conduction band was observed in sample W5A. This is not surprising if one considers the repulsive nature of the electron traps. These traps have exponentially small capture cross-sections with decreasing temperature (see eq. 3.31 or eq. 3.32) and their activation energy for releasing electrons are not simply the difference between the conduction band mobility edge and the trap levels. Further, when the sample was excited by double
Figure 5.22: The natural log of the conductivity during the de-excitation of multiple electronic trap levels in sample W5A. a) and b) denote the two regions for which the conductivity decreases with increasing temperature.
injection either at higher or lower temperatures, the "deeper" electronic trap levels were involved if a large current in the excitation process was used to produce a high local temperature. This high local temperature made the shallower trap levels ineffective but the "deeper" trap levels effective in trapping the electrons removed from the compensated acceptors. It was found in this case that samples needed to be annealed at 373 K to 400 K for hours to de-excite them to the NS. Sometimes samples have to be annealed at 450 K to 470 K for tens of hours to restore the NS. However, during these high temperature long time annealing processes the sample was kept in the air which is a reducing environment. This was one way in which the samples became aged. In order to prevent the sample from reduction, a SiO\textsubscript{2} layer was sputtered onto the sample. Unfortunately, samples W7 and W5A were badly reduced during the high temperature annealing as indicated by their decrease in color. This probably occurs with the formation of SiO\textsubscript{2} which might occur in the sputtering process. No detailed measurements of the location of the electronic trap levels could be made in the high temperature annealing processes due to the limitation of the apparatus. Considering that release of the electrons from the 0.35 eV trap level starts at about 170 K, the electronic trap levels which release electrons at around 400 K may be estimated to be 0.8 eV "below" the mobility edge of the conduction band.

In other samples, electron trap levels ("below" the conduction band edge) 0.2 eV (in nominal pure YIG), 0.31 eV and 0.34 eV (in Ca:YIG) were found. In addition, there were electron trap levels which could be emptied only at temperatures 400 K or higher in both the samples. These electron trap levels are considered to have the same origin, i.e. oxygen vacancies, as that for the
electron trap levels in the W samples.

The electronic trap levels (the oxygen vacancy levels) involved in this work are consistent with the optically measured values of the oxygen vacancy levels in YIG, as shown in Fig. 5.23, in considering that the optical transitions simply measure the differences between the oxygen vacancy levels and the conduction band edge.

5.4.2 The evolution of the Fermi level in the de-excitation process.

The activation energy of the conductivity was measured on the W samples by partially de-exciting the material by thermal annealing at various temperature values in a few steps to see if the location of the Fermi level was lifted when the conductivity of the sample was decreased in the de-excitation process (the decayed thermally-stimulated measurements). This was done as following. The sample was first cooled rapidly at some stage in the de-excitation process and then heated slowly and its conductivity was recorded as a function of temperature. This process was repeated a few times at various temperatures in the process of the de-excitation of the HCS. A typical result for sample W5B is plotted in Fig. 5.24. As can be seen, the activation energy for the conductivity and thus the Fermi level increased sequentially in the de-excitation process of the sample. At last the activation energy and the conductivity were restored to their values in the NS and this was checked every time in the experiments as the criterion to make sure the sample was in the NS before any new experimental step would be taken with it. The gradual lifting of the Fermi level in the de-excitation process of the sample confirms the prediction by our model.
Figure 5.23: The optically measured oxygen vacancy levels in impurity doped YIG, cited from Ref. 61.
Figure 5.24: $\ln \sigma$ vs. $1000/T$ for sample W5B measured from the decayed thermally-stimulated conductivity measurements. The activation energies for the conductivity measured at various stages of the de-excitation process of the HCS are as following: $E_{a1} = 0.05 \, \text{eV}(at \, T = 165 \, K)$, $E_{a2} = 0.1 \, \text{eV}$ (at $T = 194 \, K$) and $E_{a3} = 0.4 \, \text{eV}(at \, T = 238 \, K)$. 
CHAPTER VI

