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**Effects of oxygen vacancies on the magnetic and the electrical
properties of Ca-substituted yttrium iron garnet**

Song, Yong Jin, Ph.D.

The Ohio State University, 1993

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EFFECTS OF OXYGEN VACANCIES ON THE
MAGNETIC AND THE ELECTRICAL
PROPERTIES OF CA-SUBSTITUTED YTTRIUM
IRON GARNET

DISSERTATION

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

By

Yong Jin Song, B.Sc, M.Sc

* * * * *

The Ohio State University

1993

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To my family and wife

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CHAPTER I

Introduction

Yttrium Iron Garnet, $Y_3Fe_5O_{12}$, is a ferrimagnetic ionic crystal with cubic structure^[1]. It has two sublattices of iron ions which are located at the tetrahedrally coordinated d-site and octahedrally coordinated a-site. Its magnetic properties are well understood with the two sublattice model of molecular field theory. It is also a magnetic semiconductor with a wide band gap and its electrical properties are modified drastically by proper doping with donor or acceptor ions^[2].

The ferrimagnetic order is due to the superexchange mechanism mediated by oxygen ions and all the intersublattice and the intrasublattice superexchange interactions are antiferromagnetic. Among those, the intersublattice interaction is the strongest and it dominates the ferrimagnetic order. In one formula unit of $Y_3Fe_5O_{12}$, three Fe^{3+} ions at the d-site are ordered in one direction and two Fe^{3+} ions at the a-site are ordered in opposite direction. At absolute zero, its magnetic moment is known to be $5\mu_B$. Y^{3+} ion at the c-site has a diamagnetic electron configuration, so that the magnetic properties are determined by the d- and a-site iron ions.

Yttrium Iron Garnet, YIG, does not have a closely packed crystal structure and the metal ions at any site can be substituted with a wide variety of magnetic

or nonmagnetic ions. Substituted Yttrium Iron Garnet exhibits various kinds of magnetic ordering : ferrimagnetic, antiferromagnetic or even ferromagnetic order^[3]. If iron ions at one of the sites are substituted with nonmagnetic ions, the intersublattice interaction gets weaker as the substitution proceeds and the iron ions at the other site show canting and eventually it turns into the antiferromagnetic order over a certain limit of the substitution due to the dominant intrasublattice interaction^[4].

The investigations on the effects of substitution have mostly been performed through the charge-compensated substitution. For example, if Si^{4+} is substituted into the d-site of the Fe^{3+} ion, Ca^{2+} of the same amount can be substituted into c-site of the Y^{3+} ion to achieve charge balance. The site preference of the substituted ion depends on the ionic radius, etc.

The charge-uncompensated substitution invokes an imbalance of electric charge and shows many interesting properties : an anomaly of magnetization near $0K$ ^[5], photomagnetic effect^[6], ferromagnetic resonance^[7] and photoinduced absorption^[8, 9], etc. To explain the phenomena, it is widely assumed that the substituted metal ions, M^{2+} is charge-compensated by the formation of Fe^{4+} ions at low temperatures and M^{4+} ions by Fe^{2+} ions^[10].

The Ca-substituted Yttrium Iron Garnet in this research is an example of the charge-uncompensated substitution. The magnetization shows a maximum under $100K$, and decreases as the temperature approaches $0K$ while the magnetization of pure YIG increases monotonically as the temperature decreases and reaches a broad plateau under $100K$. The Ca^{2+} ion acts as an acceptor and the thermopower measurement shows that Ca-substituted YIG is a p-type semiconductor. Resistivity as low as $10^2 \Omega cm$ at $300 K$ can be achieved by this substitution while the resistivity of the pure YIG is higher than $10^{12} \Omega cm$ at $300 K$.

The decrease of the magnetization of Ca-substituted YIG(Ca:YIG) as T approaches $0K$ indicates the presence of a ferromagnetic superexchange between the d- and a-site at a point of local disorder. Two models have been proposed to explain the low temperature behavior of the magnetization. The first was the Fe^{4+} model published in 1987^[11]. According to this model, there is a third sublattice of Fe^{4+} at the d-site which is ferromagnetically coupled to the neighboring a-sites, where the holes captured in this sublattice to form Fe^{4+} are delocalized at higher temperatures. The localization energy of the holes ranges from $10K$ to $40K$ ^[5]. The second model published in 1991 explains the role of the O^- ion in the superexchange^[12, 13]. The localization of a hole at O^{2-} results in O^- , and it may change the ferrimagnetic a-d coupling into ferromagnetic above a certain doping level of Ca.

As a result of this research, a third model was proposed. For the above two models, it is expected that the anomaly of the magnetization in Ca:YIG at low temperatures should decrease with the decrease of the Fe^{4+} (or O^-) content as the number of oxygen vacancies increases by thermal annealing in a reducing atmosphere. It may even disappear at a certain annealing condition. However, the experimental results in this research showed that the increase of the number of oxygen vacancies resulted in an increase in the anomaly or a significant decrease in the magnetization. This anomaly can be explained by the ferromagnetic superexchange mediated by the unpaired electrons localized at the oxygen vacancies.

Substitution of Ca into YIG is accompanied by the increase of oxygen vacancies in the lattice. Oxygen vacancies may have one or two captured electrons or remain vacant. Annealing a sample in vacuum or N_2 atmosphere increases the concentration of oxygen vacancies and it even changes the ratio of one kind of oxygen vacancy to the other.

The local ferromagnetic superexchange for the above two different models originates from the local charge imbalance. To investigate the origin of the local ferromagnetic superexchange, a series of experiments was planned and performed in this research to create a predictable charge imbalance due to oxygen vacancies in Ca-substituted YIG, and to monitor the changes in the magnetic properties. The effects of the oxygen vacancies on the electrical conduction was also monitored.

The term doping rather than substitution can be used when one is more interested in the aspects as a semiconductor. Substitution of Ca in YIG by 0.1 formula unit is not a high level in view of a substitution, but it corresponds to around $4 \times 10^{20} \text{ions/cm}^3$ which is a very heavy doping level for a semiconductor. It may naturally induce localized states in the band gap and localized band tails at the conduction band and the valence band edge. So far, the approximation of exponential band tails has been adopted to explain several interesting electrical properties of doped YIG^[14, 15], and energy levels of several donor and acceptor ions have also been suggested. Recently, a Ca-impurity band has been proposed^[15], though without any direct experimental evidences. Information on the position and the width of the impurity band for high doping concentration are not available for other impurities^[16] either.

The conduction mechanism in YIG is believed to be due to the large polaron band conduction at temperatures above $600K$, but it has not been established yet for the temperature range under $600K$ ^[17]. For n-type YIG, there are contradicting data and interpretations between small polaron hopping and large polaron band conduction. For p-type YIG, it is even less clear^[2].

One of the difficulties in investigating the conduction processes at low temperatures is that there always exists a surface layer which has higher resistance. The I-V characteristics are understood with the two-layer model^[14], in which the surface

layer experiences the space-charge-limited current^[18] at high applied voltages. The space-charge-limited current depends on the distribution of traps in the band gap, and it may even be used as a tool monitoring the defect states.

Another goal of this research is to investigate the disorder caused by the high doping level of calcium, and the charge compensation mechanism for calcium, which might be related with oxygen vacancies. The corresponding conduction mechanism and the scattering mechanism of charge carriers are also of concern.

CHAPTER II

Magnetic Properties of YIG

2.1 Crystal Structure of Yttrium Iron Garnet

The garnet structure is very complicated even though the symmetry is cubic. It belongs to O_h^{10} -Ia3d space group. The unit cell contains 8 formula units $\{A_3\}[B_2](C_3)O_{12}$ where $\{ \}$ designates the dodecahedrally coordinated c-site, $[\]$ the octahedrally coordinated a-site and $(\)$ the tetrahedrally coordinated d-site. In a unit cell, there are 24 $\{c\}$ sites which are the largest cation sites. The next largest cation sites are the 16 $[a]$ sites and the smallest cation sites are the 24 (d) sites.

The garnet structure of yttrium iron garnet, $\{Y_3\}[Fe_2](Fe_3)O_{12}$ is not a closely packed lattice. It has a volume of 236.9 Å³ per formula unit. The unit cell has a lattice constant of 12.376 Å. The openness of the structure provides a great technical advantage in that it is possible to accommodate a very wide variety of cations in the garnet structure.

In yttrium iron garnet(YIG), a total of forty Fe^{3+} ($3d^5$) ions per unit cell are distributed at d- and a-sites. The Y^{3+} ($4f^6$) closed-shell ions are located on twenty four c-sites. The arrangement of the cations is shown in Fig. 1 and the oxygen coor-

dinations of cations are illustrated in Fig. 2. $O^{2-}(2p^6)$ ions are located at the corners of each polyhedron. Each O^{2-} ion is shared by one octahedron, one tetrahedron and two dodecahedra.

The interionic distances and angles for the cation-oxygen-cation linkages are important factors for the superexchange interaction, and are listed in Tables 1 and 2.

The substitution of a wide range of cations in YIG and other garnets has been treated in exhaustive detail by Geller et al.^[4] Table 3 lists only several of them. The tetrahedral substituent ions are almost entirely those having spherical symmetry, i.e., closed shell type. The octahedral site is larger than the tetrahedral site in YIG with the distance to the surrounding oxygen ions being 2.01Å compared to 1.87Å of tetrahedral site. Accordingly, there is a large variety of ions which have been observed to substitute for Fe^{3+} at the a-site. Many, but not all, of the ions which replace Fe^{3+} in the tetrahedral site will also do so in the octahedral site.

The dodecahedral site is the largest of the three cation sites with the average distance to the oxygen ions being about 2.40Å. Therefore, a large selection of ions including all of the rare earths and alkaline earths, will occupy this site. In some cases, the preference of an ion for one site is not very strong so that it may occur in two sites at one time. Two good examples are Ga^{3+} and Al^{3+} , which occupies d- and a-site simultaneously.

2.2 Molecular Field Theory

The magnetic properties of yttrium iron garnet are determined by the Fe^{3+} ions at the tetrahedral(d) sites and octahedral(a) sites, which constitute two sublattices. There are three different superexchange interactions between iron ions. The two in-

Figure 1: The arrangement of cations in the garnet structure. After Geller^[3].

Figure 2: The oxygen coordination of cations in YIG. After Geller and Gillo^[20].

Table 1: Nearest-neighbor interionic distances in yttrium iron garnet. From Geller and Gilleo^[20, 1].

Ion	Interionic distances ($\text{\AA}$)		
Y^{3+}	$4Fe^{3+}(a)$	at	3.46
	$6Fe^{3+}(d)$	at	3.09(2), 3.79(4)
	$8O^{2-}$	at	2.37(4), 2.43(4)
$Fe^{3+}(a)$	$2Y^{3+}$	at	3.46
	$6Fe^{3+}(d)$	at	3.46
	$6O^{2-}$	at	2.01
$Fe^{3+}(d)$	$6Y^{3+}$	at	3.09(2), 3.79(4)
	$4Fe^{3+}(a)$	at	3.46
	$4Fe^{3+}(d)$	at	3.79
	$4O^{2-}$	at	1.87
O^{2-}	$2Y^{3+}$	at	2.37, 2.43
	$1Fe^{3+}(a)$	at	2.01
	$1Fe^{3+}(d)$	at	1.87
	$9O^{2-}$	at	2.68(2), 2.81, 2.87
			2.96, 2.99(2), 3.16(2)

Table 2: Angles and distances of iron–oxygen–iron linkages in yttrium iron garnet^[20].

Ions	Distances(Å)	Angles(°)
$Fe^{3+}(a) - O^{2-} - Fe^{3+}(d)$	2.01, 1.87	125.9
$Fe^{3+}(a) - O^{2-} - Fe^{3+}(a)$	2.01, 4.41	147.2
$Fe^{3+}(d) - O^{2-} - Fe^{3+}(d)$	1.87, 3.41	86.6
	1.87, 3.68	78.8
	1.87, 3.83	74.7
	1.87, 3.83	74.6

trasublattice interactions, d–d and a–a are weaker; the one intersublattice interaction, a–d is the strongest.

The interactions between the Fe^{3+} ions are mediated by O^{2-} ions through $Fe^{3+} - O^{2-} - Fe^{3+}$ linkage. This kind of exchange interaction, known as superexchange, was first recognized by Kramers^[21] and has been extensively studied since then^[22]. For this interaction, the overlap between the wavefunction of the oxygen 2p electrons (with dumbbell-shaped distribution) and the electronic distribution of the magnetic ions is the important feature. The interaction increases with the overlap and accordingly will be greater the shorter the distance is between the magnetic ions and the oxygen ion, and the closer the linkage angle is to 180°. Table 2 shows interionic distances and the angles of $Fe^{3+} - O^{2-} - Fe^{3+}$ linkages.

The understanding of a ferrimagnet was established by Néel^[23] with his two sublattice model on the basis of antiferromagnetic superexchange. The temperature

Table 3: Cations known to substitute ions at each site in yttrium iron garnet. The ions with * at the ionic radius presumably are not yet demonstrated to do so, but listed just for reference to the radii. The radii are from Shannon and Prewitt^[19]. [(HS) : high spin, C.N. : coordination number].

Site	Ion	Ionic radius(Å)
(d) C.N.(4)	$Fe^{3+}(\text{HS})$	0.49
	Si^{4+}	0.26
	Ge^{4+}	0.390
	Ga^{3+}	0.47
	Al^{3+}	0.39
(a) C.N.(6)	$Fe^{3+}(\text{HS})$	0.645
	Pt^{4+}	0.625*
	Pt^{2+}	0.80*
	Mg^{2+}	0.720
	Pb^{4+}	0.775
	Si^{4+}	0.400*
	Ge^{4+}	0.530
	Ga^{3+}	0.620
	Al^{3+}	0.535
(c) C.N.(8)	Y^{3+}	1.019
	Ca^{2+}	1.12
	Pb^{2+}	1.29

dependence of magnetization of YIG is described best by the molecular field theory for the two sublattices except in the temperature ranges very close to absolute zero where the effect of magnon excitation should be considered, and close to the Curie temperature. The molecular field coefficients for pure YIG have been obtained most accurately by Anderson^[24] by fitting the temperature dependence of the saturation magnetization data, with the two sublattice model. His value of the Curie temperature, $T_C = 559^\circ C$ is also considered as the best.

The net magnetic moment per mole of $Y_3Fe_5O_{12}$ can be expressed as the sum of the magnetic moments of the two sublattices,

$$M(T) = M_d(T) + M_a(T) . \quad (2.1)$$

The magnetic moment per mole of each sublattice can be expressed in terms of the Brillouin function,

$$M_d(T) = M_d(0)B_{S_d}(x_d) \quad (2.2)$$

and

$$M_a(T) = M_a(0)B_{S_a}(x_a) , \quad (2.3)$$

where

$$B_{S_i} = \frac{2S_i + 1}{2S_i} \coth\left(\frac{2S_i + 1}{2S_i} x_i\right) - \frac{1}{2S_i} \coth\left(\frac{1}{2S_i} x_i\right) \quad (2.4)$$

and

$$x_i = \frac{S_i g \mu_B}{kT} H_i . \quad (2.5)$$

The molecular field for the sublattices are expressed as

$$H_d = \lambda_{dd} M_d + \lambda_{da} M_a \quad (2.6)$$

and

$$H_a = \lambda_{ad} M_d + \lambda_{aa} M_a . \quad (2.7)$$

In the above equations, $\lambda_{dd}, \lambda_{aa}$ and $\lambda_{ad} = \lambda_{da}$ are molecular field coefficients, S_d and S_a are the spin quantum numbers of Fe^{3+} ions, μ_B is the Bohr magneton, and k is the Boltzmann constant. H 's and M 's are one dimensional vectors.

At 0 K, the moments per mole for the two sublattices are

$$M_d(0) = 3gS_d\mu_B N_A, \quad M_a(0) = 2gS_a\mu_B N_A, \quad (2.8)$$

where $S_d = S_a = \frac{5}{2}$ and N_A is the Avogadro's number.

Based on the data of Anderson^[24] and of Geller *et al*^[4], Dionne determined the molecular field coefficients for the best fit with the two sublattice model^[25]. Dionne's values are introduced as follows,

$$\lambda_{ad} = -97.0 \text{ mole/cm}^3, \quad \lambda_{dd} = -30.4 \text{ mole/cm}^3, \quad \lambda_{aa} = -65.0 \text{ mole/cm}^3. \quad (2.9)$$

To list the related formulas for convenience,

$$\begin{aligned} M(T) &= M_d(T) + M_a(T), \\ M_d(T) &= 8.374 \times 10^4 B_{\frac{5}{2}} \left(\frac{3.358 \times 10^{-4}}{T} H_d \right), \\ M_a(T) &= 5.583 \times 10^4 B_{\frac{5}{2}} \left(\frac{3.358 \times 10^{-4}}{T} H_a \right), \\ H_d &= -30.4 M_d - 97.0 M_a, \end{aligned}$$

and

$$H_a = -97.0 M_d - 65.0 M_a,$$

where the M 's are in emu/mole and H 's are in gauss.

In the substituted Yttrium Iron Garnets, localized canting of the spins of the iron ions can occur^[4, 26]. When the degree of substitution is not high, the two sublattice

model can still be used in analyzing the temperature dependence of the magnetization. Dionne^[25] extended the work to the substituted yttrium iron garnets, $Y_3[Fe_{2-x}M_x](Fe_{3-y}N_y)O_{12}$ where M and N are nonmagnetic ions. He found empirically that the sublattice magnetizations at 0 K are

$$M_d(0) = 3gS_d\mu_B N(1 - k_d)(1 - 0.1k_a) \quad (2.10)$$

and

$$M_a(0) = 3gS_a\mu_B N(1 - k_a)(1 - 0.1k_d^{5.4}), \quad (2.11)$$

where $k_a = \frac{x}{2}$ and $k_d = \frac{y}{3}$. These equations are valid for k_i values which are small enough that none of the sublattices makes a transition to an antiferromagnetic state.

He found that the molecular field coefficients are also functions of k_a and k_d . The equations for λ_{ij} are

$$\lambda_{dd} = -30.4(1 - 0.87k_a), \quad (2.12)$$

$$\lambda_{aa} = -65.0(1 - 1.26k_d), \quad (2.13)$$

$$\lambda_{ad} = -97.0(1 - 0.25k_a - 0.38k_d) \quad (2.14)$$

for $k_a \leq 0.35$ and $k_d \leq 0.65$.

It should be noted that Dionne used an approximation for the change of the molecular field coefficients. He assumed that the d-site substitution induces a canting in the a-sublattice^[26] so that it reduces the a-a and a-d interaction but that it does not affect the d-d interaction because the canting does not occur in the d-sublattice. For the a-site substitution, he also made a similar assumption.

Substitution of Fe^{3+} ions with nonmagnetic ions usually accompanies a change in the lattice constant. Thus, it will affect the overlap of the wavefunctions of electrons which participate in the superexchange interactions. By approximation, Dionne

ignored this effect and the possibility that a substitution may also change the intra-sublattice interaction in the sublattice where the substitution occurs.

2.3 Curie Temperature

The Curie temperature is also an important physical variable which reflects the strength of the superexchange interaction in Yttrium Iron Garnet. Many different values had been reported for the Curie temperature of YIG until Anderson^[24] reported 559 K, which is now believed to be the most accurate value for pure YIG.

Gilleo^[27, 1] found that the Curie temperature for substituted YIG is closely related to the number of $Fe^{3+}-O^{2-}-Fe^{3+}$ linkages. He also interpreted the energy $k_B T_C/n$, where n is the total number of the linkages, as the energy which may be assigned to each linkage. His model explained the substitution dependence of the Curie temperature and also the magnetization at low temperatures in substituted YIG in the early years. In the following section, Gillo's model will be reviewed.

In YIG, Fe^{3+} ions at the a -site and the d -site have six and four $Fe^{3+}-O^{2-}-Fe^{3+}$ linkages respectively. Each oxygen ion is coordinated with only one each of the tetrahedral and the octahedral ions(refer to table 1). Gilleo started from an important assumption that the Fe^{3+} ions which have zero or only one oxygen linkage do not contribute to the magnetic ordering of the substance, and empirically, he found that the curie temperature is proportional to the number of active oxygen links per active magnetic ions.

The substituted yttrium iron garnet is represented with a formula, $\{Y_{3-y-z}Me_{y+z}\}[Fe_{2-y}M_y](Fe_{3-z}M_z)$. Let k_o and k_t be the fractions of octahedral and tetrahedral

Fe^{3+} ions which are replaced by nonmagnetic ions,

$$k_o = \frac{y}{2}, k_t = \frac{z}{2}. \quad (2.15)$$

The probability, $p_n(m)$, that an ion of coordination n be linked with m ions is

$$p_n(m) = \binom{n}{m} k^{n-m} (1-k)^m, \quad (2.16)$$

where

$$\binom{n}{m} = \frac{n!}{m!(n-m)!}. \quad (2.17)$$

Therefore, the probability E that an ion be linked with none, or at most one, of the magnetic ions is

$$E = \sum_{m=0}^1 p_n(m) = nk^{n-1} - (n-1)k^n. \quad (2.18)$$

To relate the Curie temperature to the number of oxygen links, only the active ones are of interest. In YIG, there are 12 oxygen ions in one formula unit and each oxygen linkage involves two magnetic ions, so there are a maximum of 24 interactions. However, with substitution of a fraction k_i of nonmagnetic ions, a fraction $(1 - k_i)$ of the ions is magnetic and of these a fraction $[1 - E_i(k_j)]$ is active. Accordingly, the number of active interactions is

$$n(k_o, k_t) = 24(1 - k_o)[1 - E_o(k_t)](1 - k_t)[1 - E_t(k_o)]. \quad (2.19)$$

The number N of magnetic ions which actively participate in the ferrimagnetism is

$$N(k_o, k_t) = 2(1 - k_o)[1 - E_o(k_t)] + 3(1 - k_t)[1 - E_t(k_o)]. \quad (2.20)$$

The Curie temperature $T_C(k_o, k_t)$ for a substituted garnet is related to that of yttrium iron garnet, $T_C(0,0)$ by the relation

$$T_C(k_o, k_t) = \frac{5}{24} \frac{n(k_o, k_t)}{N(k_o, k_t)} T_C(0,0), \quad (2.21)$$

where $24/5$ is the number of interactions per magnetic ion per formula unit.

2.4 Substitution and Canting

The concept of canting originated from Yaffet and Kittel's work on ferrites^[28]. The ferrites have two sublattices just the same as YIG does, and the intrasublattice and intersublattice superexchanges are similar. The spinel structure of ferrites has 8 tetrahedral (or A) sites and 16 octahedral (or B) sites which are occupied by metal ions. The two different sites are coordinated by oxygen ions just the same as in YIG. All the exchange interactions (AA , AB , and BB) are antiferromagnetic and results in a ferrimagnetic ordering. Néel's two sublattice model, based on a Weiss molecular field treatment was developed for this system^[23].

There are two obvious extremes in this system as clarified by Néel. When the $A - B$ interaction is dominant, the two sublattices will be arranged antiparallel below a transition temperature. The other extreme is the case where one of the two sublattices are completely filled with nonmagnetic ions. The system will be aligned antiferromagnetically.

For the intermediate case where the sublattices are partly substituted by non-magnetic ions and the $A - A$ (or $B - B$) interaction is dominant, Néel's conclusion was that the substance remain paramagnetic down to the lowest temperatures. This problem was treated by Yaffet and Kittel^[28] a few years later. They included the possibility that each of the sublattices can be divided into two canted sublattices by an equal angle in a symmetric way. They found that the ground state of the system may have triangular arrangement of the spins on the sublattices.

The problem of their conclusion is that the sublattices themselves are uniformly canted. Their model is sometimes called a uniform canting model. Even though a substitution may change the average value of the interactions, the effect of the

substitution must be local. This interpretation is proposed by Geller *et al* based on their data for a large number of substituted YIG^[4].

Fig. 3 and Fig. 4 show the saturation magnetization at 0 K as a function of substitution content for d-site substitution and a-site substitution respectively. He discusses the results as the following. The d-site substitution induces a random canting at the a-site and vice versa. At a small substitution, substitution at the a-site causes the effect of canting more rapidly than at the d-site and it indicates that the d-d interaction is stronger than the a-a interaction. Over a certain limit of substitution for each case, i.e. for $x > 1.8$ in Fig. 3 or for $x > 0.7$ in Fig. 4, the canting increases significantly and keeps the trend of random canting. There are additional reports on the double substitution, i.e. at both the d-site and the a-site, for both the experiment^[26] and the theory^[29], but they will not be introduced here.

Nowic^[30] proposed a model based on the molecular field theory to explain the substitution dependence of the magnetization at 0 K, but this model does not contain the concept of canting. It allows only either up and down spins. Rosencwaig^[31, 29] proposed a model similar to Yafet, but different in the sense that it deals with localized canting. His model assumes a symmetric canting of two spins around a local disorder, but different sets of spins see different number of nearest neighbors which have the average canting angle. Each individual spin will be aligned in the opposite direction of the resultant local molecular field at 0 K.

A refined model following the idea of Rosencwaig's was proposed by Patton *et al*^[32], which starts from the Heisenberg Hamiltonian and minizes the free energy. In the remaining part of this section, this model will be introduced briefly.

The Hamiltonian for a magnetic system, including the Zeeman terms is

Figure 3: Spontaneous moment at 0 K vs composition for the silicon and germanium-substituted yttrium iron garnets. After Geller^[26].

Figure 4: Spontaneous moment at 0 K vs composition for the zirconium and scandium-substituted yttrium iron garnets. After Geller^[26].

$$H = - \sum_i \sum_{j(NN)} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B H_0 \sum_i S_{iz} , \quad (2.22)$$

where the J_{ij} 's are the exchange integrals, $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spins on the i and j sites, g is the Landé g -factor, μ_B is the Bohr magneton and H_0 is the z -directed applied magnetic field. The free energy is now developed for YIG with nonmagnetic substitution on the a -sites and canting of the Fe^{3+} spins on the d -sites. The model spin configuration is illustrated in Fig 5(a). The two parts of the split d -sublattice are indicated as d' and d'' .

Let the number of Fe^{3+} ions per formula unit be denoted by $q_a, q_{d'}$ and $q_{d''}$ respectively. Let the number of nearest neighbor a -ions to a d' -ion be denoted by $n_{d'a}$, and so on. The various q and n numbers are functions of substituent level. Note that $S_a = S_{d'} = S_{d''} = \frac{5}{2}$. Table 4 lists the twelve energy terms which follow from equation 2.22. The exchange integrals $J_{d'd'} (= J_{d''d''})$ and $J_{d'd''} (= J_{d''d'})$ are for d' and d'' Fe^{3+} ions.

The results of table 4 indicate a free energy of the form,

$$E = A \cos \theta + B \cos(2\theta) + C . \quad (2.23)$$

With the assumption of equivalent d' and d'' split sublattices, the conditions $n_{ad'} = n_{ad''}$, $n_{d'a} = n_{d''a}$ and $q_{d'} = q_{d''}$ lead to the the following coefficients in equation 2.23:

$$A = -2S^2[(q_a n_{ad'} + q_{d'} n_{d'a})|J_{ad'}| + g\mu_B H_0 q_{d'}/S] , \quad (2.24)$$

$$B = 2S^2[q_{d'} n_{d'd''}]|J_{d'd''}| , \quad (2.25)$$

$$C = 2S^2[\frac{1}{2}q_a n_{aa}|J_{aa}| + q_{d'} n_{d'd'}|J_{d'd'}| + g\mu_B q_a H_0/2S] . \quad (2.26)$$

Minimization of the energy in equation 2.23 will lead to an expression for a local canting angle, θ_L . It should be noted that the d' and d'' spins in this model only 'sees'

(a)

(b)

Figure 5: (a) Model spin configuration for the free energy formulation of localized canting, (b) effective field configuration for the localized, iterative canting calculation. After Patton *et al*^[32].

Table 4: Enumeration of energy terms.

Term	Energy
aa	$+ J_{aa} q_a n_{aa} S^2$
ad'	$- J_{ad'} q_a n_{ad'} S^2 \cos \theta$
ad''	$- J_{ad''} q_a n_{ad''} S^2 \cos \theta$
$d'a$	$- J_{ad'} q_{d'} n_{d'a} S^2 \cos \theta$
$d''a$	$- J_{ad''} q_{d''} n_{d''a} S^2 \cos \theta$
$d'd'$	$+ J_{d'd'} q_{d'} n_{d'd'} S^2$
$d''d''$	$+ J_{d''d''} q_{d''} n_{d''d''} S^2$
$d'd''$	$+ J_{d'd''} q_{d'} n_{d'd''} S^2 \cos 2\theta$
$d''d'$	$+ J_{d''d'} q_{d''} n_{d''d'} S^2 \cos 2\theta$
H_0a	$+g\beta H_0 S q_a$
H_0d'	$-g\beta H_0 S q_{d'} \cos \theta$
H_0d''	$-g\beta H_0 S q_{d''} \cos \theta$

the d spins which are canted at an equal angle, θ_L whereas for the random canting originally proposed by Geller, any particular d' spin sees a variety of canted d spins at different angles. By the energy minimization equation, $\partial E / \partial \theta = 0$,

$$[(q_a n_{ad'} + q_{d'} n_{d'a}) |J_{ad'}| S^2 + g \mu_B S H_0 q_{d'}] \sin \theta_L - [2 q_{d'} n_{d'd''} |J_{d'd''}| S^2 \sin 2\theta_L = 0, \quad (2.27)$$

$\cos \theta_L$ becomes

$$\cos \theta_L = \frac{(q_a n_{ad'} + q_{d'} n_{d'a}) |J_{ad'}| S + g \mu_B S H_0 q_{d'}}{4 q_{d'} n_{d'd''} |J_{d'd''}| S}. \quad (2.28)$$

This expression is for a *local canting angle* θ_L which depends on the nearest neighbor parameters $n_{d'a}$, $n_{ad'}$ and $n_{d'd''}$ at a particular site. For a -substituted YIG, $n_{d'a}$ can range from zero to four while $n_{ad'}$ is equal to three for any a -site Fe^{3+} ion. Thus $(q_a n_{ad'} + q_{d'} n_{d'a})$ can range from $(3q_a)$ to $(3q_a + 4q_{d'})$ while $2q_{d'} n_{d'd''}$ will range from zero to $8q_{d'}$. For $q_a = 2 - x$ and $q_{d'} = 1.5$, these factors range from $6 - 3x$ to $12 - 3x$ for $(q_a n_{ad'} + q_{d'} n_{d'a})$ and from zero to 12 for $2q_{d'} n_{d'd''}$ as $n_{d'a}$ is varied from zero to four.

The average canting angle can be obtained from the above equation by replacing the n parameters by their average values and observing that $q_a < n_{ad'} > = q_{d'} < n_{d'a} >$ is satisfied for garnets with a -site substitution, then :

$$\cos \theta_{L-AV} = < n_{da} > |J_{ad'}| / < n_{dd} > |J_{d'd''}|. \quad (2.29)$$

The equation 2.27 can be interpreted as an effective torque equation for a d' spin moment. The first term has the appearance of a torque that results from an a -sublattice local effective field and the z -directed applied field at the d' -site. From the energy origins of this term, it is clear that the d' and d'' sublattice local effective fields at an a -site also contribute to this term. The second term looks like a torque from the d'' sublattice local effective field at a d' -site (or vice versa). From the discussion

leading to equation 2.27, however, it is clear that both $d'-d''$ and $d''-d'$ energy terms contribute.

From the above arguments, the following effective fields may be identified :

$$\mathbf{H}_{d'a} = \frac{(q_a n_{ad'} + q_{d'} n_{d'a}) |J_{ad'}| S}{g \mu_B q_{d'}} \hat{\mathbf{k}}, \quad (2.30)$$

$$\mathbf{H}_0 = H_0 \hat{\mathbf{k}}, \quad (2.31)$$

$$\mathbf{H}_{d'd''} = \frac{2 n_{d'd''} |J_{d'd''}| S}{g \mu_B} (-\cos \theta_L \hat{\mathbf{k}} + \sin \theta_L \hat{\mathbf{i}}), \quad (2.32)$$

where $\hat{\mathbf{i}}$ and $\hat{\mathbf{k}}$ denote unit vectors perpendicular or parallel to the static field respectively.

In the above equations, $n_{d'a}$ ranges from 0 to 4 and will be set to a new variable m . For each value of m , $H_{d'a}$ has one explicit value denoted by $H_{d'a}(m, x)$ with x indicating the amount of substitution of the non-magnetic species per formula unit. $n_{ad'}$ and $n_{d'd''}$ can be set equal to their average values by an approximation. Note that $\langle n_{ad'} \rangle = \langle n_{ad''} \rangle = 3$ and $\langle n_{d'd''} \rangle = \langle n_{d'd'} \rangle = 2$. Therefore, they are written as

$$H_{d'a}(m, x) = \frac{[q_a(x) \langle n_{ad'}(x) \rangle + q_{d'}(x) m] |J_{ad'}| S}{g \mu_B q_{d'}(x)}, \quad (2.33)$$

$$H_{d'd''}(x) = \frac{2 \langle n_{d'd''} \rangle |J_{d'd''}| S}{g \mu_B}. \quad (2.34)$$

$H_{d'a}(m, x)$ is along the positive z and $H_{d'd''}(x)$ is oriented at an angle $\langle \theta_L \rangle$ with respect to the negative z axis. The above fields may be incorporated into an iterative calculation of the average canting angle and magnetization. This procedure is illustrated in Fig. 5(b).

1. In the first iteration, $\langle \theta_L \rangle$ is estimated from $\cos \theta_{L-AV}$ in equation 2.29. The fields are shown in Fig. 5(b), with $\theta_L^{(1)} = \theta_{L-AV}$. ϕ_m is the local canting angle

of a d' ion which has m nearest neighbors at the a -site. For each value of m , a value of $\cos \phi_m^{(1)}$ is obtained,

$$\cos \phi_m^{(1)} = \frac{H_{d'a}(m, x) - H_{d'd''}(x) \cos \theta_L^{(1)}}{[H_{d'a}^2(m, x) + H_{d'd''}^2(x) - 2H_{d'a}(m, x)H_{d'd''}(x) \cos \theta_L^{(1)}]^{1/2}}. \quad (2.35)$$

From this set of $\cos \phi_m^{(1)}$ values, the average canting angle is recalculated :

$$\cos \theta_L^{(2)} = \sum_{m=0}^{n_{d'a}^{max}} P_{da}(m, x) \cos \phi_m^{(1)}, \quad (2.36)$$

$$P_{da}(m, x) = (1-x)^m x^{(n_{d'a}^{max}-m)} \binom{n_{d'a}^{max}}{m}, \quad (2.37)$$

and

$$\binom{n_{d'a}^{max}}{m} = \frac{n_{d'a}^{max}!}{m!(n_{d'a}^{max}-m)!}. \quad (2.38)$$

In the above, $n_{d'a}^{max}$ is the maximum value of $n_{d'a}$.

2. The next procedure is evident. One simply replaces $\cos \theta_L^{(1)}$ by $\cos \theta_L^{(2)}$ in equation 2.35, and recalculates a new set of $\cos \phi_m^{(3)}$, and so on. As the set of $\cos \phi_m^{(i)}$ converge to some unchanging set and $\cos \theta_L^{(i)}$ converges to a certain value, the procedure will be terminated. In this way, a self-consistent set of local ϕ_m values and average $\theta_L^{(\infty)}$ value are obtained. The magnetization is then calculated from

$$|M| = M_d \cos \theta_L^{(\infty)} - M_a. \quad (2.39)$$

By adding an applied field H_0 to $H_{d'a}(m, x)$ in equation 2.35, it can easily be extended the calculation to obtain $M(H_0)$ and the incremental susceptibility, $\chi = dM/dH_0$, as a function of the field.

The theoretical predictions by this model are shown in fig. 6 for a -site substitution in YIG. The experimental data can not be fitted with a constant ratio of

Figure 6: Comparison of theoretical predictions with data on the 0 K spontaneous moment of Zr- and Sc-substituted YIG by Geller *et al*^[4]. The moment N_b in μ_B per formula unit is shown as a function of substituent level x in $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ (squares) and $\{Y_3Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ (triangles). After Patton *et al*^[32].

$J_{d'a}/J_{d'd''}$, but the ratio between 1.5 and 1.75 best describe the peak at which severe canting starts. At higher substitution level, the curves with even lower ratios fit the data better. In Rosencwaig's model, this trend is the same but his curves are more rounded and the fit occurs at a much different set of $J_{d'a}/J_{d'd''}$ ratios.

It should be noted that this trend is opposite to Dionne's results. As the substitution proceeds, Dionne's molecular field coefficient $|\lambda_{dd}|$ decreases faster than $|\lambda_{ad}|$ (refer to equation 2.12 and equation 2.12).

The substitution is usually accompanied by the corresponding change in the lattice constant. Recently, Pardavi-Horváth *et al*^[33] correlated the change in the ratio of the exchange integrals with the change in the lattice constant. Introducing the idea of changing ratio of exchange integrals to the localized canting model, they reported a better fit to the data of zero temperature magnetization for the a-site substitution as a function of the substitution level.

2.5 Localized Ferromagnetic Superexchange

The antiferromagnetic superexchange which determines the ferrimagnetic order in a ferrimagnet occurs in the $Fe^{3+}-O^{2-}-Fe^{3+}$ linkage. Fig. 7 displays the basic mechanism of the superexchange. The electron configuration of O^{2-} ion is $2p^6$, and each two of the electrons constitute a dumbbell shaped wave function with their spins in opposite directions as shown in Fig. 7 (a). Fe^{3+} has an electron configuration of $3d^5$ and the ground state of ${}^6S_{\frac{5}{2}}$. The spins of the five electrons are parallel and if a sixth electron overlaps the Fe^{3+} ion, its spin should have opposite direction to get the lowest energy state due to the exchange interaction(Fig. 7 (b)). As a result, the two Fe^{3+} ions linked by O^{2-} ions should be aligned in the opposite direction.

Fig. 8 shows the anomaly of the magnetization of Ca-substituted YIG at low temperature. Unlike for pure YIG, $4\pi M$ for Ca:YIG decreases as the temperature approaches 0 K. This phenomenon strongly indicates that there exists a ferromagnetic superexchange between a- and d-sites, which flips over a part of the d-site spins. In YIG, the net spin is parallel to the d-site spins so the decrease in the magnetization at low temperature can only be explained by the inverted d-site spins.

This anomaly was first explained by the Fe^{4+} model^[11]. Holes can be localized close to Fe^{3+} ions at the d-site to form Fe^{4+} ions and they are delocalized at high temperature. The number of the localized holes has the temperature dependence of $1 - e^{-\frac{T_0}{T}}$. The activation energy of the localization is $10\text{ K} \sim 40\text{ K}$ for different Ca concentration. The superexchange mechanism is illustrated in Fig 7(c).

The second model was the O^- model^[12]. Unlike the O^{2-} ion, the O^- ion has an unpaired electron. This model explains that the holes which compensate Ca^{2+} decrease the strength of the superexchange coupling. Over a certain concentration of Ca, the antiferromagnetic superexchange can be switched into ferromagnetic superexchange. But this model did not explain the temperature dependence of the magnetization. The corresponding mechanism is illustrated in Fig 7(d).

In this research, Ca-substituted YIG samples are annealed in N_2 atmosphere. The expected result is an increase in the number of singly charged oxygen vacancies which has one captured electron. As a result of this research, a different ferromagnetic superexchange mechanism is proposed, which is mediated by an electron captured at an oxygen vacancy. This mechanism is illustrated in Fig 7(e).

Figure 7: Superexchange mechanism for iron-oxygen(or oxygen vacancy)-iron linkages. (a) and (b) explain the mechanism of the antiferromagnetic superexchange. (c),(d) and (e) illustrate the possible ferromagnetic superexchanges.

Figure 8: Temperature dependence of the saturation magnetization : (a) pure YIG from Anderson^[24], (b) Ca:YIG.

CHAPTER III

Electrical Properties of YIG

3.1 Energy Band Sturucture

In yttrium iron garnet, the conduction band is an overlap of four subbands of iron $3d$ delocalized states, and under the band gap, there is a broad oxygen $2p$ band. There are also two narrow iron $3d$ bands of highly localized iron $3d$ electrons, which is close to the upper edge of the oxygen $2p$ band. The positions of these two localized bands relative to the oxygen $2p$ band or to the conduction band are not clearly known, because the optical transitions from these bands to the conduction band can not be identified or masked by the transitions to the exciton levels^[35], which are also localized states.

In fig. 9(a), the energy band diagram by Larson and Metselaar is shown. They proposed that the narrow band of Fe^{3+} at the tetrahedral site is located at the top of the oxygen $2p$ band, which is the valence band. In the figure, a few of the impurity levels are also shown. The energy levels of Si^{4+} and charged oxygen vacancies, which act as donors, are located close to the conduction band edge, and an acceptor level of Pb^{2+} is also shown in the figure. The energy level of Ca^{2+} is believed to be close

to the Pb^{2+} level. Although not shown in the figure, there are many levels of excited states of $3d$ electrons due to crystal field and also exciton levels around the conduction band edge.

In a disordered material, there exist localized states in the band gap, which constitute the localized band tail and also impurity bands^[37]. The concept of band edges should be replaced by that of mobility edges, where a transition from extended states to localized states occur. The energy levels of impurities are broadened and form impurity bands.

For highly doped samples, it is expected that the presence of band tails of localized states will be observed due to the disorder. Fig. 9(b) is a representation of the energy band diagram for heavily doped YIG^[36]. The model of exponential band tail is often used as an approximation for the density of states at the band tail. This model was also used in explaining the space charge limited current through the surface layer in the polycrystalline YIG samples^[14]. In this figure, $E_{c\mu}$ and $E_{v\mu}$ denote the mobility edges of conduction band and valence band respectively. Recently, Yuan *et al*^[15] reported that an impurity band of a complex of Ca^{2+} and Fe^{4+} is located between 0.3 and 0.6eV above the valence band for CaGe:YIG which is heavily doped but partly compensated. The impurity contents in YIG, even in single crystal samples, are high compared with the doping levels in conventional semiconductors, but there are only rough agreements about the positions of the impurity levels and even less information about the impurity bands and the corresponding impurity concentrations.

Figure 9: Energy band diagram of yttrium iron garnet. (a) Pure YIG. Hatched areas denote the states which are filled at 0 K (after Larsen and Metselaar^[16]). (b) Heavily doped and charge-uncompensated YIG. After Yuan^[36].

3.2 Conduction

For the conduction mechanism of yttrium iron garnet, there are two quite different interpretations. The first model is the large polaron band conduction, and the second is the small polaron hopping conduction. The conduction mechanism is also correlated with the charge compensation mechanism for the off-valency impurities.

It is widely assumed that Fe^{2+} and Fe^{4+} ions compensate tetravalent and divalent impurities respectively. In this picture, the number of Fe^{2+} ions equals the number of uncompensated tetravalent impurities if the concentration of tetravalent impurities are higher than that of divalent impurities. On the other hand, the excess divalent impurities are charge-compensated by the formation of Fe^{4+} . In this localized picture, electrical conduction occurs via hopping of localized charge carriers, where the number of charge carriers is independent of temperature and mobility is characterized by an activation energy. In the band conduction model, the number of charge carriers is activated by an ionization energy and is an exponential function of temperature, while mobility is a power function of temperature or independent of temperature.