Conclusion

This investigation into the electrical properties of the excess Ca and Ge doped yttrium iron garnet (the W samples) reveal, for the first time, the mechanisms for the conduction of this material at room and low temperatures. The proposed model that the pinning of the Fermi level in the partially compensated acceptor tail of the valence band and the moving of the Fermi level in this tail due to either the trapping of the holes in this tail or removing of the electrons from this tail to the repulsive electron traps explains the temperature and the voltage dependence of the activation energy for the conductivity of the material and the transient space charge current spectroscopy in the normal state (NS), the excitation and de-excitation process of the high conduction state (HCS), and the stationary electrical properties of the material in the HCS. In other words, the observed experimental data have confirmed the proposed mechanisms for the electrical properties of this material. The above-cited experimental effects observed on the W samples and the corresponding predictions by the proposed model are listed in table 6.1 and table 6.2.
Table 6.1. The comparison of the experimental results to the theoretical predictions on the properties of the samples in the NS.

<table>
<thead>
<tr>
<th>parameters</th>
<th>predicted</th>
<th>observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-type in NS</td>
<td>p</td>
<td>p</td>
</tr>
<tr>
<td>activation energy for</td>
<td>change with $T$</td>
<td>$\sim 0.40 \text{ eV}(200 \leq T \leq 300K)$</td>
</tr>
<tr>
<td>conductivity</td>
<td></td>
<td>$\sim 0.02 \text{ eV}(T &lt; 100 \text{ K})$</td>
</tr>
<tr>
<td>$E_a$ in NS</td>
<td>depends on $E$</td>
<td>Yes, see Table V-1</td>
</tr>
<tr>
<td></td>
<td>PF dimension can be found</td>
<td>$210 \sim 240 \text{ A}$</td>
</tr>
<tr>
<td>Hole trap effects</td>
<td>location of hole levels and density of trapped holes can be found</td>
<td>$\sim 0.36 \text{ eV}$ above valence band mobility edge</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$10^{14} \sim 10^{16}/\text{cm}^3\text{eV}$, depending on $V_{ap}$</td>
</tr>
</tbody>
</table>

Symbols used in this and next table: C-type—The type of conductivity; $E$—electric field; $E_a$—activation energy for the conductivity of the sample; e-traps—repulsive electron traps; C-mobility edge and V-mobility edge—conduction and valence band mobility edge respectively; I oscillation—current oscillation; and f—frequency.
Table 6.2. The comparison of the experimental results to the theoretical predictions on the properties of the samples in the HCS.

<table>
<thead>
<tr>
<th>parameters</th>
<th>predicted</th>
<th>observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>excitation of HCS by light and ( \mathcal{E} )</td>
<td>1. rate varies: ( 1 - e^{-t/\tau} ) to ( t ) to ( t^{1/2} ) after initiation of HCS</td>
<td>Yes, see Fig. 5.7 and 5.8</td>
</tr>
<tr>
<td></td>
<td>2. rate depends on ( \mathcal{E} )</td>
<td>rate reduced more than 10 times when ( \mathcal{E} ) reduced by two</td>
</tr>
<tr>
<td>starting time of excitation</td>
<td>chaotic</td>
<td>observed</td>
</tr>
<tr>
<td>excitation of HCS by double injection</td>
<td>I oscillation of low ( f ) before in HCS</td>
<td>( f: 10^2 \sim 10^3 ) ( Hz )</td>
</tr>
<tr>
<td>conductivity</td>
<td>higher than in NS</td>
<td>about 5 orders of magnitude</td>
</tr>
<tr>
<td>( E_a ) in HCS</td>
<td>lower than in NS</td>
<td>( \sim 0.02 ) ( eV )</td>
</tr>
<tr>
<td>hole trap effect</td>
<td>disappear</td>
<td>Yes</td>
</tr>
<tr>
<td>de-excitation of HCS by thermally annealing at some ( T )</td>
<td>70, 170, 240, 400,..( K ), depending on e-traps involved</td>
<td></td>
</tr>
<tr>
<td>location of e-trap levels</td>
<td>can be found in annealing process</td>
<td>( 0.02 \sim 0.8 ) ( eV ) “below” C-mobility edge</td>
</tr>
<tr>
<td>change of ( E_a ) in de-excitation</td>
<td>lifting</td>
<td>0.02 to 0.09 to 0.15 to 0.40 ( eV )</td>
</tr>
<tr>
<td></td>
<td>gradually</td>
<td>above V-mobility edge</td>
</tr>
</tbody>
</table>
Other electrical properties of Ca excess CaGe:YIG, such as the electrical contacts with Au and In, the space charge limited current in the material, are explained well by the proposed model in combination with the appropriate theories reviewed in chapter II.