3.2.1 Band Conduction

The d.c. conductivity is the sum of contributions of electrons and holes,

$$\sigma = ne\mu_e + pe\mu_h, \quad (3.1)$$

where n and p denote the number densities of electrons and holes respectively, and μ_e and μ_h are the corresponding mobilities. The concentrations n and p can be written in terms of the Fermi energy E_F , the energies at the band edges E_c and E_v , and

the effective densities of states N_c and N_v of the conduction band and valence band, respectively:

$$n = N_c \exp\left(-\frac{E_c - E_F}{kT}\right), \quad (3.2)$$

$$p = N_v \exp\left(-\frac{E_F - E_v}{kT}\right), \quad (3.3)$$

where N_c and N_v are

$$N_c = 2 \left(\frac{m_e^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} = (2.54 \times 10^{19} \text{ cm}^{-3}) \left(\frac{m_e^*}{m_e} \right)^{\frac{3}{2}} \left(\frac{T}{300} \right)^{\frac{3}{2}}, \quad (3.4)$$

$$N_v = 2 \left(\frac{m_h^* kT}{2\pi\hbar^2} \right)^{\frac{3}{2}} = (2.54 \times 10^{19} \text{ cm}^{-3}) \left(\frac{m_h^*}{m_e} \right)^{\frac{3}{2}} \left(\frac{T}{300} \right)^{\frac{3}{2}}. \quad (3.5)$$

In the above equation, m_e denotes the electron mass, $\hbar$ denotes Plank's constant, m_e^* and m_h^* denote effective masses of electrons and holes respectively.

The temperature dependence of mobility is determined by the scattering mechanism of charge carriers. The scattering mechanisms and the corresponding temperature dependences of mobility are listed in table 5.

The temperature dependence of Seebeck coefficient is also an important criterion for the conduction mechanism. When a temperature gradient exists in a substance for an open circuit configuration, an electric field is built up to balance the charge accumulation at the cold electrode.

$$\mathbf{E} = Q \nabla T. \quad (3.6)$$

The proportionality constant Q is known as the thermoelectric power(thermopower) or the Seebeck coefficient. For an extrinsic semiconductor, the temperature dependence of the thermopower is

$$Q_e = -\frac{k}{e} \left(\ln \frac{N_c}{n} + r_e \right) = -\frac{k}{e} \left[\frac{E_c - E_F}{kT} + r_e \right], \quad (3.7)$$

$$Q_h = +\frac{k}{e} \left(\ln \frac{N_v}{p} + r_h \right) = +\frac{k}{e} \left[\frac{E_F - E_v}{kT} + r_h \right]. \quad (3.8)$$

Table 5: Various scattering mechanisms of charge carriers and temperature dependence of mobility.

Scattering Mechanism	Mobility
Acuostical lattice scattering	$\mu \sim T^{-\frac{3}{2}}$
Optical lattice scattering	$\mu \sim (e^{\frac{\theta_l}{T}} - 1)$
Ionized impurity scattering	$\mu \sim T^{\frac{3}{2}}$
Neutral impurity scattering	$\mu \sim \text{temperature-independent}$

The r_h and r_e are transport constants, which depend on the scattering mechanism. When both of holes and electrons contribute to conduction,

$$Q = \frac{\sigma_e Q_e + \sigma_h Q_h}{\sigma_e + \sigma_h} . \quad (3.9)$$

The transport constants are listed in table 6.

Hall mobility in the extrinsic range is defined as

$$\mu_H = R\sigma , \quad (3.10)$$

where R is the Hall coefficient. In an n-type semiconductor, the Hall coefficient is written as

$$R = -\frac{r_H}{ne} , \quad (3.11)$$

where the Hall factor, r_H , depends on the scattering mechanism ^[40]. The Hall factor is

$$r_H = \frac{3\pi}{8} = 1.18, \quad \text{for accoustic lattice scattering,} \quad (3.12)$$

$$r_H = \frac{315\pi}{512} = 1.93, \quad \text{for ionized impurity scattering.} \quad (3.13)$$

Table 6: Transport constants for different scattering mechanisms [39].

Scattering mechanism	r
acoustical lattice scattering	2
ionized impurity scattering	4 (or 3.2)
polar scattering	3
neutral impurity scattering	2.5

In the above equations, the order of magnitude of r_H is 1. Therefore, when the value of the drift mobility is not available, the Hall mobility may be used in investigating the conduction mechanism of the material.

If both electrons and holes are present, the expressions for the Hall coefficient is

$$R = \frac{r_H}{e} \frac{-n\mu_e^2 + p\mu_h^2}{(n\mu_e + p\mu_h)^2} . \quad (3.14)$$

For a magnetic conductor, there is an anomalous Hall effect superposed on the ordinary Hall effect in the temperature region below the Curie point. The Hall resistivity is written as^[41]

$$\rho_H = R_0 B + R_s M , \quad (3.15)$$

$$\frac{\rho_H}{\rho} = \mu_H B + \frac{R_s}{\rho} M , \quad (3.16)$$

where R_0 is the normal Hall coefficient, R_s is the anomalous Hall coefficient, B is the magnetic field, M is the magnetization and ρ is the resistivity.

In some magnetic semiconductors, the electrical properties are strongly influenced by the magnetic properties. Such an interaction can be caused by various

mechanisms, *e.g.* exchange splitting of the bands or spin disorder scattering influencing the mobility. For YIG, however, the electrical properties are influenced very little by the magnetization.

3.2.2 Large Polaron Band Conduction

The mobilities of charge carriers in YIG are small, on the order of $0.1\text{cm}^2/\text{Vsec}$. Therefore, the charge carriers are regarded as polarons. If the lattice distortion induced by the charge carrier extends over distances larger than the lattice constant, the large polaron band model can be applied. In this case, there is a lower limit for the drift mobility^[38].

$$\mu = \frac{e\tau}{m^*}, \quad (3.17)$$

$$\mu \geq 5 \left(\frac{m_e}{m^*} \right)^{\frac{1}{2}} \left(\frac{300}{T} \right)^{\frac{1}{2}}, \quad (3.18)$$

where m^* is the effective mass of the polaron and τ is the momentum relaxation time. Larsen *et al*^[17] estimated the lower limit of the mobility for large polaron to be about $1\text{cm}^2/\text{Vsec}$. The values of N_c and N_v can be determined from equations 3.4 and 3.5 interpreting m_e^* and m_h^* as the corresponding effective masses of polaron respectively. The temperature dependence of the mobility in table 5 does not change for each scattering mechanism.

At high temperatures, where accoustic lattice scattering is a dominant scattering mechanism, $N_c\mu_e$ is temperature independent and the temperature dependence of the conductivity for the band conduction is

$$\sigma = ne\mu_e \propto \exp\left(-\frac{E_c - E_F}{kT}\right) \quad (3.19)$$

for n -type semiconductor. However, the temperature dependence of conductivity

will be different if a different scattering mechanism is dominant, e.g. in a lower temperature range.

Equations 3.7 and 3.8 for thermopower also apply to the large polaron band conduction with the corresponding changes for the effective masses. The transport constants r for the Seebeck coefficients are about 2 in the large polaron model.

3.2.3 Small Polaron Hopping Conduction

In a crystalline *element*, there is a sharp condition for polaron formation to occur. But in ionic solids, there will always be some deformation of the surroundings for a carrier, so that some self-trapping is always possible. If the interaction between the charge carrier and the lattice is strong and the band is narrow, the charge carrier can be trapped in its own self-generated polarization field in the ionic lattice. This is the case of the small polaron, where the charge carrier becomes localized within a radius close to the lattice constant.

At low temperatures, it behaves like a particle with enhanced effective mass and a mean free path l tending to infinity as the temperature tends to zero. In this case, small polaron band conduction prevails.

The small polaron is strongly scattered by phonons. At a temperature near $\frac{1}{2}\Theta_D$, where Θ_D is the Debye temperature, l becomes comparable with the distance between the possible sites where charge carriers can move, and at higher temperatures thermally activated hopping sets in. For hopping conduction, the mobility has the form :

$$\mu \propto \exp\left(-\frac{W_H}{kT}\right), \quad (3.20)$$

where W_H is the hopping energy. The effective density of states in this case is twice

the concentration of the cations available at a site for the small polaron, considering the spin degeneracy. For YIG, small polaron hopping via the octahedral sites would mean $N = 8.4 \times 10^{21} \text{ cm}^{-3}$ [17].

The mobility of the small polaron is expected to be small. Bosman^[38] estimated the upper limit of the mobility as

$$\mu \ll \frac{1}{4\pi} \frac{ea^2}{\hbar} \frac{\hbar\omega_0}{kT}, \quad (3.21)$$

where a is the lattice constant, and ω_0 is the phonon frequency. In the case where $a \simeq 3\text{\AA}$ and $kT = \hbar\omega_0$, it follows that

$$\mu \ll 0.1 \text{ cm}^2/\text{Vsec}. \quad (3.22)$$

At high temperatures $T > \frac{1}{2}\Theta_D$, an approximate formula for the mobility is

$$\mu = \text{constant} \cdot \frac{1}{T^{\frac{3}{2}}} \exp\left(-\frac{U}{kT}\right), \quad (3.23)$$

where U is the activation energy of the mobility.

In crystalline materials, a characteristic of polaron motion is the difference between E_σ , the activation energy for conduction, and E_Q , that for the thermopower. For n -type material, the thermopower is expressed as

$$Q = -\frac{k}{e} \left(\frac{E_Q}{kT} + r \right). \quad (3.24)$$

It is expected that $E_\sigma = E_c - E_F + W_H$ and $E_Q = E_c - E_F$, where W_H is the hopping energy. The transport constant, r , for the small polaron is very small : $r \sim 0$.

3.2.4 Experimental Results

For a high temperature range between 600 K and 1500 K , it is well established by Larson *et al*^[17] that the conduction in YIG is due to a large polaron band conduction and the dominant scattering mechanism is acoustic phonon scattering. They

performed extensive experiments on the conductivity and the thermopower for both p -type and n -type YIG and also on the intrinsic conductivity. A p -type YIG can make a transition to an intrinsic semiconductor and even to an n -type YIG by controlling the oxygen partial pressure and creating oxygen vacancies, which act as a donor and compensate the acceptor ions in the p -type samples.

For the condition of intrinsic conduction, the equation for the conductivity,

$$\sigma = \sigma_0 \exp\left(-\frac{E}{kT}\right), \quad (3.25)$$

fits their data well with $\sigma_0 = (6.0 \pm 0.13) \times 10^3 (\Omega cm)^{-1}$ and $E = 1.43 \text{ eV}$. The temperature dependence of the band gap energy E_g is described by

$$E_g = E_g^0 + \beta T, \quad (3.26)$$

where β is a constant. The values of E_g and β are given as

$$E_g^0 = 2.86 \text{ eV}, \quad \beta = -8 \times 10^{-4} \text{ eV/K}. \quad (3.27)$$

Their analyses also gave,

$$\mu_h N_v e^{r_h} = 3.0 \times 10^{21} (\text{V sec cm})^{-1}, \quad (3.28)$$

$$\mu_e N_c e^{r_e} = 5.2 \times 10^{20} (\text{V sec cm})^{-1} \quad (3.29)$$

and

$$\beta/k + r_h + r_e = -5.4, \quad (3.30)$$

$$r_e + \ln g_e = 2.7, \quad (3.31)$$

where g_e is the g -factor of electrons. For p -type YIG, an equation similar to eq. 3.31 was not available. For the large polaron model, they had $g_e = 2$ and $r_e = 2$, which is indicative of an acoustic phonon scattering. They estimated that $N_c = 4.6 \times 10^{20} \text{ cm}^{-3}$

and $\mu_e = 0.15 \text{ cm}^2/\text{Vsec}$ at 1000 K , which is a little low for the large polaron model which predicts $\mu_e \geq 0.7 \text{ cm}^2/\text{Vsec}$. They concluded that their high temperature data favors the large polaron model.

In the temperature range below 600 K , a satisfactory interpretation has not been found yet. The resistivity of n -type Si -doped YIG is about $10^4 \Omega\text{cm}$ with activation energy near 0.3 eV . The resistivity of p -type Ca -doped YIG is down to $10^2 \Omega\text{cm}$ at 40°C with activation energies between 0.2 and 0.4 eV . In polycrystalline samples of n -type YIG, activation energies in the range of $0.5 \sim 0.9 \text{ eV}$ were also reported. No anomaly in the $\log \rho$ vs $1/T$ plots is observed at the Curie temperature in Si -doped YIG.

Measurements of thermopower for Si -doped YIG^[41] show that the activation energy, E_Q , differs from E_p which is an activation energy of the resistivity. These differences are expected in the small polaron hopping model. The Hall mobility of Si -doped YIG by Bullok and Epstein^[42] has a temperature independent value of $\mu_H \sim 0.1 \text{ cm}^2/\text{Vsec}$, but the value obtained by Ksendzov *et al*^[41] has a temperature dependence which favors a large polaron mechanism. The thermopower measured by Ksendzov *et al* shows a maximum at 250 K and decreases with increasing temperature, which leads to the interpretation that an impurity conduction occurs at low temperatures.

As described above, there are contradicting data for n -type YIG under 600 K and no agreement has been established on the conduction mechanism. For p -type YIG, it is even less clear. The data on the thermopower and the Hall mobility are very limited.

3.3 Oxygen Vacancies

Oxygen vacancies exist in every oxide crystals including yttrium iron garnet. The concentration of oxygen vacancies in YIG has been evaluated by several authors. It varied between 0.0006 and 0.03 in formula unit in as-grown single crystals, and between 0.004 and 0.01 in polycrystalline materials. From the study of local vibrational modes in the IR spectrum, Andlauer and Tolksdorf^[43] discussed that oxygen vacancies compensate Pb^{2+} , which is also an acceptor ion, and that the abundance of the singly charged oxygen vacancies is up to 20 % of the total amount of oxygen vacancies in their YIG samples. They also proposed that charge compensation of M^{2+} (a metal ion with valency +2) by O^- is not plausible.

Measurements of the photomagnetic effect and lattice constant indicate that above about 1100 K, additional oxygen vacancies are formed in the garnet lattice^[44]. Reversible weight changes of YIG during the annealing process at high temperatures and in low oxygen partial pressure were observed by Metselaar *et al*^[45]. From this thermogravimetric measurements, they obtained the oxygen vacancy concentration as a function of temperature for different oxygen partial pressures. The data are shown in fig. 10.

Oxygen vacancies act as donors according to the equilibrium reaction :

In the above equations, the Kröger–Vink notation^[46] is used, where dots indicate effective positive charges, primes indicate effective negative charges and subscripts indicate the atomic site of the defect. As can be seen in the above equations, oxygen vacancies may have three different charged states : oxygen vacancy which is empty

Figure 10: The oxygen vacancy concentration $[V_O]$ in cm^{-3} as a function of the reciprocal temperature, at four different values of the partial oxygen pressure : + 10^{-1} atm , o 10^{-2} atm , x 10^{-3} atm , □ 10^{-4} atm . After Metselaar and Huyberts^[45].

($V_{\ddot{O}}$), oxygen vacancy which has one captured electron ($V_{\dot{O}}$), oxygen vacancy which has two captured electrons (V_O). The energy levels of oxygen vacancies are also shown in Fig. 9.

3.4 Effects of Surface Layer

As grown samples of YIG, either n -type or p -type, have a surface layer of higher resistivity which has a thickness of the order on 300 Å^[47]. For example, a sample of YIG which was grown by Liquid Phase Epitaxy with a thickness 5 μm , may have a surface layer for which the resistance is 10 times as high as that of the bulk. This means that the surface layer has a resistivity which is on the order of 10^3 times that of the bulk.

When a voltage is applied to a sample, the surface layer usually shows a transient current which drops rapidly at a time scale of 1 $msec$ and continues to decrease for a period as long as 1000 sec . This phenomenon is known to be due to the surface layer but not due to the non-ohmic contact.

The thickness of the surface layer can be reduced by chemical etching with acids or by ion-milling, but a surface layer with different characteristics from the bulk can not be removed completely. It always exists in YIG samples.

Another characteristic of the surface layer is the fast diffusion of oxygen vacancies along the surface layer^[48]. The surface layer can easily be reduced or oxydized at a low temperature of 250°C, while reduction of oxidation of the bulk occurs above 900°C. A diffusion distance of oxygen along the surface layer, $\sim 0.5 mm$ in 25 hour at 250°C has been observed^[49].

It is quite probable that the above characteristics of the surface layer masked the bulk properties of the YIG samples. Sintered polycrystalline samples of YIG usually have even thicker surface layer at the grain boundary with higher concentrations of impurities, which are expected to be compensated as well.

3.4.1 Two Layer Model

Space-charge-limited current at the surface layer was first analyzed in polycrystalline YIG samples by Larson and Metselaar^[14]. They analysed their data with the assumption that there exist a thin surface layer with higher resistivity at the grain boundaries. Their data and theoretical fits are shown in Fig. 11(a). The equivalent circuit of the model is also shown in Fig. 11(b).

The surface layer which has a similar magnitude of resistance to that of the bulk is thinner than the bulk by a factor of $\frac{1}{100}$. Therefore, the electric field in the surface layer is much higher than that in the bulk. Furthermore, the surface layer has lower concentration of charge carriers at thermal equilibrium. Over a certain limit of applied voltage, the electric field in the surface layer exceeds the highest limit of ohmic range and injection of excess charge carriers occurs in the surface layer.

A simple description of the space-charge-limited current in n-type material is

$$n > n_0 , \quad (3.34)$$

$$J \propto V^\alpha, \quad \alpha > 1 , \quad (3.35)$$

where n_0 is the density of electrons at thermal equilibrium. Space charge limited current may have a different functional dependence of current vs applied voltage depending on the energy distribution of traps in the material.

(a)

(b)

Figure 11: DC I-V characteristic of polycrystalline YIG (a) and equivalent circuit diagram of the two layer model (b). After Larson *et al*^[14].

3.5 Space Charge Limited Current

The phenomenon of space charge limited current were extensively studied in 1950's for steady state currents^[50, 51], and in early 1960's for transient currents^[52]. Since then, further developments have been established^[18] and this phenomenon has served as a useful tool in investigating traps, localized states, and so on, in insulators and semiconductors.

Space charge limited current is characterized by a carrier concentration, which is higher than that in thermal equilibrium, by injection of charge carriers. For n -type material,

$$n(x) > n_0 , \quad (3.36)$$

where n_0 is the carrier concentration at thermal equilibrium. It should be noted that $n(x)$ is a function of position. Instead of a Fermi level, E_F , a quasi-Fermi level $F(x)$ should be used in describing $n(x)$ because the material is not in thermal equilibrium.

Usually, an ohmic contact for a certain type of charge carrier will be a blocking contact for another. Under a special consideration of contacts, both type of charge carriers may be injected into the material, one from each electrode. This phenomenon is called double injection. When a space charge limited current flows through a material, there exists a transient current at the beginning which approaches a steady state current. In this section, the discussion of the space charge limited current will be limited to DC steady state current of single carriers in one dimension.

Choosing a simple geometry where the cathode lies at $x = 0$ and the anode is at $x = L$. The equations which characterize this problem are

$$J = e\mu n\mathcal{E} = \text{constant} , \quad (3.37)$$

$$\frac{\epsilon}{e} \frac{d\mathcal{E}}{dx} = n - n_0 + \sum_j (n_{tj} - n_{tj,0}) , \quad (3.38)$$

$$n(x) = N_c \exp \frac{F(x) - E_c(x)}{kT} ; \quad n_{tj}(x) = \frac{N_{tj}}{1 + \frac{1}{g_j} \frac{N_j}{n(x)}} , \quad (3.39)$$

where the diffusion current is neglected. Equation 3.38 is the Poisson's equation for this problem. In the above equations, ϵ is the permittivity, J is the current density, E is the electric field, n_{tj} is the density of electrons trapped at the j th trap level, $n_{tj,0}$ is the same variable at thermal equilibrium, g_j is the degeneracy of the trap level and $N_j = N_c \exp \frac{E_{tj} - E_c}{kT}$, where E_{tj} is the energy level of the trap. These equations are subject to the boundary condition,

$$\mathcal{E}(0) = 0 . \quad (3.40)$$

As an approximation, the cathode is assumed to be an infinite reservoir of electrons available for the injection, which leads to the boundary condition.

3.5.1 The Perfect Trap-Free Insulator

This is an analog of the thermionic vacuum diode, where n_0 and all n_{tj} 's are zero. The equations for this problem are

$$\frac{\epsilon}{e} \frac{d\mathcal{E}}{dx} = n , \quad (3.41)$$

$$J = e\mu n\mathcal{E} , \quad (3.42)$$

The two equations are combined to give

$$\frac{\epsilon}{e} \mathcal{E} \frac{d\mathcal{E}}{dx} = \frac{J}{e\mu} \quad (3.43)$$

and this equation is can be integrated with the boundary condition in eq. 3.40 to give

$$\mathcal{E}(x) = \left(\frac{2J}{e\mu} \right)^{\frac{1}{2}} x^{\frac{1}{2}} , \quad (3.44)$$

$$V(x) = \int_0^x \mathcal{E}(x) dx = \left(\frac{8J}{9\epsilon\mu} \right)^{\frac{1}{2}} x^{\frac{3}{2}}, \quad (3.45)$$

$$n(x) = \frac{\epsilon}{e} \frac{d\mathcal{E}}{dx} = \frac{1}{e} \left(\frac{\epsilon J}{2\mu} \right)^{\frac{1}{2}} x^{-\frac{1}{2}}. \quad (3.46)$$

Taking $x = L$ and $V = V(L)$ in equation 3.45, the following current-voltage characteristic is obtained

$$J = \frac{9}{8} \epsilon \mu \frac{V^2}{L^3}. \quad (3.47)$$

The total injected charge can be obtained by integrating $n(x)$.

$$Q = eA \int_0^L n(x) dx = \frac{3}{2} \frac{\epsilon A}{L} V, \quad (3.48)$$

$$Q = CV, \quad C = \frac{3}{2} \frac{\epsilon A}{L}, \quad (3.49)$$

where A is the area of the crosssection. Equations 3.47 and 3.49 give an interesting interpretation. The total injected charge is proportional to V , as if it were a parallel plate capacitor with $C = \frac{3}{2} \frac{\epsilon A}{L}$. The electric field is also proportional to V so that $J \propto V^2$.

3.5.2 The Trap-Free Insulator with Thermal Free Carriers

A solid which is free of traps is represented by the equation,

$$\frac{\epsilon}{e} \frac{d\mathcal{E}}{dx} = n(x) - n_0. \quad (3.50)$$

Thermally generated electrons of concentration n_0 also contribute to the current. This equation, with equation 3.37, can be solved to give the exact analytic solution but its physical meaning cannot be readily be seen from the solution. In the following, only a qualitative interpretation will be given.

At low applied voltages, $n - n_0$ in equation 3.50 will be close to zero and the current will follow Ohm's law. At a sufficiently high voltage, the charge density

of injected carrier, $n_i = n - n_0$, will be much higher than n_0 and $n - n_0$ can be approximated by n . In this case, the current voltage characteristic will be the same as equation 3.47. In the intermediate range, a crossover from Ohmic to $J \propto V^2$ will occur at a voltage, V_X , where the total injected charge equals the thermally generated charge.

$$en_0LA = CV_X, \quad V_X = \frac{2en_0L^2}{3\epsilon}. \quad (3.51)$$

3.5.3 Single Level Traps

Traps in semiconductors are classified into two groups according to the position of their energy levels with respect to the Fermi level. Shallow traps are those with energy levels above the Fermi level and the deep traps are those below the Fermi level. For either kind of traps, the Poisson's equation becomes

$$\frac{\epsilon}{e} \frac{d\mathcal{E}}{dx} = (n - n_0) + (n_t - n_{t,0}). \quad (3.52)$$

For shallow traps with the condition $E_t - F > 4kT$,

$$n_t = \frac{N_t}{1 + \frac{1}{g} \exp\left(\frac{E_t - F}{kT}\right)} \approx gN_t \exp\left(-\frac{E_t - F}{kT}\right), \quad (3.53)$$

$$\frac{n}{n_t} = \frac{N_c \exp\left(-\frac{E_c - F}{kT}\right)}{gN_t \exp\left(-\frac{E_t - F}{kT}\right)} = \frac{N_c}{gN_t} \exp\left(-\frac{E_c - E_t}{kT}\right) = \theta, \quad (3.54)$$

where θ is a constant. Substituting equation 3.54 into equation 3.52,

$$\frac{\epsilon}{e} \frac{d\mathcal{E}}{dx} = \left(\frac{1}{\theta} + 1\right)(n - n_0) \approx \frac{1}{\theta}(n - n_0). \quad (3.55)$$

The only difference from the trap-free problem is a factor θ on the right hand side of the equation. Therefore the solution

$$J = \frac{9}{8} \theta \epsilon \mu \frac{V^2}{L^3} \quad (3.56)$$

will be valid beyond the Ohmic range. Above a certain critical voltage, V_{TFL} , all of the traps will be filled and Equation 3.52 will be reduced to that of the ideal trap free insulator for which

$$n \gg -n_0 + (n_t - n_0) , \quad (3.57)$$

$$\frac{\epsilon}{e} \frac{d\mathcal{E}}{dx} \approx n . \quad (3.58)$$

The current voltage characteristic for the case of shallow traps is shown in Fig. 12 as curve II. It also shows the I-V characteristic for deep traps. For deep traps, the intermediate stage of trap filling process does not exist and the current jumps from the Ohm's law to the trap-free V^2 law around the V_{TFL} .

3.5.4 Traps Distributed in Energy

A disordered system usually has a band tail with an unknown density of states. In that case, the band tail of localized states may be approximated with an exponential function.

$$\mathcal{N}_t(E) = \frac{N_t}{kT_t} \exp\left(\frac{E - E_c}{kT_t}\right) . \quad (3.59)$$

This equation is normalized so that the total number density of traps is N_t . T_t is a constant which characterizes the distribution. In the intermediate range of I-V characteristic, just above the Ohmic range, it is assumed that nearly all of the injected charges are trapped in the localized states, i.e. $n_{ti} \gg n_i$, where n_{ti} denotes the density of injected charges which are trapped in the localized states, and n_i denotes the density of charge carriers in the conduction band. Then, the Poisson's equation becomes

$$\frac{\epsilon}{e} \frac{d\mathcal{E}}{dx} = n_{ti}(x) , \quad (3.60)$$

Figure 12: The current-voltage characteristics of a perfect insulator and insulators with single level traps. I corresponds to the deep traps, and II corresponds to the shallow traps. The perfect insulator switches from the Ohm's law to the trap-free square law directly. After Lampert^[18].

$$n_{ti}(x) = \int_{F_0}^{F(x)} \mathcal{N}_t(E) dE, \quad (3.61)$$

where F_0 is the Fermi level in thermal equilibrium. Equation 3.61 shows the number density of the newly occupied traps by the movement of the quasi-Fermi level.

The solution of the equation shows

$$J = N_c \mu e^{1-l} \left[\frac{\epsilon l}{N_t(l+1)} \right]^l \left(\frac{2l+1}{l+1} \right)^{l+1} \frac{V^{l+1}}{L^{2l+1}}, \quad (3.62)$$

$$F(x) = kT_t \ln \left[\frac{(l+1)^2}{l(2l+1)} \frac{eN_t L^2}{\epsilon V} \left(\frac{x}{L} \right)^{\frac{1}{l+1}} \right], \quad (3.63)$$

where $l = T_t/T$. Note that l is a function of temperature. Equation 3.62 is a solution for the intermediate range of the applied voltage. Above the trap-filled limit, this system will also follow the trap-free square law.

3.5.5 Trap Filled Limit

In Fig. 12, the transition from either the Ohmic range or the intermediate range to the trap-free square law is illustrated as an abrupt change but a real transition may occur gradually. Actually, it depends on the ratio of the total number of traps to the thermally generated charge carriers. It also depends on the position of the trap level or the distribution of traps.

Regardless of the above criteria, the transition should occur at a high electric field on the order of 10^5 V/cm. However, whether it is observed or not in a certain material depends on the material properties. A competing mechanism such as heating or electrical breakdown may occur before the material reaches the region of the trap-free square law behavior.

CHAPTER IV

Modeling

4.1 Magnetic Properties

The energy of the Fe^{3+} ions in yttrium iron garnet can be expressed with the Heisenberg Hamiltonian. The exchange integrals in the Heisenberg Hamiltonian can be calculated from the experimentally determined molecular field coefficients of the two sublattice model.

In the substituted Yttrium Iron Garnets, localized canting of the spins of the iron ions occur^[4, 26]. When the level of substitution is not high, the two sublattice model can still be used in analyzing the temperature dependence of the magnetization^[25].

The samples in this experiment have some impurities which were included into the crystal structure during the growth procedure. Furthermore, they have been annealed in nitrogen atmosphere to test the effects of oxygen vacancies. As a result, they have much higher level of local disorder in the crystal structure. It is not appropriate to apply the macroscopic two sublattice model by Néel to explain the anomaly in temperature dependence of the magnetization in the Ca:YIG samples. They have local disorders which is either inherent by the growth procedure or created by the

thermal annealing .

A model of microscopic molecular field theory is proposed in this section. The relationship between the Heisenberg Hamiltonian and the macroscopic two sublattice model is also clarified.

4.1.1 Heisenberg Hamiltonian and the Molecular Field Theory

The energy of a spin S_i in a magnetic system can be expressed with the Heisenberg Hamiltonian :

$$H_i = -2 \sum_j J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B \mathbf{S}_i \cdot \mathbf{H} , \quad (4.1)$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spins on the i and j sites, J_{ij} 's are the exchange integrals, g is the Landé g -factor, μ_B is the Bohr magneton, and $\mathbf{H}$ is the external field. When an external field is applied in the z -direction, the energy of the magnetic system is

$$H = - \sum_i \sum_{j, NN} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_B H_0 \sum_i S_{iz} . \quad (4.2)$$

The free energy per formula unit of Yttrium Iron Garnet, $Y_3[Fe_2](Fe_3)O_{12}$ at $H_0 = 0$ is

$$E_{fmu} = -J_{dd}q_d n_{dd} S^2 + J_{ad}q_a n_{ad} S^2 + J_{da}q_d n_{da} S^2 - J_{aa}q_a n_{aa} S^2 \quad (4.3)$$

where q_a denotes the occupation number of spins at the a -site in formula units and n_{ad} is the number of d -site nearest neighbors of an a -site spin. For YIG, the occupation number and the number of nearest neighbors are $q_d = 3, q_a = 2, n_{dd} = 4, n_{aa} = 8, n_{da} = 4, n_{ad} = 6$ and S is $\frac{5}{2}$ for both d - and a -site iron ions. Note that $J_{ad} = J_{da}$.

The molecular field equations for the two sublattice system are

$$\mathbf{H}_d = \lambda_{dd} \mathbf{M}_d + \lambda_{ad} \mathbf{M}_a , \quad (4.4)$$

$$\mathbf{H}_a = \lambda_{ad}\mathbf{M}_d + \lambda_{aa}\mathbf{M}_a , \quad (4.5)$$

where

$$M_d = N_A q_d g \mu_B S , \quad (4.6)$$

$$M_a = N_A q_a g \mu_B S , \quad (4.7)$$

where N_A is the Avogadro's number. The free energy per mole can also be described in a different way^[28] :

$$E = -\frac{1}{2}(\mathbf{M}_d \cdot \mathbf{H}_d + \mathbf{M}_a \cdot \mathbf{H}_a) , \quad (4.8)$$

where units of M_d and M_a are magnetic moments per mole. Substituting the molecular field equations into the above equation,

$$E = -\frac{1}{2}\lambda_{dd}M_d^2 + \lambda_{ad}M_dM_a - \frac{1}{2}\lambda_{aa}M_a^2 , \quad (4.9)$$

and

$$E = N_A E_{fmu} . \quad (4.10)$$

Combining eq. 4.3, eq. 4.6, eq. 4.9 and eq. 4.10,

$$N_A J_{dd} q_d n_{dd} S^2 = \frac{1}{2} \lambda_{dd} (N_A q_d g \mu_B S)^2 . \quad (4.11)$$

From this equation,

$$J_{dd} = \frac{q_d}{2n_{dd}} N_A (g \mu_B)^2 \lambda_{dd} . \quad (4.12)$$

Similarly,

$$J_{aa} = \frac{q_a}{2n_{aa}} N_A (g \mu_B)^2 \lambda_{aa} \quad (4.13)$$

and

$$J_{ad} = \frac{q_a q_d}{q_a n_{ad} + q_d n_{da}} N_A (g \mu_B)^2 \lambda_{ad} . \quad (4.14)$$

Dionne's molecular field coefficients can be converted into exchange integrals using the above formulas :

$$J_{ad} = -5.02 \times 10^{-15} \text{erg} = -36.4K ,$$

$$J_{dd} = -2.36 \times 10^{-15} \text{erg} = -17.1K ,$$

$$J_{aa} = -1.68 \times 10^{-15} \text{erg} = -12.2K .$$

Equation 4.1 can be transformed into the molecular field equations. At $\mathbf{H} = 0$,

$$H_i = -g\mu_B \mathbf{S}_i \cdot \left(\frac{2}{g\mu_B} \sum_{j,NN} J_{ij} \mathbf{S}_j \right) . \quad (4.15)$$

The term in the parentheses is interpreted as the molecular field :

$$\mathbf{H}_i = \frac{2}{g\mu_B} \sum_{j,NN} J_{ij} \mathbf{S}_j . \quad (4.16)$$

For Yttrium Iron Garnet,

$$\langle H_{dz} \rangle = \frac{2}{g\mu_B} (J_{dd} n_{dd} \langle S_{dz} \rangle + J_{ad} n_{da} \langle S_{az} \rangle) \quad (4.17)$$

and

$$\langle H_{az} \rangle = \frac{2}{g\mu_B} (J_{ad} n_{ad} \langle S_{dz} \rangle + J_{aa} n_{aa} \langle S_{az} \rangle) . \quad (4.18)$$

Incorporating the Brillouin function, eq.(2.4), the temperature dependence of a spin at a certain site can be calculated :

$$\langle S_{iz}(T) \rangle = S_i B_{S_i} \left(\frac{S_i g \mu_B}{kT} \langle H_{iz} \rangle \right) . \quad (4.19)$$

For substituted Yttrium Iron Garnets, the spins at a certain site will have different values of n_{ij} 's. Nowic^[30] adopted this idea in explaining the substitution dependence of the magnetization for substituted YIG and for substituted Rare-Earth Iron Garnet, and achieved a limited success. He also used the model in explaining the temperature dependence of the magnetization for $\{Y_{0.75}Ca_{2.25}\}[Fe_2](Fe_{0.75}Si_{2.25})O_{12}$ qualitatively.

4.1.2 Proposed Model – Microscopic Molecular Field Theory

Ca:YIG thin films grown by Liquid Phase Epitaxy have impurities such as lead and boron from the flux materials and also platinum which is dissolved into the melt from the crucible. The samples may have inherent oxygen vacancies during the growth procedure due to the substitution of Ca. Furthermore, the samples may have vacancies of iron ions.

The *Pt* impurity is known to replace Fe^{3+} ions at the octahedral site. This is an *a*-site substitution, and each *Pt* atom produces six broken *a*-*d* links for the *d*-site Fe^{3+} ions. The Platinum atoms in the crystal are assumed to be diamagnetic. This will be discussed in Chapter VI.

The anomaly of the temperature dependence of the magnetization in Ca:YIG indicates that there exists a kind of ferromagnetic superexchange in the substance. In our formulation, it is assumed that the ferromagnetic superexchange is mediated by the singly charged oxygen vacancy ($V_O^\cdot$). If it is due to the other mechanism, i.e. via Fe^{4+} or O^{2-} , a minor correction will be needed.

There exist two kinds of oxygen vacancies in Ca:YIG. One is the empty oxygen vacancy which is denoted by $V_O^\cdot$ in the Kröger-Vink notation, and the other is $V_O^\cdot$ which has one captured electron. Because each O^{2-} ion contributes to only one *a*-*d* link, each $V_O^\cdot$ will break only one *a*-*d* link.

Each *d*-*d* interaction is mediated by four oxygen ions (Table 2). If there is an oxygen vacancy around a *d*-site Fe^{3+} , it may change the *d*-*d* interaction. This means that if a *d*-site Fe^{3+} ion has an oxygen vacancy of any kind, one of its four *d*-*d* interaction should be affected. The effects of $V_O^\cdot$ and $V_O^\cdot$ will be different. These

effects will also be included in our formulation.

First, the molecular fields at the normal d -site and a -site are described as

$$H_{dN} = \frac{2}{g\mu_B} \{4J_{dd}S_{dAv} + 4J_{ad}S_{aAv}\}, \quad (4.20)$$

$$H_{aN} = \frac{2}{g\mu_B} \{6J_{ad}S_{dAv} + 8J_{aa}S_{aAv}\}, \quad (4.21)$$

where S_{dAv} and S_{aAv} denote the average spins of all the different d -sites and all the different a -sites respectively. In the above equations, H_{dN} and H_{aN} are used rather than $\langle H_{dN} \rangle$ and $\langle H_{aN} \rangle$ for simplicity.

Next, the d -site Fe^{3+} ions which have different sets of nearest neighbors will be considered. The molecular field at the Fe^{3+} ion at the d -site which has one ferromagnetic a - d link due to $V_{\dot{O}}$ is

$$H_{dI} = \frac{2}{g\mu_B} \{[3J_{dd} + (J_{dd} + \Delta J'_{dd})]S_{dAv} + (3J_{ad} + J_I)S_{aAv}\}, \quad (4.22)$$

where J_I denotes the exchange integral for the ferromagnetic superexchange mediated by $V_{\dot{O}}$, and $\Delta J'_{dd}$ denotes the change in d - d interaction due to the $V_{\dot{O}}$. Depending on the strength of J_I , the Fe^{3+} ion at this site may be inverted, i.e. flipped over in the opposite direction, at low temperatures. The molecular fields at two different d -site Fe^{3+} ions with single broken link are

$$H_{dA} = \frac{2}{g\mu_B} \{4J_{dd}S_{dAv} + 3J_{ad}S_{aAv}\}, \quad (4.23)$$

$$H_{dV} = \frac{2}{g\mu_B} \{[(3J_{dd} + (J_{dd} + \Delta J''_{dd}))S_{dAv} + 3J_{ad}S_{aAv}\}, \quad (4.24)$$

where $\Delta J''_{dd}$ denotes the change in the d - d interaction due to $V_{\ddot{O}}$. d -site Fe^{3+} ions with two broken a - d links may also exist with appreciable probability.

$$H_{dAA} = \frac{2}{g\mu_B} \{4J_{dd}S_{dAv} + 2J_{ad}S_{aAv}\}, \quad (4.25)$$

$$H_{dVA} = \frac{2}{g\mu_B} \{[(3J_{dd} + (J_{dd} + \Delta J''_{dd}))S_{dAv} + 2J_{ad}S_{aAv}\}, \quad (4.26)$$

where H_{dAA} denote the molecular field at the d -site which has two broken links by a -site substitutes. Likewise, H_{dVA} represent the d -site field with one $V_O^{\cdot\cdot}$ and one substitute at the a -site. There may exist Fe^{3+} ions which have one $V_O^{\cdot\cdot}$ and one $V_O^{\cdot}$ at their a - d links, or two $V_O^{\cdot}$'s at their a - d links, and so on, but the cases with small probability were not included in this formulation.

The Fe^{3+} ions at the a -site may also have a disorder around them. Then,

$$H_{aV} = \frac{2}{g\mu_B} \{5J_{ad}S_{dAv} + 8J_{aa}S_{aAv}\}, \quad (4.27)$$

$$H_{aA} = \frac{2}{g\mu_B} \{6J_{ad}S_{dAv} + 7J_{aa}S_{aAv}\}, \quad (4.28)$$

where H_{aV} or H_{aA} denote the molecular fields at the a -site Fe^{3+} ions which have single broken a - d links or single broken a - a links respectively.

In the above formulation, only the Fe^{3+} ions with single abnormal link are considered, except in equation 4.25 and 4.26. The density of the lattice imperfections are not high in this experiment, thus only the first order perturbation is considered with the two exceptions for H_{dAA} and H_{dVA} .

Let f_{di} and f_{aj} be the contents of a certain Fe^{3+} ions, in formula unit, at the d -site and a -site respectively. Then the average spins, S_{dAv} and S_{aAv} can be calculated as the following :

$$S_{dAv} = \frac{1}{3 - V_d} [(3 - V_d - \sum_i f_{di})S_{dN} + \sum_i f_{di}S_{di}], \quad (4.29)$$

$$S_{aAv} = \frac{1}{2 - V_a} [(2 - V_a - \sum_j f_{aj})S_{aN} + \sum_j f_{aj}S_{aj}], \quad (4.30)$$

where S_{di} or S_{aj} denotes the spin (statistical mean) at a certain d -site or a -site respectively, and V_d and V_a denote the contents of vacancies or substitutes in d - and a -site respectively.

A spin is related to its molecular field by the Brillouin function :

$$S_{di}(T) = SB_S\left(\frac{Sg\mu_B}{kT}H_{di}\right), \quad (4.31)$$

$$S_{aj}(T) = SB_S\left(\frac{Sg\mu_B}{kT}H_{aj}\right). \quad (4.32)$$

In the above equations, $S = \frac{5}{2}$. If Fe^{4+} is the origin of the ferromagnetic a - d interaction, the corresponding change to the spin values in equation 4.31 should be made.

Finally, the total spin per formula unit and the magnetic moment per mole can be calculated,

$$S_{total} = (3 - V_d)S_{dAv} - \frac{1}{5}f_{dI}S_{dI} + (2 - V_a)S_{aAv}, \quad (4.33)$$

$$M_{total} = N_A g \mu_B S_{total}, \quad (4.34)$$

where N_A is the Avogadro's number and μ_B is the Bohr magneton. The term $-\frac{1}{5}f_{dI}S_{dI}$ is included to take into account the paramagnetic spin of the electron in V_O . Because the distance of the O^{2-} ion to the d -site Fe^{3+} ion is closer than the $O^{2-}-Fe^{3+}$ (a -site) distance (table 2), it is assumed for an approximation that the electron in V_O is also more closely linked to the d -site Fe^{3+} ion so that its spin direction is antiparallel to that of the d -site Fe^{3+} .

The equations from 4.20 to 4.32 are simultaneous nonlinear equations. The other difficulty in applying the above formulas to experimental data is that the magnetization is a smooth function of temperature, so a deliberate choice on the number of equations and the number of parameters is needed to get the best fit to the experimental data.

4.2 Charge Dynamics in Ca-substituted YIG

It is a well known fact that oxygen vacancies always exist in an oxide crystal, but it is nearly impossible to determine the accurate concentration of oxygen vacancies with any experimental tool. In most of the cases, the amount of oxygen vacancies are comparable to or less than the systematic error of the experimental tool, such as EPMA and so on, which has an accuracy on the order of 1% of the oxygen content.

It was found that the amount of oxygen vacancies is closely related to the charge balance inside the crystal. Thus, we propose a systematic way of testing the origin of the ferromagnetic superexchange, and the dominant mechanism for the charge compensation in p -type YIG.

4.2.1 Ca-substituted YIG

In writing the formula of Ca:YIG, many authors wrote it simply as

$$\{Y_{3-x}Ca_x\}Fe_5O_{12} \quad (4.35)$$

because the content of oxygen vacancies was unknown. Another expression might be

$$\{Y_{3-x}Ca_x\}Fe_5O_{12-\frac{x}{2}} \quad (4.36)$$

considering that CaO supplies one O^{2-} ion per Ca^{2+} ion during the crystal growth, whereas Y_2O_3 supplies 1.5 O^{2-} ions per Y^{3+} ion.

No perfect crystal exists. Even in pure YIG, oxygen vacancies are formed. Therefore, the formula of Ca:YIG should be written in the following way :

$$\begin{aligned} & \{Y_{3-x}Ca_x\}Fe_5O_{12-\frac{x}{2}-z} + \left(\frac{1}{2}x + z\right)(\text{oxygen vacancy}) \\ & = (3-x)\left(\frac{1}{2}Y_2O_3\right) + \frac{5}{2}Fe_2O_3 + xCaO - z\left(\frac{1}{2}O_2\right) \end{aligned} \quad (4.37)$$

The total content of oxygen vacancies is $w = \frac{1}{2}x + z$, depending on how many oxygen atoms are added or subtracted during the crystal growth. Whether $z > 0$ or $z < 0$ for as-grown samples has not been confirmed by experiment. The possibility of taking out or adding only O^{2-} ions is ruled out by the charge neutrality of the crystal.