A new technique, the transient space charge limited current spectroscopy (TSLCS) method, has been developed in this work for the measurements of the majority carrier (hole in this work) trap effects in the high resistive solids. If an injecting contact for the minority carriers (electrons in this work) and a blocking contact for the majority carriers were available, the method can also be applied to measure the minority trap effects.

The sensitive dependence of the excitation rate of the HCS on the electric field indicates the repulsive nature of the electron traps which take part in inducing the HCS. Contrasting experiments of exciting the HCS were done on samples of Ge:YIG, Ca:YIG, Ge excess GeCa:YIG and nominally pure YIG to argue that the positively charged oxygen vacancies are likely the sources of these traps. It was found that the HCS can be realized in all of these materials except for Ge:YIG and that the responsible electron trap levels for the HCS in these materials fall in the same range (0.1 - 0.8 eV "below" the conduction mobility edge) as in the Ca excess CaGe:YIG materials (see §5.4.1). The energy range of these electron trap levels are close to the optically measured energy range of the oxygen vacancies in YIG (see Fig. 5.23). The oxygen vacancies are general lattice defects in YIG and their concentrations are much higher in p-type YIG than in n-type YIG because of the electrical neutrality condition of the materials. In the heavily doped Ge:YIG($Y_3Fe_{5-y}O_{12}$, $y = 0.1$) used in this work, the concentration of
the oxygen vacancies would be small and the Fermi level is pinned in the impurity band which is far from the valence band. In this case it is difficult to move the Fermi level close to the valence band to have a p-type HCS. In the Ge excess GeCa:YIG, the concentration of ion Ge$^{4+}$ is only a little more than that of ion Ca$^{2+}$ (about 0.02 ions per formula). Any inhomogeneity in the composition of this material may result in the condition necessary for the realization of the p-type HCS: partially compensated p-type conduction and sufficient oxygen vacancies available to serve as the repulsive electron traps. As observed in experiments (see §5.3.2), thermopower in the HCS of this material is vanishingly small. This has been explained as due to the possible coexistence of the n-type and p-type portions in the material when this material was excited by double injection method into the high conduction state. Based on the arguments given above and the analysis on the electrical nature of the oxygen vacancies in §3.2.1, the repulsive electron traps can be attributed to the oxygen vacancies. In addition, if there are repulsive hole traps available in the n-type YIG, it would be possible to realize the n-type high conduction state.