Another aspect of adding or subtracting oxygen atoms is

Removing an oxygen atom leaves two electrons in the crystal. On the other hand, adding one neutral oxygen atom results in a deficiency of two electrons inside the crystal. The valency of the oxygen vacancies may also change as the following :

Fig. 13 shows the content of various charged centers in $Ca_{1.0}:YIG$. The content of various charged centers are plotted as a function of w , which is the total amount of oxygen vacancies. Though such a high substitution is not possible, 1.0 formula unit(fmu) of Ca -substitution is assumed for the purpose of illustration.

Consider the diagram starting from $w = 0.5$. According to equation 4.37, this point corresponds to $z = 0$. At this point, all the oxygen vacancies will be $V_O^{\bullet\bullet}$. For the following arguments, the content will be expressed in formula unit. Moving to the left of the graph from this point, adding oxygen atoms, z varies from 0 to -0.5 so that the number of $V_O^{\bullet\bullet}$ decrease from 0.5 to 0 and the deficiency of electrons will vary from 0 to 1. The deficiency of electrons may result in the presence of either Fe^{4+} or O^- . It means the creation of those charged centers from 0 to 1 in fmu as w varies from 0.5 to 0.

Figure 13: The contents of various charged centers in $Ca_{1.0}:YIG$: (a) O^- or Fe^{4+} ions, (b) $V_O^{\bullet\bullet}$, (c) $V_O^{\bullet}$, and (d) V_O . w denotes the total amount of oxygen vacancies, and V_O , $V_O^{\bullet}$, $V_O^{\bullet\bullet}$ denote neutral (2 electrons), singly positive(1 electron) and doubly positive(empty) vacancies respectively.

Moving to the right from $w = 0.5$, i.e. taking oxygen atoms out from the crystal, the number of electrons left inside the crystal varies from 0 to 1.0 as w varies from 0.5 to 1.0. The energy level of V_O with two electrons is much higher than that of $V_O^\cdot$ with only one electron due to the mutual interaction of the two electrons. Therefore, the extra electrons will fill up $V_O^{\cdot\cdot}$ until all the $V_O^{\cdot\cdot}$ are converted to $V_O^\cdot$. This procedure will continue until w reaches 1.0. V_O is not produced during this process. Over the limit of $w = 1.0$, the number of $V_O^\cdot$ will stay constant and the number of V_O will begin to rise.

As discussed in Chapter 2, the localized ferromagnetic superexchange may be due to either Fe^{4+} or O^- ions. These cases are only possible for $w < 0.5$. On the other hand, if a sample with $w > 0.5$ shows the anomaly, the mechanism of the ferromagnetic superexchange will be due to $V_O^\cdot$. At $w = 0$, there will be no such exchange interaction and the anomaly of magnetization at low temperatures would not be observed.

It should be noted that there is a basic difference between the Fe^{4+} and the O^- models. Fe^{4+} should have four ferromagnetic $a-d$ linkages, whereas O^- ion serves for only one $a-d$ linkage among the four d -site Fe^{3+} ions.

Whether the as-grown crystals have w smaller than 50 % of the Ca content or not, taking out oxygen atoms and observing the corresponding change may give a clue to the mechanism for the anomaly in Ca:YIG. The content of oxygen vacancies can be increased by annealing the crystal in vacuum or in N_2 atmosphere at high temperature, i.e. by reducing the sample. An observation of the reverse process is expected to be more difficult. It is known that the content of oxygen vacancies does not decrease easily by annealing in oxygen atmosphere^[43].

4.2.2 Charge Compensation in *p*-Type YIG

Ca^{2+} is substituted into the dodecahedral site (*c*-site). The normal valency of *c*-site is +3, which is considered to be neutral in the Kröger-Vink notation. By this notation, Ca^{2+} ion is expressed as Ca' , which means singly negative. Fe^{4+} ion can also be written as Fe' . Because Ca' ion causes a charge unbalance, it may be either balanced by one of its neighbors or it may keep its valency just as the donors and acceptors do in silicon at low temperatures.

It should be pointed out that YIG is an ionic crystal, while silicon is a covalent crystal. An acceptor ion in silicon, e.g. B^{3+} , keeps its valency at low temperatures with one missing bond. If it catches a thermally excited electron from the valence band, it completes the four covalent bonds with its neighbors. The energy level of this excited electron is identified as the acceptor level, which is close to the valence band of silicon^[53].

In ionic crystals, the bonding originates from the electrostatic forces between ions with closed shell. Thus, Ca^{2+} ion in the Y^{3+} ion's site should be balanced by some other charged center. Though Ca -doped YIG is known as *p*-type, it is evident that Ca^{2+} ion cannot serve as an acceptor for itself. A negative Ca' ion cannot capture an electron as an acceptor does in silicon.

Ca' may be balanced by the formation of Fe' or Fe^{4+} as many authors have assumed. However, if Ca' is coordinated with either $V_O^{\bullet\bullet}$ or $V_O^{\bullet}$ among its 8 nearest neighbor O^{2-} ions, it can be charge-compensated at a closer distance. Moreover, $V_O^{\bullet\bullet}$ can compensate two Ca' ions globally. The distance of $Y^{3+}-O^{2-}$ link is 2.37 Å or 2.43 Å, whereas the distance of $Y^{3+}-Fe^{3+}$ linkage varies from 3.09 Å to 3.79 Å. If the as-grown samples lie in the range of $w > x/2$ (refer to equation 4.37), the dominant

mechanism for the charge compensation will be due to oxygen vacancies.

Even though Ca^{2+} does not serve as an acceptor for itself, Ca:YIG is p -type. The activation energy of conduction has been reported in the range of $0.2 \sim 0.4 eV$. Therefore a picture is needed to identify the energy level of an acceptor. The trapping center of the excited electron may be the Fe^{4+} ion which is associated with Ca^{2+} [15]. However, $V_O^{\bullet\bullet}$ can also trap an electron. The energy level of $V_O^{\bullet\bullet}$ in Fig. 9 is too high to be an acceptor level, but the energy level of $V_O^{\bullet\bullet}$ will depend on the number and the kinds of its nearest neighbor. In YIG, an O^{2-} ion is coordinated with two Y^{3+} ions, one d -site Fe^{3+} ion and one a -site Fe^{3+} ion. The energy level of $V_O^{\bullet\bullet}$ which is coordinated with, and compensates the Ca^{2+} ion will be different from that of $V_O^{\bullet\bullet}$ with Y^{3+} ion, which is neutral within the concept of Kröger and Vink.

Thus, the mechanism for the charge compensation, the identification of the acceptor level, and the origin of the superexchange are closely related. Through this experiment for the correlations between oxygen vacancies and the magnetic and the electrical properties, a certain answer to the above questions is expected.

CHAPTER V

Experiment

5.1 Crystal Growth

The samples of Yttrium Iron Garnet(YIG) thin films were grown by Liquid Phase Epitaxy on a substrate of Gadolinium Galium Garnet(GGG). The flux materials are PbO and B_2O_3 . The composition of the melt for growing Ca:YIG samples are shown in table 7.

Before weighing, the chemicals were dehydrated by annealing between $200^\circ C$ and $400^\circ C$ in air. The samples are grown in oxygen atmosphere with O_2 flow. The inner diameter of the furnace was $6.9cm$ and the flow rate of oxygen was $0.9\ l/min$. The melt was homogenized at 1050° , being stirred with a rotating platinum stirrer at $30rpm$ for an hour. After homogenization, the temperature of the melt was lowered to the stand-by temperature at $980^\circ C$. When the substrate was ready, the temperature of the melt was lowered to the growth temperature, which ranged from $950^\circ C$ to $880^\circ C$.

The saturation temperature of the melt was measured by dipping small pieces of substrate and observing the crystalization on the surface of the substrate. The

Table 7: Composition of melt for the growth of Ca:YIG samples.

Chemical	mol %	wt %
Y_2O_3	0.522	0.565
Fe_2O_3	10.440	7.988
B_2O_3	4.743	1.582
PbO	83.950	89.773
CaO	0.345	0.093

saturation temperature of the melt with the composition in table 7 was $976 \pm 1^\circ C$.

The procedure of controlling the temperature, as a function of time, of the 3-zone electric tube furnace is shown in Fig. 14. The long term stability of the temperature inside the melt was better than $1.2^\circ C$ and the short term fluctuation of temperature, e.g. for 10 minutes, was less than $0.3^\circ C$. The temperature uniformity inside the melt is $\pm 0.5^\circ C$ along the depth, $0.8cm$, of the melt, of which the weight of the batch was $100g$. A platinum crucible was used, and the substrate holder was also made of platinum.

The thin films of YIG were grown for $2 \sim 10 min$. During the growth, the sample was rotated at $30 rpm$. At the end of each growth, The sample was raised quickly to just over the surface of the melt, and turned rapidly at $400 rpm$ to drop off the remaining melt from the sample surface. If a drop of melt remains on the surface of the sample, crystal growth proceeds further inside the melt drop so that the thickness uniformity gets worse. After the growth, the sample was cleaned in boiling acid, which is a diluted solution of nitric acid and acetic acid. The volume ratio of constituents of the solution was $H_2O : HNO_3 : CH_3COOH = 2 : 1 : 1$.

Figure 14: The procedure of the temperature control for the furnace. The temperature at the crucible is plotted as a function of time until it reaches the growth temperature.

The growth rate depends on the growth temperature and the rotation speed during the growth. The thickness of the sample which was grown at 900°C for 5 minutes ranges from 4.2 to $4.7\ \mu\text{m}$.

The impurity contents of YIG samples which were grown by LPE depend on the melt composition and the growth temperature. The samples grown from the melt with composition in Table 7 were analyzed by Electron Probe Microanalysis (EPMA), and the impurity contents are listed as a function of growth temperature (T_g) in Table 8. As reported earlier, the lower the growth temperature, the higher the impurity contents.

Table 8: Impurity contents in formula unit as a function of growth temperature (T_g).

$T_g\ (^{\circ}\text{C})$	Ca	Pb	Pt
950	0.09	0.03	0.04
940	0.12	0.03	0.05
900	0.20 ± 0.01	0.05 ± 0.01	0.11 ± 0.01
880	0.23	0.06	0.12

5.2 Sample Preparation and Characterization

The lattice constant of the samples were measured by X-ray diffractometer. The thickness of the samples were measured by scanning electron microscope and by an optical interference method, which will be described in a later section.

The samples were cut into rectangular pieces of dimension, $(5 \pm 1) \times (5 \pm 1)\ \text{mm}^2$ for both magnetic and electrical measurements. The size of a sample was measured

with digital vernier calipers, with 0.01mm resolution. The lengths were measured at several different places and averaged. The estimated error of the area of the samples was $\pm 2\%$.

5.2.1 Lattice Constant

The lattice constant of the samples was measured with Scintag PAD V X-ray Diffractometer. Unlike powder samples, the samples are single crystal thin films grown on (111) plane of Gadolinium Gallium Garnet, so the samples should be aligned very carefully to get the diffraction spectra.

Fig. 15 shows a schematic diagram of the X-ray Diffractometer. The X-ray source is fixed, the reference plane S is scanned by the angle θ , and the detector is scanned by 2θ . Fig. 15(b) and (c) show the angular coordinates ϕ and χ of the plane S' , which is fixed at the sample holder, with respect to the reference plane. By adjusting ϕ and χ , the plane of the thin film should be aligned parallel to the reference plane accurately.

When the peak from the (888) plane of the GGG substrate could be separately identified, it was used as a standard for the alignment of the sample. The lattice constant of GGG is $12.383 \text{ \AA}$. For a sample with thickness about $7\mu\text{m}$, or for the sample of which the lattice constant is close to that of GGG, the peak from the GGG substrate could not be separately identified. In this case, the sample was aligned so that the peak from the (888) plane of YIG has a maximum intensity. The diffraction peaks from the sample are shown in Fig. 16.

After the alignment, 2θ for the diffraction peak from the (888) plane was mea-

Figure 15: Block diagram of X-ray diffractometer.

Figure 16: X-ray diffraction spectra from a sample of Ca:YIG thin film on the GGG substrate. (a) A wide angle scan, (b) peaks from the (888) planes of YIG and GGG (at 119.083°).

sured, and the lattice constant was calculated with the equations,

$$d = \frac{\lambda}{2 \sin \theta} , \quad (5.1)$$

$$a = 8\sqrt{3} d , \quad (5.2)$$

where d is the separation of the (888) plane and a is the lattice constant. The wavelength of the X-ray is 1.54060 Å. The accuracy of the lattice constant measurement was better than 0.001 Å.

5.2.2 Thickness

The thickness of the YIG thin films can be measured using a scanning electron microscope (SEM). To measure the thickness, a small piece of sample is broken into two pieces and the surface at the cross-section is observed with SEM after an appropriate coating on the surface of the sample to be observed with a conducting material, e.g. gold or carbon. The error in thickness by this method was about 5%, so an optical method was used in the later experiments.

When the optical absorption of a thin film is measured, interference peaks due to the multiple reflection inside the film are superposed to the absorption spectra. For the thin films with thickness of 4 to 5 μm , the peaks are observed in a wavelength range from about 600 to 2000 nm . The absorption curve of a Ca:YIG sample is shown in Fig. 17. The thickness of the film, t , can be calculated with the equation^[54],

$$t = \frac{1}{2} \frac{m}{n_2/\lambda_2 - n_1/\lambda_1} \quad (5.3)$$

where λ_1 and λ_2 are the wavelengths of the 0 th and m th interference peaks respectively. The starting and the ending peaks are chosen at around 2 μm and 0.8 μm respectively, where the error of the refractive indices seems to be the least using pure

Table 9: Refractive index of YIG. After McCollum *et al*^[55] and Johnson *et al*^[56].

λ (after McCollum <i>et al</i>)	n	λ (after Johnson <i>et al</i>)	n
0.509	2.416	1.4	2.209
0.546	2.363	1.6	2.200
0.589	2.329	1.8	2.194
0.633	2.310	2.0	2.188
		2.5	2.177
		3.0	2.168
		3.5	2.158
		4.0	2.148

YIG's values^[55, 56]. The refractive indices of pure YIG are listed in Table 9. At the wavelengths where the refractive indices are not available, interpolated values were used. The estimated error in measuring the thickness with this method is 1 or 2 % for samples with thicknesses of about 5 μm .

There is also an empirical formula for the refractive index of YIG^[57],

$$n_{\lambda} = 2.171 + 0.05062/\lambda^2 \quad (\lambda \text{ in } \mu m) . \quad (5.4)$$

5.2.3 Annealing

The annealing of the samples was done in a nitrogen atmosphere or in an oxygen atmosphere in a tube furnace with inner diameter of 7 *cm*. During the annealing process, an O_2 or N_2 gas flow rate of 0.9 *l/min* was used. The temperature range for the annealing was 600 ~ 1000°C in nitrogen and 900 ~ 1200°C in oxygen atmosphere.

Figure 17: Interference peaks due to multiple reflection inside the YIG thin film. The peaks are superposed to the absorption spectra.

The time for the annealing was from 6 to 8 hours.

Although fast oxygen diffusion has been reported[48, 49], it seems that the diffusion process is along the surface of YIG film. The diffusion process of oxygen through the bulk is rather a slow process. Metselaar *et al*[45] reported that a 6 hour annealing in a temperature range of $900 \sim 1400^{\circ}C$ is enough to get an equilibrium for the thermogravimetric measurements on their samples, which had been crushed into fine powders with electro-hydraulic crusher. The grain sizes of the powders were not reported.

5.3 Measurement of magnetization

A PAR model 155 vibrating sample magnetometer is used to measure the magnetization of the samples. A block diagram of the apparatus is shown in Fig. 18. The sample holder is placed at the bottom of the vibrating sample rod between the pole faces of a magnet. The sample rod vibrates at a nominal frequency of 82 Hz . Pickup coils are mounted on the magnet pole faces and a set of capacitor plates are mounted at the other end of the sample rod just under the vibrating head.

During the operation, the signal from the pickup coils is compared with the signal from the vibrating capacitor. The error signal is incorporated into a negative feedback loop which adjusts the d-c voltage applied to the capacitor plates so that the capacity-generated signal nulls the signal from the pickup coils. At equilibrium, the d-c voltage applied to the capacitor is measured. By this nulling method, the output is only dependent on the magnetic moment of the sample and is independent of the vibrating frequency and amplitude.

The magnet power supply is controlled by a computer and the data from the

lock-in amplifier and the gaussmeter are also taken by the computer. The delay time of 35 seconds between the setting of a new magnetic field and the acquisition of a data point was required to get a stable output from the magnetometer.

A liquid helium dewar of Janis model 153 was used for low temperature measurements, and a high temperature oven of PAR model 151 was used for high temperature measurements. For the control and measurement of temperature, two GaAlAs diodes were used for the low temperature measurements and a Chromel–Alumel thermocouple was used for the high temperature measurements.

For the high temperature measurements, boron nitride(*BN*) sample holder was used. The boron nitride sample holder has a shape of a cup, which was designed for powder samples. Two vertical slots were cut on the opposite sides of the cup so that it can accept and hold a sample of a rectangular shape. The dimension of the slots is about $0.7\text{mm} \times 6\text{mm}$. During the high temperature measurement, the samples annealed in nitrogen were kept in the nitrogen or helium atmosphere. The samples annealed in oxygen were measured in air.

The saturation magnetization of a sample was measured with the applied magnetic field parallel to the plane of the thin film, which is an easy direction of the magnetization. A hysteresis curve for a Ca:YIG sample on GGG substrate is plotted in Fig. 19. The signal from the substrate and the sample holder is superposed on that of the Ca:YIG film. The magnetic moment of the sample is saturated above 0.15 KG , whereas the sum of the signals from the substrate (paramagnetic) and the sample holder (diamagnetic) is paramagnetic and follow a straight line. From the intercepts by the linear regression for the range of saturation, the saturation magnetic moment is measured. The short term stability of this measurement, for a few hours, is as good as 0.5 %, while the systematic error is about 1 %. The long term stability

Figure 18: Block diagram of the vibrating sample magnetometer.

Figure 19: Magnetic moment vs applied field, at room temperature, for a Ca:YIG thin film on a GGG substrate. The signal from the substrate and from the sample holder can be figured out by linear regression for the ranges of saturation. From the intercepts, saturation magnetic moment of the sample is obtained.

for a day or two is estimated to be 1 or 2 % .

5.4 Electrical Measurement

5.4.1 Measurement of Resistivity

Fig. 20 shows the configuration of the thin film of YIG on GGG substrate with electrodes on it. For electrode materials, gold and nickel were used. It is known that gold and platinum make Ohmic contact with *p*-type YIG^[17, 36]. A necessary condition for an electrode material to have an Ohmic contact with a *p*-type semiconductor is that its work function be larger than that of the semiconductor. Nickel has a work function of about 5 eV, which is similar to the values of *Pt* or *Au*, and the I-V characteristic of the samples with *Ni* electrodes did not show any difference from those with gold electrodes. Therefore, *Ni* was chosen as a substitute for gold or platinum.

Nickel was coated on the sample surface by vacuum deposition by Joule heating. Twisted tungsten wires were used as a heater. The current through the heater during the deposition was about 55 A. Use of a flat boat with high current of about 200 A was avoided to prevent the sample from the possible heating and the annealing in vacuum.

A mask was used for the vacuum coating to provide the geometry of the electrode pads. The mask was made of a copper plate which has two square holes of $4 \times 4\text{mm}$ with sharp edges. A tiny wire with thickness between 25 and 100 μm was put across each of the square holes so that the wire divides each hole in half. The wire was attached to the sample side of the mask so that the wire would be kept parallel and close to the sample surface. A sharp image of the wire could be obtained at the edges

of the deposited material with the above design. For most of the samples, the distance between the electrode pads was about $70\ \mu\text{m}$ and the length of the gap between the electrode pads was $4\ \text{mm}$ following the dimension of the mask.

For the measurement of the resistivity, the sample was placed on the cold finger using vacuum grease for a thermal contact, and kept in a vacuum in the range of 10^{-6} torr . An Air Products model LT-3-110 helium refrigerator with adjustable helium flow was used. The temperature difference between the YIG film and the cold finger is estimated to be less than $0.5\ \text{K}$ and the temperature stability of the cold finger is about $\frac{1}{100}\ \text{K}$. A Keithley K181 Nanovoltmeter was used for voltage measurement and a Keithley K617 Electrometer was used as a voltage source and also as an ammeter. The control of the voltage source and data acquisition were done by a computer through GPIB interfaces. I-V characteristics of a sample at different temperatures were measured down to $140\ \text{K}$, where the resistance of the sample is very high. The data were analyzed to get the resistances of the bulk and of the surface layer separately.

The leakage current of the apparatus was measured at different conditions, and is shown in Table 10. The second column of the table, $I_{l,out}$, was measured by disconnecting the plug of the triaxial cable from the outlet of the cryostat : it represent the leakage current outside the cryostat. Accordingly, it was measured at room temperature and is independent of the sample temperature. The third and the fourth columns represent the leakage current of the whole system, including the wiring at the cold finger. The lowest temperature for a reasonable data set can be determined referring to the data of a sample and to this table.

Fig. 20 also illustrates the surface layer of YIG film and the equivalent circuit diagram for the two-layer model. Fig. 21 shows typical I-V characteristics for a

(a)

(b)

Figure 20: Sample configuration with electrodes on it (a). The surface layer is illustrated in the diagram. The equivalent circuit diagram is also shown in (b).

Table 10: Leakage current through the apparatus for measuring I-V characteristics.

V(volts)	$I_{l,out}(A)$ (295 K)	$I_{l,total}(A)$ (300 K)	$I_{l,total}(A)$ (260 K)
1	3.3×10^{-14}	1.3×10^{-13}	4.7×10^{-14}
10	4.8×10^{-14}	1.1×10^{-12}	1.2×10^{-13}
100	2.5×10^{-13}	1.0×10^{-11}	8.8×10^{-13}

sample which has a thick surface layer. The curves are characterized with three different regions. The first is the range of low applied voltages which looks like an Ohmic range and has a slope of about 1.02. The second is an intermediate range of applied voltage with variable slopes. The third is a range of high applied voltage, which seems to have a larger slope than the ohmic range. In the first region, the resistance of the surface layer dominates and the slope, the total resistance, is mostly due to the surface layer. This phenomenon is common to samples having a thick surface layer. In the third region, injected space charges to the surface layer reduce the resistance of the layer greatly and the resistance of the bulk has a dominant contribution to the total resistance. In Fig. 21, the resistance of the surface layer at low applied voltages is estimated to be higher than that of the bulk by a factor of 10.

The effects of the surface layer can be reduced by etching the surface of the YIG film^[47], but the presence of a surface layer cannot be completely removed. It seems to be an inherent property of the surface of YIG as an oxide semiconductor. If a certain sample seems to have a thick surface layer, the surface can be etched by an etchant to reduce the thickness. The best etchant for YIG is phosphoric acid. With 8.6 % H_3PO_4 solution boiling at $100^\circ C$, an etching rate of $47 \text{ \AA}/min$ was observed.

Figure 21: I-V characteristic of $\text{Ca}_{0.10}\text{:YIG}$ without any surface treatments. The resistance of the surface layer is larger than the bulk of YIG film by a factor of 10, though its thickness is an order of $\frac{1}{100}$ of the sample thickness.

Another way of reducing the surface effects is treating the sample surface in acids, which seems to be an oxidation process. The effects of the surface treatments are shown in Fig. 22. The effects of the treatments in boiling sulfuric acid and in a diluted solution of acetic acid and nitric acid at two different conditions are compared. The best surface condition was obtained with the boiling solution of nitric acid and acetic acid, which is used as a cleaning solution for the crystal growth.

The effects of the surface layer is not only the high resistance, but also a transient current which decays with a long time constant. This effect is prominent at low applied voltages under 1 volt. A time constant as long as 1000 sec was observed for a sample which had not been treated for the surface condition. With the above treatment, the transient current dropped within 1 % of its initial value in 20 seconds. For the measurement of I-V characteristics, this delay time was reflected in the computer program between the application of a voltage and the subsequent data acquisition.

5.4.2 Thermopower

When a temperature gradient exist in a semiconductor in an open circuit configuration, charge carriers accumulate at the cold end of the material and an internal field is built up to oppose further movement of the carriers,

$$\mathbf{E} = Q \nabla T , \quad (5.5)$$

where Q is the thermopower. Integrating the above formula,

$$\int_1^2 \mathbf{E} \cdot d\mathbf{r} = \int_1^2 Q \nabla T \cdot d\mathbf{r} , \quad (5.6)$$

$$\Delta V = -Q \Delta T . \quad (5.7)$$

Q is positive for p -type semiconductor, and negative for n -type semiconductor. This means that the hot end of the sample shows a lower potential for a p -type semi-

Figure 22: Effects of different surface treatments on I-V characteristics of $\text{Ca}_{0.16}\text{:YIG}$ at 300 K : (a) etched in 125°C H_2SO_4 for 100 sec, (b) treated at room temperature in diluted $\text{HNO}_3 + \text{CH}_3\text{COOH}$ solution in ultrasonic cleaner for 30 minutes, (c) treated in diluted $\text{HNO}_3 + \text{CH}_3\text{COOH}$ solution at 125°C for 2.5 hrs.

conductor, and vice versa. Even if Q is not measured as a function of temperature, measuring the sign of Q is an important tool for testing the type of a semiconductor.

For the measurement of the thermopower, the cold finger in the cryostat was made with two copper blocks. The copper blocks were separated with thin teflon plates ($t < 0.1 \text{ mm}$), and each block had a separate heater wire. A sample with a 1 mm gap between the electrode pads was prepared and tested. A reasonable value of Q was measured at 300 K , but it was impossible at 260 K due to the high resistance of the sample. However, even the samples with a $70 \mu\text{m}$ gap could be tested for the sign of Q , at 300 K , with this design of cold finger.

CHAPTER VI

Data and Discussion

The samples used in this study are listed in Table 11. All the samples were grown by LPE in this laboratory except the samples with substrate number 168012, which were grown at CNR in Italy. The samples listed in the table, except those mentioned above, were grown at 900°C from the same melt (Table 7) with rotation rate 30 *rpm*, and showed the same composition within experimental error of EPMA.

The formula for these samples can be written as

$$\{Y_{2.75}Ca_{0.20}Pb_{0.05}\}(Fe_{4.69}Pt_{0.11})O_{11.4} . \quad (6.1)$$

In converting the atomic percents from EPMA results, the sum of the contents of the ions at dodecahedral site was set to 3 because the *c*-site has the largest radius and seems to have the least amount of vacancies. The errors in iron and oxygen contents in the above formula are estimated to be about 2 % of their total amounts. The errors in the impurity contents are listed in Table 11. The content of boron, which is not included in the table, varies from 0 to 0.8 in fmol even for the samples grown at the same conditions. The variation may be due to the difficulty of detecting the signals from the light atoms in EPMA.

Table 11: The characterization of samples used in this study.

Sample	Substrate No.	Impurity Content			Thickness (μm)
		Ca	Pb	Pt	
C3,F3,R3	9104252	0.20 ± 0.01	0.05 ± 0.01	0.11 ± 0.01	4.2
D3,E3,Q3	9110033				4.6
A1	9112024				3.5
T3,U3,W3	9202121				5.0
J6,K6	168012*	0.16 ± 0.01	0.04 ± 0.01	0.01	4.3

* furnished by Inst. Sol. St. Elec. CNR, Rome, Italy.

In Equation 6.1, the sum of the d - and the a -site ions in fm_u is 4.8, for which the error is estimated to be ± 0.1 . It is less than 5 even though the error of this quantity is considered. This may be considered as an indication of the presence of the iron ion vacancies. Similar results can be found in a report by Larson^[58] for which the EPMA analysis was done for Si -doped YIG grown by LPE. If the above conversion method from the atomic percent of EPMA data to fm_u is used for their data, the sum of the d - and the a -site ions ranges from 4.79 to 4.95 in fm_u for their samples.

The samples with the same substrate number were cut from the same substrate. The samples, C3, R3, and Q3 were used for the study of the electrical properties and all of the others were used for magnetic measurements.

6.1 Magnetic Properties

6.1.1 Data

The temperature dependence of the magnetization was measured for the samples listed in Table 12. The error in measuring the volume of a sample ranges from 3 to

Table 12: Samples with different annealing conditions. The temperature dependence of $4\pi M$ was measured for these samples.

Sample	Condition	Substrate No.
D3A	as grown	9110033
D3B	1000°C, O_2 , 7hrs	
E3C	900°C, N_2 , 6hrs	
E3D	1000°C, N_2 , 7hrs	
F3E	960°C, N_2 , 7hrs	9104252

4 %. This error propagates to the error of the magnetization. For the purpose of comparison, the sample D3A was annealed successively to get D3B, E3C, and finally E3D. While loading the sample, which was annealed at 900°C in N_2 , to the high temperature setup of the magnetometer, a corner of the sample was broken so it was renamed to E3C. The broken edge was nearly perpendicular to the plane so the volume of E3C was recalibrated by measuring their masses with a chemical balance. In general, the third character in the name of a sample corresponds to the annealing condition of the sample. F3E was cut from another substrate, but the only difference is that the error in its volume may be added in comparing the magnetization.

Fig. 23 shows the measured magnetizations as a function of temperature. The as-grown sample shows the same results as curve (a) for the D3B sample within experimental error and is not plotted. Curve (b) for the E3C sample shows a slight decrease over the whole temperature range compared to curve (a) and it also shows a decrease in the slope of low temperature magnetization under 30 K. It has long been believed that oxygen vacancies will cause only minor changes to the magnetization of YIG^[57], but curves (c) and (d) for the F3E and the E3D samples show a significant change over the whole temperature range. The Curie temperature is a good measure of the strength of the exchange interaction while the zero temperature magnetization

Figure 23: The temperature dependence of the magnetization of $\text{Ca}_{0.20}\text{:YIG}$. The sample conditions are : (a) $\circ$ – annealed in O_2 at 1000°C (D3B), (b) $\bullet$ – annealed in N_2 at 900°C (E3C), (c) $\diamond$ – annealed in N_2 at 960°C (F3E), (d) $\square$ – annealed in N_2 at 1000°C (E3D). The samples were annealed for 6 ~ 7 hours at the above conditions.

Table 13: Samples annealed in oxygen atmosphere.

Sample	Substrate No.	Condition	a (Å)
T3B	9202121	1000°C, O_2 , 7hrs	12.384
U3B		1100°C, O_2 , 7hrs	12.385
W3B		1200°C, O_2 , 7hrs	12.381

is a good measure of the amount of substitution for Fe^{3+} in YIG or a reflection of the spin ordering. Fig. 23 indicates a remarkable change for the parameters mentioned above.

The lattice constant of unannealed D3A sample was measured to be 12.390 ± 0.001 Å, while the lattice constant of F3E sample (annealed in N_2 at $960^\circ C$) was 0.023 Å smaller, and the lattice constant of E3D sample (annealed in N_2 at $1000^\circ C$) was 0.032 Å smaller. The lattice constant of the GGG substrate, measured to be 12.382 ± 0.001 Å, remained unchanged by the annealing. It is interpreted that this decrease in net lattice size as the annealing temperature is increased is an indication of the creation of oxygen vacancies in the annealing process.

As a counterpart to the above experiments, a set of samples were annealed in oxygen atmosphere. The annealing temperatures were $1000^\circ C$, $1100^\circ C$ and $1200^\circ C$. The annealing conditions and the lattice constants are listed in Table 13. Instead of annealing a sample successively, the volume of the samples was recalibrated using the magnetometer. The short time reproducibility of the magnetometer for 3~4 hours is as good as 0.5%, so the method is expected to give a good calibration for the purpose of comparison.

The magnetization curves are shown in Fig. 24. Curve (a) for the T3B sample can be considered as a reference because the magnetization curve for the sample

Figure 24: The magnetization vs temperature for the $\text{Ca}_{0.20}\text{:YIG}$ annealed in oxygen atmosphere. The sample conditions are : (a) $\circ$ – annealed in O_2 at 1000°C (T3B), (b) $\bullet$ – annealed in O_2 at 1100°C (U3B), (c) $\diamond$ – annealed in O_2 at 1200°C (W3B). The samples were annealed for 7 hours at the above conditions.

annealed at 1000°C in O_2 is the same as that of the as-grown sample within experimental error as stated before. Curve (b) for the sample U3B annealed at 1100°C shows only a slight decrease from the curve (a) over the whole temperature range. Curve (c) for the sample W3B annealed at 1200°C shows an additional change, but a characteristic of this change is that the curves look like a reduction or magnification of one another along the ordinate. The Curie temperatures are nearly the same. The lattice constants in Table 13 show another feature of the oxygen annealing. The sample annealed in 1100°C does not show any change within experimental error. The change in the lattice constant of the sample annealed at 1200°C is only slightly larger than the experimental error.

The above observations result in an important interpretation that the change in the magnetization for the samples annealed in N_2 at or under 1000°C is not due to other effects than those of oxygen vacancies. On the other hand, very little change in the lattice constants and no change in the shape of the magnetization curve in oxygen annealed samples also lead to another important interpretation. The strengths of the exchange interactions do not change appreciably by the oxygen annealing up to 1200°C . A slight decrease in the magnetization can be attributed to the change of sites of Fe^{3+} ions from d -sites to a -sites. In the EPMA results in equation 6.1, the sum of the d - and the a -site ions is 4.8, which is less than 5.0. It suggests that there exist some vacancies of Fe^{3+} ions. The diffusion of iron ions may occur through these vacancies well above 1000°C . The observations support the above interpretations.

6.1.2 Magnetization and Lattice Constant

Zero temperature magnetization is a good measure of spin ordering because the effect of phonons is removed. The samples annealed in nitrogen show a dramatic change in

the magnetization at 4 K . For now, the magnetization at 4 K will be considered as the zero temperature magnetization as an approximation.

The samples have platinum substitution of 0.11 fmu at the a -site, and the corresponding effect of canting at the d -site spins can be estimated. Following Patton's model(section 2.4), the average canting angle of the d -site spins for a -site substitution by 0.1 fmu is only 0.02° . Following this model, the effect of canting is negligible. Dionne's empirical formula also gives another way of estimating the effect. Following equation 2.10, the expected change for the same substitution is a decrease of 1.1 % for the d -site magnetic moment, which corresponds to 80 G of $4\pi M$.

Table 14 shows the magnetization at 4 K for different annealing conditions. The samples are those described in Table 12, which were successively annealed. The decrease of the $4\pi M$ for E3D sample(annealed in N_2 at $1000^\circ C$) with respect to D3B is as much as 560 G. This huge change in $4\pi M$ cannot be attributed to the effect of canting. By Patton's model(section 2.4), the change in the magnetization due to canting is less than 0.1 % even for the a -site substitution up to 0.6 fmu. Therefore, the observed change in $4\pi M$ due to the nitrogen annealing can only be interpreted as an increase of the number of the inverted spins at the d -site due to a ferromagnetic superexchange.

The expected change due to the annealing in nitrogen is the increase of the content of oxygen vacancies as discussed in the last section. The increase in the total amount of oxygen vacancies corresponds to an increase of the charged oxygen vacancies, $V_O^\bullet$, or a decrease in Fe^{4+} (or O^-). Therefore, the above experimental results suggest that the dominant mechanism for the ferromagnetic superexchange is due to the singly charged oxygen vacancies, at least, for the above sample conditions.

Table 14: The magnetization and the content of inverted spins at 4 K for different annealing conditions. The number of inverted spins is expected to match the number of ferromagnetic linkages, i.e. due to $V_O^\bullet$, or Fe^{4+} , or O^- .

Sample	Condition	$4\pi M$ (G) at 4 K	Inverted spins(fmu)
D3B	1000°C, O_2	2600±20	0.03±0.01
E3C	900°C, N_2	2550	0.04
F3E	960°C, N_2	2200	0.12
E3D	1000°C, N_2	2040	0.16

In Table 14, the estimated contents of inverted spins at 4 K are also listed. The substitution of $Pt_{0.11}$ at the a -site will change $4\pi M$ to 2730 G at 0 K following Néel's model, while the pure YIG value is 2460 G corresponding to $5\mu_B$ per formula unit. However, the differences between 2730 G and the $(4\pi M)_{4K}$ values listed in Table 14 cannot be attributed solely to the inverted spins at the d -site, because there may be an unbalance between the contents of vacancies of iron ions at the d -site and at the a -site.

There is a way for estimating the content of inverted spins for the D3B sample, which was annealed in O_2 at 1000°C. In Fig. 23, the magnetization of D3B shows a maximum at about 40 K. For the proposed $V_O^\bullet$ model, the inverted spins will have an energy lower than 40 K for their ordered state, and their spin directions become random at around 40 K from that of the ordered state at 0 K. The change in $4\pi M$ for this transition is 1970 G/fmu. To get the above conversion factor, it has been assumed that the paramagnetic spin of $V_O^\bullet$ is more closely bound to the d -site Fe^{3+} ion than to the a -site Fe^{3+} and the sum of the magnetic moments of Fe^{3+} ion and the $V_O^\bullet$ is $4\mu_B$. It was already noted that the position of O^{2-} ion, where $V_O^\bullet$ is located, is closer to the d -site than to the a -site. These arguments may apply to the O^- model, although the authors of the model did not mention the temperature dependence of

the magnetization.

The arguments above do not apply to the Fe^{4+} model. In that model, the hole is localized close to the Fe^{3+} ion at 0 K to form Fe^{4+} ion and becomes delocalized at higher temperatures so that Fe^{4+} ion returns to the normal Fe^{3+} ion^[11]. The net change of the magnetic moment for this process, i.e. from zero temperature to the delocalization temperature, is $9\mu_B$ per formula unit and it corresponds to a change of 4430 G/fmu for $4\pi M$.

The content of inverted spins for the D3B sample was calculated following the arguments given above for the V_O model. It should be noted that the magnetization of pure YIG shows very little change in this temperature range, i.e. from 0 K to 40 K. If the Fe^{4+} model is followed, the content of inverted spins will be reduced by a factor of $\frac{4}{9}$. For other samples, the values of D3B sample were used as a reference and the changes from those were calculated. If a normal spin of Fe^{3+} ion with $5\mu_B$ switches to an inverted spin, the net change in the magnetic moment is $9\mu_B$ for all the three models, if the above assumption for the paramagnetic spin is followed for V_O and O^- models.

For the D3B sample which has $Pt_{0.11}$ at the a -site, there follows an interesting observation. The zero temperature $4\pi M$ by Néel's model for the above samples is 2730 G, and the zero temperature value of $4\pi M$ of D3B sample is 2600 G. If the difference is converted into the content of inverted spins with a change of $9\mu_B$ per spin, it gives 0.03 fmu. Within experimental error, it is the same as the value in Table 14, which means that the difference from the value of Néel's model is due mostly to inverted spins. This suggests that even if there exist vacancies of Fe^{3+} ions, the concentrations of the vacancies at the d -site and at the a -site are closely balanced in this sample.

Table 15: Magnetization at 4 K and lattice constant for different annealing conditions.

Sample	$4\pi M(G)$	a (Å)	Condition	Substrate No.
D3A	2610	12.390	as grown	9110033
D3B	2600	—	1000°C, O_2	
E3C	2550	—	900°C, N_2	
E3D	2040	12.358	1000°C, N_2	
C3K	—	12.389	as grown	9104252
F3E	2200	12.367	960°C, N_2	
A1A	—	12.388	as grown	9112024
A1G	2300	12.370	930°C, N_2	
J6A	2380	12.378	as grown	168012
K6D	2140	12.364	1000°C, N_2	

To investigate the correlation of the change in $4\pi M$ at 4 K to the change in the lattice constant, further experiments were done for samples having different thicknesses or with different Ca content. The results are shown in Table 15. The sample A1G which is thinner than the other samples (refer to Table 11) shows a larger change in both the magnetization and lattice constant compared to the expected values by an interpolation from the E3C and the F3E samples, considering the annealing temperatures for those. It suggests that the annealing times for the D, E, F samples which are thicker than the A samples might not have been enough to reach thermal equilibrium at their annealing temperatures. The sample K6D, which is from CNR in Italy, has lower Ca content (0.16 fmu) and even much lower Pt content (0.04 fmu) than the samples grown in this laboratory. Its change in $4\pi M$ from the as-grown state is only 240 G compared to 570 G of E3D even though both are annealed at the same temperature of 1000°C. It indicates that the amount of oxygen vacancies created by annealing is not only a function of temperature but also a function of Ca and Pt contents.

The results in Table 15 are plotted in Fig. 25. Even though the samples have different *Ca* content and thicknesses, the data points seem to lie on a straight line. If they are fitted with a straight line,

$$|\Delta(4\pi M)| = A|\Delta a| + B, \quad (6.2)$$

the result is $A = (1.8 \pm 0.1) \times 10^4 \text{ G/\AA}$ and $B = -(15 \pm 13) \text{ G}$. The intercept is close to zero, i.e., the straight line passes through the origin within experimental error. This result leads to an important interpretation. Referring to Fig. 13, increasing the total concentration of oxygen vacancies across $w = 0.5$ should result in a transition of one ferromagnetic superexchange to another. At $w = 0.5$, the number of inverted spins should be zero. If the as-grown sample lies in the range of $w < 0.5$, as the total number of oxygen vacancies increases, the number of the inverted spins will decrease at first, reach zero at $w = 0.5$ and then it will increase. If this is the case, the straight line in Fig. 25 should have a nonzero intercept. However, this is not observed within experimental error.

The above observation strongly suggests that the as-grown samples lie in the range of $w \geq 0.5$, i.e. they have charged oxygen vacancies. Redefining w as the ratio of the total content of oxygen vacancies to the sum of *Ca* and *Pb* contents, the range with $w \geq 0.5$ is where the oxygen vacancies are dominant charge compensators for Ca^{2+} and Pb^{2+} ions. Ca^{2+} and Pb^{2+} have ionic radii of 1.12 Å and 1.29 Å respectively, which are larger than the radius, 1.019 Å of Y^{3+} . Though $V_O^{\bullet\bullet}$, which is doubly positive, may compensate two Ca^{2+} ions globally, it is not expected that each $V_O^{\bullet\bullet}$ is coordinated with two Ca^{2+} or Pb^{2+} ions or combination of those as nearest neighbors because of their large radii. Therefore, other kinds of intervening compensators may exist in between $Ca-V_O^{\bullet\bullet}-Ca$ coordinations. For the purpose of charge compensation, $Ca^{2+}-V_O^{\bullet}$ seems to be more satisfactory because they compensate each other. This

Figure 25: Change of $4\pi M$ at 4 K vs change of lattice constant. The changes were calculated with respect to the as-grown sample or oxygen annealed sample at 1000°C. The samples corresponding to the data points are : (a) $\circ$ - E3D(1000°C in N_2), (b) $\triangle$ - F3E(960°C in N_2), (c) $\square$ - A1G(930°C in N_2), (d) $\diamond$ - K6D(1000°C in N_2),

may be the reason for such a large change in the amount of oxygen vacancies observed in this experiment, but not for the *Si*-substituted YIG.

In Fig. 25, the slope of the straight line passing through the origin and the data points can be found more accurately adding the origin as another point for the linear regression. The slope is

$$\Delta|4\pi M|/\Delta|a| = (1.78 \pm 0.03) \times 10^4 \text{ G}/\text{\AA} . \quad (6.3)$$

In the $V_{\dot{O}}$ model, the ratio of the change in $4\pi M$ to the change in the content of $V_{\dot{O}}$ is

$$\frac{\Delta(4\pi M)}{\Delta[V_{\dot{O}}]} = -4.43 \times 10^3 \text{ G}/fmu , \quad (6.4)$$

where $[V_{\dot{O}}]$ denotes the content of $V_{\dot{O}}$. Let $[V_{O,total}]$ denote the sum of the oxygen vacancies of different kinds, then $\Delta[V_{\dot{O}}]/\Delta[V_{O,total}] = 2$ following the arguments in section 4.2. The above equations can be combined to give the following rates,

$$\frac{\Delta a}{\Delta[V_{O,total}]} = -0.50 \text{\AA}/fmu = -1.18 \times 10^{-22} \text{\AA} cm^3 , \quad (6.5)$$

$$\frac{\Delta a}{\Delta[V_{\dot{O}}]} = -0.25 \text{\AA}/fmu . \quad (6.6)$$

The errors in the constants in equations 6.5 and 6.6 are estimated to be about 2 % .