The band type conduction of Ca excess CaGe:YIG in the temperature range between 300 $K$ and 200 $K$ may be directly confirmed by comparing the activation energies for the conductivity and the Seebeck coefficient of the material. Efforts have been made to measure the Seebeck coefficient of the material as a function of temperature. Unfortunately, good data has not been obtained because of the unsolved problem of having, at the same time, good thermal contacts and a good electrical insulation between the sample holder and the sample. This may be one possible area for further investigation on
The fine structure of the proposed energy bands and the band tails in Ca excess CaGe:YIG is difficult to study by optical absorption spectroscopy since the localized iron ion states give rise to many lines in the energy gap of YIG. A possible alternative study is proposed as following. Any garnet not containing the transition metal ions, heavily doped with Ca in excess of Ge if possible, may be used to study the fine structure of the impurity tails of the bands since the garnet has the same crystallographic structure as CaGe:YIG but has no iron ions to give rise to the undesirable lines of absorption spectrum. In this case, it is expected to be possible to observe the HCS and other effects which are observed in CaGe:YIG. The data on the band structure of such a garnet may be used to justify the proposed band model for CaGe:YIG in the present work.

If the sandwich-type electrical contacts of transparent electrodes to the thin film sample were available, it would be possible, with a reasonable accuracy, to apply the TSLCS method to measure the density of hole trap levels when the sample is in the NS and to apply the trap free SCL method (see eq. 2.19, 2.20) to measure the concentration and the mobility of holes in the valence band when the sample is in the HCS. If an injecting contact for electrons and a blocking contact for holes were available, the TSLCS method can be applied to measure the repulsive electron trap levels directly.

The competition between trapping holes near the electrode and removing electrons from the compensated acceptors to the repulsive electron traps results in a chaotic behaviour of the excitation of the HCS, i.e. the excitation may start earlier or later under the same conditions. More research is needed.
to understand the details of this competition process.
## APPENDIX A

The checklist of the symbols used in the dissertation

<table>
<thead>
<tr>
<th>SYMBOLS</th>
<th>MEANING</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A(E), A_0$:</td>
<td>Density of states as a function of energy, the coefficient in this distribution function.</td>
</tr>
<tr>
<td>$a$:</td>
<td>Absorption coefficient of light.</td>
</tr>
<tr>
<td>$B, B_2, B_3$:</td>
<td>Constants.</td>
</tr>
<tr>
<td>$C, c$:</td>
<td>Constant, capacitance, velocity of sound.</td>
</tr>
<tr>
<td>$b$:</td>
<td>Rate of changing temperature.</td>
</tr>
<tr>
<td>$E$:</td>
<td>Energy.</td>
</tr>
</tbody>
</table>
$E_{c\mu}$, $E_{v\mu}$: ... Mobility edges of the conduction and the valence bands respectively.

$E_{f0}$, $E_{f}$: ............................................................ Fermi energy in the equilibrium and the non-equilibrium systems respectively.

$E_A$: ........................................ Activation energy of conduction.

$E_\mu$, $E_{\mu h}$: ... Activation energies of mobilities in the band conduction and the hopping conduction respectively.

$E_{sh}$, $E_{PP}$, $E_m$: .... Activation energies of mobilities due to the short range lattice fluctuations, the long range fluctuations of the potential of impurity charges, and the magnetic disorders respectively.

$E_{te}$, $E_{th}$: ........ Electron trap level and hole trap level respectively.

$E_r$: ................................................. Recombination level.

$E_{RP}$: ........................................ Repulsive electron trap level.
\( E_b \): Barrier height of the repulsive electron trap.

\( E_{fe} \): Quasi-Fermi level of electrons.

\( e_i \): Emission rate of electrons from the repulsive electron traps or emission rate of holes from the hole traps.

\( \varepsilon \): Electric field intensity.

\( f \): Frequency.

\( I \): Electric current.

\( I_l \): Light intensity.

\( I_s \): Saturation electric current.

\( h, \hbar \): Plank constants.

\( J \): Electric current density.

\( k \): Boltzmann constant.
L: ........................................ Width of the conduction channel.

l: .............. Dimension of the long range potential fluctuations.

$m_e, m_e^*, m_h^*$: Mass of electron and effective mass of electron and hole respectively.

$N_{e_l}, N_{v_h}$: ........................................ Density of states equivalent at the edges of the conduction and the valence bands respectively.