6.1.3 Temperature Dependence of Magnetization

In the substituted YIG, the Fe^{3+} ions may have a different number of nearest neighbors depending on the local disorder. The temperature dependence of each spin will be quite different. The substitution is also accompanied by a change of lattice constant which may affect the strength of the exchange interaction. As a preliminary argument, the correlations among the degree of substitution, the change in

exchange integrals, and the lattice constant will be discussed and then the corresponding changes of the temperature dependence of each spin with different number of neighbors will be compared qualitatively.

To estimate the changes in the above characteristics, assume an a -site substitution with 0.2 fmu ($k_a = 0.1$). According to Dionne's formulae 2.12 and 2.14, the substitution will result in a change of the molecular field coefficients,

$$\Delta\lambda_{dd}/\lambda_{dd} = -0.087, \Delta\lambda_{ad}/\lambda_{ad} = -0.025. \quad (6.7)$$

According to equations 4.12, 4.13 and 4.14, the exchange integrals are proportional to the corresponding molecular field coefficients. The ratio of an exchange integral to the corresponding value of pure YIG is defined as

$$C_{ij} = \frac{J_{ij}}{J_{ij}^0}, \quad (6.8)$$

where i and j denote a - or d -site and J_{ij}^0 denotes the exchange integral of the pure YIG. With this notation, the substitution of 0.2 fmu in the a -site corresponds to $C_{dd} = 0.913$ and $C_{ad} = 0.975$.

Dionne's analysis on the a -site substitution was done for the $\{Y_{3-x}Ca_x\}[Fe_{2-x}Zr_x](Fe_3)O_{12}$ samples, for which the lattice constants were measured later as a function of substitution level by other authors^[59]. The ratio of the change of lattice constant to the substitution level is $\Delta a/\Delta x = 0.16 \text{ \AA/fmu}$. The substitution of $x = 0.2$ fmu corresponds to an increase of lattice constant, $\Delta a = 0.032 \text{ \AA}$.

To see the change of the temperature dependence of the spins at the d -site with different number of neighbors, the energies of the spins are listed in Table 16 for three different sets of C_{ij} 's for a -site substitution. Refer to Section 4.1 for the Heisenberg Hamiltonian of a spin and the values J_{ij} 's. Though Dionne's results show a decrease

Table 16: Energy of spins at 0 K with different number of nearest neighbors. The energies of the spins at the d -site for three different sets of exchange integrals corresponding to a -site substitution with 0.2 fmu are illustrated. n_{ij} denotes the number of the j -site nearest neighbors of an i -site Fe^{3+} ion. The unit of the energy is K .

n_{da}	n_{dd}	$C_{ad} = 0.97$	$C_{ad} = 1.00$	$C_{ad} = 1.03$
		$C_{dd} = 0.91$	$C_{dd} = 1.00$	$C_{dd} = 1.09$
4	4	-990	-970	-940
4	3	-1180	-1180	-1180
3	4	-550	-510	-470
3	3	-740	-720	-710
2	4	-100	-55	-5
2	3	-300	-270	-240

in the molecular field coefficients regardless of the type of the lattice constant change, i.e. for either increase or decrease, the case with larger exchange integrals than the pure YIG values is also illustrated.

The energy in Table 16 can be considered as an activation energy for the spin to change from the aligned state to a random state, under the condition that the spins at its neighbor do not change. This condition holds approximately for the spins with small ordering energy of under 100 K because the spins at its neighbor decays much more slowly. However, this interpretation does not hold for the spins with higher energies because their neighbors also change appreciably as the temperature changes. In pure YIG, the d -spins have the ordering energy of 970 K but the Curie point is 559 K . This example illustrates the situation well. However, the energies listed in Table 16 can still be used as a criterion for how fast a specific local spin becomes random as the temperature increases. It should be noted that the spin with $n_{da} = 2$ and $n_{dd} = 4$ has a very low energy, which varies appreciably as the exchange integrals change.

For a normal spin at the a -site, the absolute value of the energy is 1510 K which is much higher than that of a d -site spin because it has six a - d interactions which are the strongest among the superexchange interactions in YIG. Even if an a -site spin has one missing nearest neighbor at the d -site, the energy is still higher than that of d -site spins which means that the spin decays more slowly than that at the d -site as the temperature increases.

Applying the above arguments to the temperature dependence of $4\pi M$ in Fig. 23, a qualitative interpretation for the behavior of spins can be obtained. The low temperature behavior of D3B sample indicates that inverted spins with small exchange energy exist in this sample. The energy of the spins can be estimated to be about 40 K . For the F3E sample and E3B sample, the magnetization decreases very fast up to 100 K which points to the presence of spins with very low energy. These spins should be at the d -site and are identified as those with $n_{da} = 2$ and $n_{dd} = 4$. In most cases, the a -site spins become disordered slowly. If an ordered spin at 0 K decays and finally becomes random at higher temperature, the change in the magnetic moment is $5\mu_B$, which results in a change of $|\Delta(4\pi M)| = 2460\text{ G/fmu}$ in YIG. Using this criterion, the amount of the d -site spins with two missing a - d linkages can also be estimated.

In Fig. 26, the fitted results are shown in solid lines with the experimental results. The proposed model explains the low temperature behavior of magnetization in Ca-substituted YIG for the D3B sample(1000°C , O_2) and the E3C sample(900°C , N_2), which show the presence of inverted spins. It also explains the rapid decrease of magnetization at low temperatures for the F3E sample(960°C , N_2) and the E3D sample(1000°C , N_2), which is due to the d -site Fe^{3+} ions with two missing a - d linkages.

In Fig 27 and Fig. 28, the temperature dependences of the z -components of spins having different numbers of nearest neighbors and with different kinds of superexchange interactions are shown. For the definition of the environment of these spins, refer to Section 4.1. There are similar behaviors of the curves for the D3B and the E3D samples. Among the up-state spins, S_{dN} decreases the slowest and S_{dA} , S_{dVA} and S_{dAA} follow in that order. The behavior of S_{dV} is very close to that of S_{dA} so it is not shown in the figures. Among the down-state spins, $|S_{aA}|$ decreases the slowest and S_{aN} , S_{aV} and S_{dI} follow in that order. However, there are marked differences between the two samples. For the D3B sample, the change of inverted spin S_{dI} is much faster, at low temperatures, than those of S_{dAA} and S_{dVA} which are the spins with two missing a - d linkages. The effect of S_{dI} can be observed while the presence of S_{dAA} and S_{dVA} is hidden at low temperatures. The opposite phenomena occur for the E3D sample. A similar change in the spin ordering energy due to substitution was illustrated in Table 16. This difference originates from the change of exchange integrals, which is attributed to the change of lattice constant due to the annealing in nitrogen. This is a clear manifestation that the change in the lattice constant is correlated to the change in exchange integrals, or overlap of wavefunctions of the ions which participate in the superexchange.

As discussed earlier in Section 4.1.2, there are many parameters to be determined in this model while the experimental data show smooth curves. Therefore, most of the parameters among f_{di} and f_{aj} 's were determined from statistical arguments with EPMA data and with the $[V_O]$ obtained in the last section. First, the total content of oxygen vacancies was calculated as

$$[V_{O,total}] = \frac{1}{2}([Ca^{2+}] + [Pb^{2+}]) + \frac{3}{2}([Pt] + [V_{Fe}]) \quad (6.9)$$

where $[V_{Fe}] = [V_{Fe,d}] + [V_{Fe,a}]$ is the total content of iron vacancies, which is to be

Figure 26: The raw data and the results of the fit by the microscopic molecular field theory. The solid lines denote the fitted results with the proposed model and the marks denote the raw data. The samples are : $\circ$ - D3B, $\bullet$ - E3C, $\diamond$ - F3E and $\square$ - E3D.

Figure 27: The temperature dependence of the z -component of various spins in D3B sample.

Figure 28: The temperature dependence of the z -component of various spins in E3D sample.

estimated during the fitting procedure. It is assumed that Pt and V_{Fe} induce oxygen vacancies at one and half times their total amount because they replace Fe^{3+} which accompanies 1.5 oxygen atoms during the crystal growth procedure. Since $[V_{\dot{O}}]$ is known, $[V_{\ddot{O}}]$ is obtained as the difference between $[V_{O,total}]$ and $[V_{\dot{O}}]$.

Each $V_{\ddot{O}}$ supplies one missing a - d link and each of Pt or $V_{Fe,a}$ supplies six missing a - d links to the d -site spins. The a -site imperfections, i.e. Pt or $V_{Fe,a}$ may induce double missing a - d links to the d -site spins, but the six missing links which each of them supplies are not statistically independent. Therefore, the estimation of f_{dAA} was done in the following way. If an a -site imperfection has another a -site imperfection among its eight nearest neighbor, the pair produces two S_{dAA} 's, while if an a -site imperfection is coordinated with another among the six second nearest neighbors, one S_{dAA} results. When summing up the number of S_{dAA} 's, the effect of double counting should be considered. f_{dAA} is then calculated as

$$\begin{aligned} f_{dAA} &= \frac{1}{2} ([Pt] + [V_{Fe,a}]) \{8p_1(1-p_1)^7 \times 2 + 6p_1(1-p_1)^5\}, \\ p_1 &= \frac{[Pt] + [V_{Fe,a}]}{2}. \end{aligned} \quad (6.10)$$

f_{dVA} was used as a parameter for the F3E and E3D samples, which enables the estimation of the total content of oxygen vacancies, and hence the minimum content of $[V_{Fe}]$, but it was set to be zero for the D3B and E3C samples as an approximation. The details for the calculation of the other f_i or f_j 's are in the subroutine 'GETMFPAR' of the program in Appendix A. Actually, the $V_{\ddot{O}}$ acts as a charge compensator for other imperfections such as Ca^{2+} and Pb^{2+} ions, and possibly for Pt and V_{Fe} so that it can not be treated statistically. $[V_{Fe,d}] = [V_{Fe,a}]$ was assumed following the discussion in the last section and $f_I = [V_{\dot{O}}]$.

The important parameters obtained by the fitting, or used as known variables

are listed in Table 17. $\Delta C'_{dd}$ which is associated with V_O could not be determined so it was excluded for the fitting. $\Delta C''_{dd}$ could only be determined for the F3E sample and E3D sample, and any value in a wide range of $-0.1 < \Delta C''_{dd} < -0.3$ gave a good fit so that it was set to -0.2 . The F3E sample is from a different substrate from the other samples, so a different value for $[V_{Fe}]$ was allowed.

The values of V_{Fe} verifies, independent of the result by EPMA, that an order of 0.1 *fmu* of iron vacancies exist in the samples which were grown by Liquid Phase Epitaxy. The large value of f_{dVA} suggests that the oxygen vacancies aggregate preferentially around a certain site as the lattice shrinks.

Concerning the errors in the C_{ij} 's, an important feature of the molecular field theory should be discussed. For a data set of $4\pi M$ vs T , a unique solution of C_{ij} 's does not exist and a few different sets of C_{ij} 's may exist that give reasonable fits to the experimental data. For this reason, Dionne might have assumed that J_{aa} does not change ($C_{aa} = 1$) by the *a*-site substitution (refer to Section 2.2). Therefore, the values of C_{ij} 's which most nearly satisfy the criteria established by the Dionne's formulae and the lattice constant change (refer to Equation 6.7) upon substitution were chosen and the resulting values of C_{ij} are listed in Table 17.

The values of the C_{ij} 's are not satisfactory to the expectation that a linear relationship between the lattice constant and the exchange integrals could be obtained. It may be due to the fact that not enough number of terms were included in the formulation or due to unsatisfactory estimation for the f_{ij} 's. Oxygen vacancies may be the major compensators for negative lattice imperfections, in the sense of the Kröger and Vink notation, including *Pt* atoms and iron vacancies. Their distribution might not be statistically independent, as suggested by the interpretation of the large f_{dVA} for the E3D and F3E samples. However, the overall change of exchange integrals from

Table 17: The parameters determined by the fit with the microscopic molecular field theory.

Sample	D3B	E3C	F3E	E3D
C_{ad}	0.96	0.96	1.06	1.03
C_{dd}	0.68	0.69	1.11	1.14
C_{aa}	0.90	0.89	0.97	0.75
$ C_I $	1.655	1.668	1.71	1.71
$\Delta C''_{dd}$	-0.2	-0.2	-0.2	-0.2
f_I	0.03	0.04	0.12	0.16
f_{dVA}	0	0	0.25	0.40
f_{dAA}	0.08	0.08	0.06	0.10
$[V_{Fe}]$	0.10	0.10	0.04	0.14

the D3B sample to the E3D sample indicates an increase of the exchange integrals as the lattice constant decreases due to the creation of oxygen vacancies. Another observation is that the d - d interaction decreases by roughly 20 % with the presence of an intervening $V_O^{\cdot\cdot}$ inside the d - d linkage.

In the formulation above, Pt was assumed to be diamagnetic, which means no contribution to the magnetization of YIG. For many years, platinum has been believed to exist as Pt^{4+} in YIG^[60, 61], which is paramagnetic. However, a systematic research on the valency of platinum could not be found. Platinum atom has electron configuration of $5d^9 6s^1$. In silicon, which is a host crystal of valency +4, platinum has a valency of +1, or 0, or -1^[62, 63]. In an EPR study of Pt^- in silicon, Anderson *et al*^[64] assumes that Pt^- has an electron configuration of a platinum atom with $5d^{10}$ configuration trapped in a negatively charged vacancy. In view of the extensive studies on the platinum impurity in Si , the valency of Pt in YIG should be questioned.

6.2 Electrical Properties

I-V characteristics of the samples were measured for the Q3, R3 and C3 samples described in Table 11. The effect of the surface layer was greatly reduced in the I-V characteristics by the surface treatment described in Chapter V, but was still observed. A way of analysis was found to separate the signal of the bulk from that of the surface layer. By this analysis, the resistivity of the bulk was obtained and analyzed to investigate the conduction mechanism in Ca-doped YIG.

6.2.1 I-V Characteristics

The $\text{Ca}_{0.20}\text{YIG}$ samples which were grown in this laboratory were used for the electrical measurements. The samples were annealed in various annealing conditions described in Table 18. The samples C3K, C3L, C3M, and R3E are different pieces from the same substrate, but the samples Q3B, Q3C and Q3D are the same piece from the substrate 9110033. After the I-V characteristics of the Q3B sample were measured, the electrodes were etched away and the sample surface was etched by 500 Å to remove the possible effect of diffusion of electrode material into the surface, that may be induced by the electric field. Thereafter, the sample was annealed to get the sample Q3C. The same procedure was followed to get the sample Q3D.

The I-V characteristics were measured with applied voltages between 0.005 and 100 V in the temperature range from 300 K to 140 K. The resistance of Q3D sample was very high so that it was measured up to 330 K.

In Fig. 29, the I-V characteristics of the C3K sample are shown. The surface treatment of this sample was very good so that the I-V characteristics in this figure

Table 18: Samples with different annealing conditions.

Sample	Condition	Substrate No.
C3K	as-grown	9104252
C3L	600°C, N_2 , 8hrs	
C3M	800°C, N_2 , 6hrs	
Q3B	1000°C, O_2 , 7hrs	9110033
Q3C	900°C, N_2 , 7hrs	
Q3D	1000°C, N_2 , 7hrs	
R3E	960°C, N_2 , 7hrs	9104252

seem to be nearly Ohmic.

The I–V characteristics of Ca:YIG samples are characterized with three different regions(refer to Fig. 21) : the apparent Ohmic region at low applied voltages, the intermediate region with variable slope, and the third region at high applied voltages. The slope in the $\log I$ vs $\log V$ plot in the third region is nearly a constant which is larger than one. It suggests that the surface layer may be above the trap-filled-limit of space charge limited current. Therefore, it was assumed that the space charge limited current through the surface layer is above the trap filled limit in the high voltage region . The validity of this assumption will be confirmed if the signal from the surface layer which is separated from that of the bulk under this assumption satisfy the trap-free square law, i.e $I \propto V^2$.

The equivalent circuit diagram of the two layer model was illustrated in Fig. 20 in Chapter V. It was also assumed that the bulk of the sample is still Ohmic in this voltage range, which is fairly reasonable. The electric field inside the bulk is under $10^4 V/cm$ considering the geometry of the sample. Even if the bulk property deviates from the Ohmic behavior, it would be a minor effect compared to the surface layer

Figure 29: I-V characteristics of C3K sample at different temperatures. The I-V characteristics seem to be nearly Ohmic due to the surface treatment.

effect. Under this assumption, the voltage and the current will satisfy

$$V = V_B + V_S , \quad (6.11)$$

$$V = RI + \alpha I^{0.5} , \quad (6.12)$$

where R is the resistance of the bulk and α is a constant which depends on the total number of the traps in the surface layer. The advantage of this method is that the trap free square law holds above the trap filled limit regardless of the trap distribution. It should be noted that in the intermediate region, the slope of the $\log I$ vs $\log V$ plot depends on the trap distribution, which is not known.

Equation 6.12 was used to fit the raw data for I-V characteristics at various temperatures between 140 and 300 K, and R and α were determined. The raw data and the results of the analysis for the surface layer are shown in Fig. 30 for the Q3B sample. The three or four data points of the surface layer from the highest voltage satisfy the trap free square law, i.e. their slope is close to 2. The data for the I-V characteristics were taken before this analysis was found so no special attention was paid to the number of the data points which can be used for this analysis. The data points were taken in logarithmic voltage steps so that only three or four data points between 10 V and 100 V could be used for this analysis. However, equation 6.12 has only two parameters and the number of the available data points were three or four so the analysis could be done. The slope of the $\log I$ vs $\log V$ curve for the surface layer obtained by this analysis were between 1.9 and 2.1 in this voltage range, which supports the assumption that the surface layer satisfies the trap free square law at high voltages for the samples used in this study.

Fig. 31 shows the ratios of V_B/V and V_S/V of the Q3B sample at the same temperatures shown in Fig. 30. At the applied voltage of 10 V, only 83 % of the total voltage is applied to the bulk at 160 K. It gets even worse at higher temperatures :

Figure 30: I-V characteristics of Q3B sample which show the raw data and those of the surface layer obtained by the analysis. The three data points of the surface layer from the highest voltage show a slope close to two.

Figure 31: Voltage ratios, V_B/V and V_S/V of Q3B sample at two different temperatures. The two data points from the lowest voltage at 140 K, for each of the bulk and the surface layer, are erroneous because of the low current through the sample. For these data points, the leakage current through the apparatus is not negligible.

about 70 % out of the total voltage, 10 V, applied to the bulk at 240 K. This effect can also be seen in Fig. 30 comparing V_S with V at the same current. Generally, the ratio, V_S/V increases as the temperature increases.

Another important interpretation of the results is that the current measured at low voltages, e.g. under 1 V, reflects mostly the properties of the surface layer, but not of the bulk. This analysis explains clearly the difficulties which people have had for the studies in the electrical properties of YIG.

6.2.2 Conduction in Ca-doped YIG

The resistance of the bulk was separated from that of the surface layer as described in the last section. The resistivity of the bulk was calculated considering the geometry of the samples and shown as a function of temperature in Fig. 32 for various annealing conditions.

Any effect of nitrogen annealing on the magnetization, within experimental error, was not observed with annealing temperature under 800°C , which is interpreted to mean that no appreciable change in the amount of oxygen vacancies occurred by the annealing process. However, in Fig. 32, the resistivity of the C3M sample which was annealed in N_2 at 800°C is lower than that of the as grown sample(C3K) over the whole temperature range. The resistivity of the sample C3L which was annealed in N_2 at 600°C does not show any difference from that of C3M within experimental error, and was not shown in this figure. Even further decreases in the resistivity are observed for sample Q3B which was annealed in O_2 at 1000°C . This decrease of the resistivity from C3K through Q3B is interpreted to be unrelated to the change in the amount of oxygen vacancies. It may be due to the degree of charge compensation

Figure 32: Resistivity vs temperature for $\text{Ca}_{0.20}\text{:YIG}$ with various annealing conditions. The sample conditions are : * - as grown(C3K), ▽ - 800°C in N_2 (C3M), ○ - 1000°C in O_2 (Q3B), ● - 900°C in N_2 (Q3C), □ - 960°C in N_2 (R3E), ◇ - 1000°C in N_2 (Q3D). The samples were annealed for 6 ~ 8 hrs at the above conditions.

inside the crystal, which will be discussed later.

Sample Q3B has the lowest resistivity. On annealing this sample in nitrogen, a dramatic increase in the resistivity was observed. The resistivity of sample Q3C(annealed at $900^\circ C$ in N_2) shows a slight increase, but samples R3E and Q3C, which were annealed at $960^\circ C$ and $1000^\circ C$ in N_2 , show huge changes. While the resistivity of sample Q3B at $300 K$ is $1.3 \times 10^3 \Omega cm$, those of Q3C, R3E, and Q3D samples are $2.3 \times 10^3 \Omega cm$, $3.7 \times 10^5 \Omega cm$, $8 \times 10^9 \Omega cm$, respectively. This change is clearly due to the increase of the charged oxygen vacancies, $V_O^\bullet$, for which the mechanism will be discussed later.

Another feature of the temperature dependence of the resistivity in Fig. 32 is that the data points of each sample are not on a straight line. The term activation energy is defined as the energy in the equation, $f = f_0 \exp(\pm \frac{\Delta E}{kT})$, if the variable f follows the temperature dependence in that equation either exactly or approximately. Using the above definition, the activation energies of the resistivity for the samples were calculated at different temperatures as the slopes at these points. The slope at each point was approximated as the slope of the straight line passing through the two adjacent points. The results are listed in Table 19.

Table 19: Activation energy(eV) of resistivity at different temperatures for the samples with various annealing conditions.