$N_a, N_d$: .... Concentrations of the acceptors and donors respectively.

$N_{e_t}, N_{h_th}$: Concentrations of the repulsive electron traps and the hole traps respectively.

$n$: ............... Concentration of electrons in the conduction band.

$n_a$: ........ Concentration of electrons compensating(occupying) the acceptors.

$n_t$: ........ Concentration of electrons in the repulsive electron traps.
\( p_0, p \): Concentrations of holes in the valence band in equilibrium and in non-equilibrium system respectively.

\( p_t \): Concentration of holes in the hole traps.

\( q \): Charge of electron.

\( R \): Resistance.

\( S_{tc}, S_{te} \): Capture and escape cross-sections respectively.

\( T \): Temperature.

\( T_c, T'_c \): Characteristic temperatures for the distributions of the density of states.

\( t \): Time, thickness of thin layers.

\( V \): Volume.
$V$: ................................................................. Voltage, volt.

$v$: ................................................................. Velocity, constant.

$v_d$: ................................................................. Drift velocity.

$W$: ...................... Length of conduction channel, band width.

$w$: ................................................................. Constant.

$\mu_{fh}, \mu_{hh}$: .......... Mobilities of holes in the band and the hopping conduction respectively.

$\epsilon_s, \epsilon_{\infty}$: ... Static and high frequency dielectric constants respectively.

$\eta$: .......................... Coupling constant of polaron with lattice.

$\rho$: ................................................................. Resistivity.

$\sigma$: .......................... Conductivity, capture or escape cross section.
\( \gamma_{ec}, \gamma_{ea} \): Capture and escape coefficients respectively.

\( \Delta, \delta, \psi \): Energy differences.

\( \tau_e \): Life time of electrons in their capture process by the repulsive electron traps.

\( \tau_r \): Life time of electrons in their recombination process with the holes in the tail of the valence band.

\( \xi \): Constant.

\( \beta \): Quantum yield.

NS: Normal state.

HCS: High conduction state.
The density of states equivalent of the valence band

In the approximation of the effective mass of electrons in the valence band of a semiconductor, the energy of an electron near the maximum of the valence band can be expressed as

\[ E(\vec{k}) = E_v - \frac{h^2 \kappa^2}{2m_h^*}, \tag{1} \]

where \( \kappa \) is the wave vector, \( E_v = E(\kappa_0) \), and \( \kappa_0 \) is taken as zero; \( m_h^* = -m_e^* \) = \( (\frac{1}{h^2} \frac{\partial^2 E}{\partial \kappa^2} |_0)^{-1} \) is the effective mass of a hole while \( m_e^* \) is the effective mass of an electron in the valence band.

The density of states of the valence band near the energy maximum can be deduced from the equation

\[ \text{Number of total states} = 2V \frac{h^3}{\hbar^3} \int 4\pi \kappa^2 d\kappa, \tag{2} \]

where \( V \) is the volume of the semiconductor and the integral is over the whole valence band within the effective mass approximation, to be

\[ g(E) = 2\pi V \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} (E_v - E)^{1/2}. \tag{3} \]

The concentration of holes in the valence band is then calculated as

\[ p = \int_{-\infty}^{E_v} g(E)[1 - f(E)] dE, \tag{4} \]
where \( f(E) = 1/[1 + \exp(E - E_f)] \) with \( E_f, k, T \) being the Fermi level, the Boltzmann constant, and the temperature respectively. When \( E_f - E \gg kT \), \( p \) can be approximately evaluated as

\[
p = 2\left(\frac{2\pi m^*_h kT}{\hbar^2}\right)^{3/2} \exp\left(-\frac{E_f - E_v}{kT}\right),
\]

where the pre-exponential coefficient

\[
N_v = 2\left(\frac{2\pi m^*_h kT}{\hbar^2}\right)^{3/2},
\]

is called the density of states equivalent of the valence band.
LIST OF REFERENCES