Sample	300 K	240 K	200 K	160 K
C3K(as grown)	0.32	0.32	0.30	0.27
C3M($800^\circ C, N_2$)	0.32	0.32	0.30	0.27
Q3B($1000^\circ C, O_2$)	0.32	0.31	0.29	0.27
Q3C($900^\circ C, N_2$)	0.34	0.32	0.30	0.29
R3E($960^\circ C, N_2$)	0.44	0.42	0.39	—

The activation energies in Table 19 are not constants even within the temperature range of $200 \sim 300 \text{ K}$. It strongly suggests that the dominant scattering mechanism of charge carriers is not the acoustic lattice scattering as expected, if the conduction is due to band conduction.

The conductivity in p -type YIG is expressed as

$$\begin{aligned}\sigma &= pe\mu_h = N_v \exp\left(-\frac{E_F - E_v}{kT}\right)e\mu_h \\ &\propto \mu_h(T)T^{\frac{3}{2}} \exp\left(-\frac{E_F - E_v}{kT}\right),\end{aligned}\quad (6.13)$$

if band conduction is assumed. The temperature dependences of mobility for different scattering mechanisms are listed in Table 5 in Chapter III. To find the temperature dependence of mobility, the data for the resistivity were fitted with the following equation,

$$\sigma = AT^\alpha \exp\left(-\frac{\Delta E}{kT}\right), \text{ or } \rho = A^{-1}T^{-\alpha} \exp\left(\frac{\Delta E}{kT}\right). \quad (6.14)$$

There are three parameters, A^{-1} , α and ΔE in this analysis. These parameters were obtained by a fit to the data and the values for α and ΔE are listed in Table 20. The data points only in the temperature range of $200 \sim 300 \text{ K}$ were used for this analysis. Under 200 K , it is probable that a different conduction mechanism may contribute to the resistivity^[36]. Therefore, the data points under 200 K were excluded in this analysis. The data for the Q3D sample were also excluded in the analysis because the resistivity of this sample is so high that the accuracy is much lower than other's.

In Table 20, α is close to 3 for C3K, C3L, C3M samples and larger than 3 for the other samples. $\alpha = 3$ means that $\mu \propto T^{\frac{3}{2}}$ and the corresponding scattering mechanism is due to ionized impurities. For all the other scattering mechanisms in Table 5, the exponent of T in the mobility is less than or equal to zero. In other words, α should be less than or equal to 1.5 for any other scattering mechanism. The high

Table 20: Parameters by the fit with equation $\rho = A^{-1}T^{-\alpha} \exp(\frac{\Delta E}{kT})$.

Sample	α	$\Delta E (eV)$
C3K(as grown)	2.9	0.25
C3L(600° C, N_2)	2.7	0.25
C3M(800° C, N_2)	3.1	0.25
Q3B(1000° C, O_2)	4.3	0.22
Q3C(900° C, N_2)	5.4	0.21
R3E(960° C, N_2)	6.0	0.29

values of α for Q3B, Q3C and R3E samples may be due to the narrow temperature range for the fit. However, the high exponents of those samples do not favor other scattering mechanisms more than the ionized impurity scattering. Therefore, it can be concluded that the data for these samples favor the ionized impurity scattering as the dominant scattering mechanism.

Based upon the arguments above, the data for the resistivity were fitted again with $\alpha = 3$ to get ΔE , the position of the Fermi Energy with respect to the valence band edge and the parameter A which is dependent on the effective mass of a hole and also the number of charged impurities. The parameters by this fit are listed in Table 21 and the bulk resistivities calculated with these parameters are plotted in Fig. 33. In this figure, the fit is very good between 200 K and 300 K, but the data points under 200 K show lower resistivity than the theoretical curve. This may be an indication of an onset of a transition to another conduction mechanism or an error due to the surface current. The resistance of the Q3D sample was very high so that the leakage current through the apparatus was as high as 15 % at 300 K. Therefore, only the approximate value of ΔE is listed in Table 21.

With a little further calculation, the physical meaning of the parameter A will

Figure 33: Data and theoretical fit for the temperature dependence of the resistivity for $\text{Ca}_{0.20}\text{:YIG}$. The calculated values are plotted with solid lines and the raw data are plotted with different symbols. Ionized impurity scattering was assumed, and the data points between 200 K and 300 K were used for the fit. The symbols for the raw data are : * - as grown(C3K), o - 1000°C in O_2 (Q3B), • - 900°C in N_2 (Q3C), □ - 960°C in N_2 (R3E), ◇ - 1000°C in N_2 (Q3D).

Table 21: Parameters by the fit with equation $\rho = A^{-1}T^{-3} \exp(\frac{\Delta E}{kT})$. Ionized impurity scattering was assumed.

Sample	$A^{-1}(\Omega cm K^3)$	$\Delta E (eV)$
C3K(as grown)	8.47×10^6	0.25
C3L($600^\circ C, N_2$)	5.98×10^6	0.25
C3M($800^\circ C, N_2$)	5.70×10^6	0.25
Q3B($1000^\circ C, O_2$)	2.56×10^6	0.25
Q3C($900^\circ C, N_2$)	2.87×10^6	0.26
R3E($960^\circ C, N_2$)	1.04×10^7	0.36
Q3D($1000^\circ C, N_2$)	—	0.8 ± 0.1

become clearer. The mobility can be expressed as

$$\mu_h = \mu_{h,300K} \left(\frac{T}{300K} \right)^{\frac{3}{2}}. \quad (6.15)$$

This equation can be combined with the expression of conductivity.

$$\begin{aligned} \sigma &= pe\mu_h \\ &= 2 \left(\frac{m_h^* k \cdot 300K}{2\pi\hbar^2} \right)^{\frac{3}{2}} \left(\frac{T}{300K} \right)^{\frac{3}{2}} \exp\left(-\frac{E_F - E_v}{kT}\right) e \mu_{h,300K} \left(\frac{T}{300K} \right)^{\frac{3}{2}} \\ &= (4.06 \text{ coul/cm}^3) \mu_{h,300K} \left(\frac{m_h^*}{m_e} \right)^{\frac{3}{2}} \left(\frac{T}{300K} \right)^3 \exp\left(-\frac{E_F - E_v}{kT}\right). \end{aligned} \quad (6.16)$$

Combining equations 6.14 and 6.16,

$$\left(\frac{m_h^*}{m_e} \right)^{\frac{3}{2}} \mu_{h,300K} = (6.65 \times 10^6 K^3) A \quad (6.17)$$

Using this equation, the data in Table 21 were converted into the mobility at 300 K with a factor which depends on the effective mass of a hole. These results are listed in Table 22.

In Table 22, the mobility increases with thermal annealing for C3L and C3M samples and reaches a maximum for the Q3B sample. Thereafter, it decreases as the

number of charged oxygen vacancies increases in Q3C and R3E samples. The increase of mobility following from C3K through Q3B can be interpreted as a decrease in the number of the ionized impurity scattering centers. The decrease of the mobility from Q3B to R3E is interpreted as an increase in the number of scattering centers.

The annealing effect in N_2 for C3L and C3M samples is not related with the creation of oxygen vacancies. The measurement on the magnetic properties showed that the number of $V_O^\bullet$ does not change within experimental error by a thermal annealing at or under $800^\circ C$ in N_2 , while an increase in $[V_O^\bullet]$ was observed in Q3C and R3E sample. It also showed that the annealing at $1000^\circ C$ in O_2 does not affect the temperature dependence of $4\pi M$ within experimental error, hence the number of charged oxygen vacancies, $[V_O^\bullet]$. Therefore, the increase in the mobility from the C3K sample (as-grown) to Q3B ($1000^\circ C$, O_2) can be interpreted as having a better charge compensation by the thermal annealing, i.e. a decrease in the number of the charged centers, while the decrease in mobility from Q3B sample to R3E ($960^\circ C$, N_2) can be attributed to the increase of $[V_O^\bullet]$. In view of the growth time, 5 min of the samples by LPE, which is not long enough to get the best charge compensation, this interpretation is reasonable.

If the scattering is due to the ionized impurities, the mobility is related to the number of charged impurities as^[40]

$$\mu = \frac{3.68 \times 10^{20} cm^{-3}}{N_I} \frac{1}{Z^2} \left(\frac{\epsilon_r}{16} \right)^2 \left(\frac{T}{100K} \right)^{\frac{3}{2}} \left(\frac{m^*}{m_e} \right)^{-\frac{1}{2}} [f(\beta)]^{-1}, \quad (6.18)$$

where N_I is the number of impurity atoms with charge Ze , ϵ_r is the relative permittivity, and $f(\beta)$ is a function related to the momentum relaxation time. There are two expressions for $f(\beta)$: one by Brooks and Herring^[65], and the other by Conwell

Table 22: Mobility at 300 K of $\text{Ca}_{0.20}\text{:YIG}$. $\left(\frac{m_h^*}{m_e}\right)^{\frac{3}{2}} \mu_{h,300K}$ is listed for different annealing conditions. Though m_h^* is an unknown constant, the change in mobility can be compared.

Sample	$\left(\frac{m_h^*}{m_e}\right)^{\frac{3}{2}} \mu_{h,300K} \left(\frac{\text{cm}^2}{\text{Vsec}}\right)$
C3K(as grown)	0.78
C3L(600°C, N_2)	1.11
C3M(800°C, N_2)	1.17
Q3B(1000°C, O_2)	2.60
Q3C(900°C, N_2)	2.32
R3E(960°C, N_2)	0.64

and Weisskopf^[66]. By Brooks and Herring,

$$f_{BH}(\beta_{BH}) = \ln(1 + \beta_{BH}^2) - \frac{0.434 \beta_{BH}^2}{1 + \beta_{BH}^2},$$

$$\beta_{BH} = \left(\frac{\epsilon_r}{16}\right)^{\frac{1}{2}} \frac{T}{100K} \left(\frac{m^*}{m_e}\right)^{\frac{1}{2}} \left(\frac{2.08 \times 10^{18} \text{cm}^{-3}}{n}\right)^{\frac{1}{2}}. \quad (6.19)$$

where n is the density of electrons. By Conwell and Weisskopf,

$$f_{CW}(\beta_{CW}) = \log(1 + \beta_{CW}^2),$$

$$\beta_{CW} = \frac{1}{Z} \frac{\epsilon_r}{16} \frac{T}{100K} \left(\frac{2.35 \times 10^{19} \text{cm}^{-3}}{N_I}\right)^{\frac{1}{3}}, \quad (6.20)$$

where the log is to the base 10. Brooks and Herring's formula has an unknown n (or p in this case) in the expression of the mobility, while Conwell and Weisskopf's does not. In a calculation of mobility vs impurity concentration with $m^* = m_e$, $Z = 1$, and $\epsilon_r = 16$, the $\log \mu$ vs $\log N_I$ plot by Brooks and Herring's formula deviates from a straight line significantly around $N_I = 10^{18} \text{cm}^{-3}$, while the plot by Conwell and Weisskopf's nearly keeps a constant slope in this range^[40]. For the above reasons, the latter was chosen in the following analysis.

In Table 22, the mobility decreases by a factor of $\frac{1}{4}$ from Q3B sample to R3E, while $[V_O]$ changes from 0.03 to 0.12 in fmu (refer to Table 14). It seems that there is a definite correlation between $[V_O]$ and the mobility. Therefore, the mobility due to V_O was calculated using the conversion factor $4.22 \times 10^{21} cm^{-3}/fmu$ from fmu to cm^{-3} , $Z = 1$ and $\epsilon_r = 18$ ^[14]. The results are listed in Table 23.

If there are other scattering centers, the mobility can be obtained with the equation,

$$\frac{1}{\mu} = \frac{1}{\mu_1} + \frac{1}{\mu_2}, \quad (6.21)$$

where μ_1 and μ_2 are contributions of the different scattering centers respectively. In the analysis for the temperature dependence of the magnetization, it was found that an aggregation of oxygen vacancies occurred for the samples annealed at $960^\circ C$ and $1000^\circ C$ in N_2 . This aggregation may introduce some error in the mobility and hence the effective mass of the R3E sample in Table 23 in addition to the uncertainty due to the error in $[V_O]$, which is smaller in R3E than in Q3B and Q3C samples. Considering the uncertainties in this experiments, the effective mass which is the ratio of column 2 to column 3 in Table 23 is relatively close for the three samples. Therefore, it is interpreted that the contribution of other scattering centers is minor under the conditions of Q3B, Q3C and R3E samples.

Before proceeding to further analyses, the applicability of the Conwell and Weiskopf's formula should be questioned. Usually in conventional semiconductors, the semiconductors become degenerate beyond the doping level of $10^{18} cm^{-3}$, and the Brooks-Herring's calculation deviates from the Conwell and Weiskopf's significantly in this doping range^[40]. Therefore, the validity of either model for a very high doping level, which is of the order of $10^{20} cm^{-3}$ for this experiments, is not clearly known.

For now, the effective masses of Q3B and Q3C in Table 23 will be accepted and

Table 23: Mobility at 300 K of $\text{Ca}_{0.20}\text{YIG}$ and effective mass of a hole. $\left(\frac{m_h^*}{m_e}\right)^{\frac{1}{2}} \mu_{h,300K}$ is listed for different annealing conditions. $\mu_{h,300K}^{Exp}$ is the value obtained by the fit to the resistivity data, and $\mu_{h,300K}^{Th}$ is the one calculated by Conwell and Weisskopf's formula^[66] assuming the major scattering center is V_O . The effective mass was calculated dividing the second column by the third column.

Sample	$\left(\frac{m_h^*}{m_e}\right)^{\frac{1}{2}} \mu_{h,300K}^{Exp} \left(\frac{cm^2}{Vsec}\right)$	$\left(\frac{m_h^*}{m_e}\right)^{\frac{1}{2}} \mu_{h,300K}^{Th} \left(\frac{cm^2}{Vsec}\right)$	$\frac{m_h^*}{m_e}$
Q3B(1000°C, O_2)	2.60	28.5	0.091
Q3C(900°C, N_2)	2.32	23.6	0.098
R3E(960°C, N_2)	0.64	12.2	0.052

approximated as $m_h^* \approx 0.1 m_e$. With this effective mass, the mobilities at 300 K for C3K and Q3B samples are 25 and 82 $\frac{cm^2}{Vsec}$ respectively. These values are two orders of magnitude larger than the reported values of *Si*-doped YIG, which is an order of 0.1 $\frac{cm^2}{Vsec}$. With this value of effective mass, the charge carrier density, p can be calculated using the Fermi energy listed in Table 21. p ranges from 5×10^{13} for Q3B to 7×10^{11} for R3E.

One of Larson's high temperature results above 600 K (Section 3.2.4) showed

$$\mu_h N_v e^{r_h} = 3.0 \times 10^{21} (V sec cm)^{-1},$$

for *p*-type YIG. The scattering is due to acoustical lattice scattering for this temperature range ($T > 600 K$). With this equation, the contribution of the acoustical lattice scattering to the mobility at 300 K can be calculated. Using $m_h^* = 0.1 m_e$ and $r_h = 2$,

$$N_v = 8.03 \times 10^{17} cm^{-3}, \quad (6.22)$$

$$\mu_h^A = 5.1 \times 10^2 \frac{cm^2}{V sec}. \quad (6.23)$$

This value is an order of magnitude larger than the mobility due to ionized impurity scattering. Therefore, the mobility at 300 K is

$$\begin{aligned}\frac{1}{\mu_h} &= \frac{1}{\mu_h^I} + \frac{1}{\mu_h^A} \\ &\approx \frac{1}{\mu_h^I},\end{aligned}\tag{6.24}$$

where μ_h^I and μ_h^A denote the mobilities due to the impurity scattering and due to the acoustical lattice scattering respectively. The dominant contribution to the scattering of charge carriers is done by the ionized impurity scattering at 300 K and even higher contribution by this mechanism at lower temperatures. The temperature at which the transition from the impurity scattering to the acoustical lattice scattering occurs can be estimated with the condition, $\mu_h^I \approx \mu_h^A$. The temperatures are 800 K for C3K sample and 550 K for Q3B sample. However, a sharp transition is not expected, rather it will be a slow transition within $\pm 200^\circ K$ around the transition temperature estimated above.

The above arguments indicate that Larson's results are not inconsistent with the analysis of Conwell and Weisskopf's formula under the assumption of a dominant contribution of V_O to the ionized impurity scattering. The effective mass by this analysis is much smaller than that expected for a polaron. The value of $m_h^* = 0.1 m_e$ is similar to the values for broad bands rather than that of the narrow and highly localized iron 3d bands. The valence band might be the broad oxygen 2p band. This observation raises a question about Larson's band diagram (Fig. 9), where the narrow band of Fe^{3+} at the tetrahedral site is located at the top of the valence band.

6.2.3 Surface Layer

In Section 6.2.1, the effect of a surface layer on the I-V characteristics was analyzed and the voltage ratio V_S/V was plotted in Fig. 31 as a function of applied voltage. On the other hand, an analysis of V_S/V as a function of temperature will clarify the temperature dependence of the error in the bulk resistivity if the voltage drop V_S at the surface layer is not considered or ignored. As discussed before, the I-V characteristic of Ca:YIG has three different regions. Most of the former data might have been obtained at the low voltage region because the I-V characteristic in this region seems to be Ohmic, while the high voltage region should be used to give a better approximation for the bulk properties because V_S/V is relatively small in this region.

The voltage ratio, V_S/V , for the Q3B sample in the two regions mentioned above is shown in Fig. 34. In the low voltage region, the voltage drop at the surface layer changes from about 55 % at 150 K to 83 % at 300 K. With a thicker surface layer, an even larger percentage would be expected. This observation shows that the surface layer masks the bulk properties completely in the low voltage region. Furthermore, the ratio changes appreciably as the temperature changes. In the high voltage region, the effect is smaller but still on the order of 10 %, which is also dependent on temperature.

There are two other observations for the surface layer effect. The first is that the transition in the I-V characteristic from the low voltage region to the intermediate region or from the intermediate to the high voltage region occurs at a voltage independent of temperature (refer to Fig. 21). The second is that the activation energy of the resistance in the low voltage region is very close to that in the high voltage region. For example, the activation energy, around room temperature, for the resistance of

the C3K sample is 0.302 eV with $V = 0.5\text{ volts}$, and 0.309 eV with $V = 50\text{ volts}$. The error in the above activation energies is $\pm 0.003\text{ eV}$. While they are very close, there is a small noticeable difference.

In this experiment, the samples annealed in N_2 above 900°C showed an increase of both resistivity and activation energy. The resistivity of the surface layer is estimated to be about 10^3 times as high as the bulk resistivity. Then, a higher activation energy for the resistance is expected at the low voltage region where the effect of the surface layer is dominant, however the activation energy in the high voltage region is very close to or even higher than that.

For the I-V characteristic, the onset of the intermediate region occurs with the condition, $n - n_0 \approx n_0$ where n_0 is the carrier concentration in thermal equilibrium. The applied voltage with this condition is generally dependent on temperature, but this is not observed.

The two observations are common to all the samples which were tested. It can be interpreted that the charge carriers in the surface layer are not those in thermal equilibrium inside the surface layer, even at the low applied voltages. They may be carriers diffused from the bulk. These phenomena are not clearly understood and need further studies.

6.2.4 Impurity Band

By annealing the samples in nitrogen atmosphere, the concentration of singly charged oxygen vacancies, $[V_O^\bullet]$ increased and a change in the position of the Fermi level was observed. $[V_O^\bullet]$ was measured from the analysis of the magnetization, and $E_F - E_v$ was measured from the analysis of the resistivity. The results are listed in Table 24.

Figure 34: The voltage drop at the surface layer as a function of temperature. V_s/V with $V = 0.5$ volts in the low voltage region and with 50 volts in the high voltage region are plotted.

Table 24: The concentration of singly charged oxygen vacancies and the corresponding position of Fermi level.

Sample	$[V]$ ($fm\mu$)	$E_F - E_v$ (eV)
Q3B(1000°C, O_2)	0.03	0.25
Q3B(900°C, N_2)	0.04	0.26
Q3B(960°C, N_2)	0.12	0.36
Q3B(1000°C, N_2)	0.16	0.8 ± 0.1

In the samples used in this experiment, $[Ca^{2+}] = 0.20 \text{ } fm\mu = 8 \times 10^{20} \text{ } cm^{-3}$ and $[Pb^{2+}] = 0.05 \text{ } fm\mu = 2 \times 10^{20} \text{ } cm^{-3}$. Under this high level of doping, the formation of impurity bands is naturally expected. As discussed in Section 4.2, the Ca^{2+} or Pb^{2+} ions cannot behave as acceptors for themselves. They should be compensated by $V_{\ddot{O}}$, $V_{\dot{O}}$ or by Fe^{4+} . The analyses thus far show that $V_{\ddot{O}}$ and $V_{\dot{O}}$ are dominant charge compensators to Ca^{2+} or Pb^{2+} ions. Therefore, the rise of the Fermi level corresponding to the increase of $[V_{\dot{O}}]$ in Table 24 strongly suggests that an impurity band of oxygen vacancies is being filled as the annealing temperature increases.

Oxygen vacancies may have different environments. They may be coordinated with Ca^{2+} ions or Pb^{2+} ions to compensate them. An O^{2-} ion in YIG is coordinated with one d -site Fe^{3+} ion, one a -site Fe^{3+} ion and two Y^{3+} ions. A variety of different environments of oxygen vacancies can be imagined.

The experimental results reported so far manifest that the Ca -doped YIG has the lowest resistivity and the lowest activation energy. Therefore, it is assumed that the impurity band with the lowest energy is due to empty oxygen vacancies, $V_{\ddot{O}}$, associated with Ca^{2+} . The rapid change of occupation number of this band to form $V_{\dot{O}}$ in the range of $0.25 \text{ eV} < E_F - E_v < 0.35 \text{ eV}$ shows the presence of the impurity band centered at about 0.3 eV above the valence band edge.

The real situation is expected to be more complicated than the model proposed in Section 4.2, but as an approximation, the total density of states for one electron oxygen vacancies is assumed to be

$$[V_{O,total}] = \frac{1}{2}[Ca] + \frac{1}{2}[V_O] . \quad (6.25)$$

Then, the ratio of occupied states to the total number of states is

$$f = \frac{[V_O]}{[V_{O,total}]} = \frac{[V_O]}{\frac{1}{2}[Ca^{2+}] + \frac{1}{2}[V_O]} . \quad (6.26)$$

The ratios are 0.26, 0.33, 0.75 and 0.89 for Q3B, Q3C, R3E and Q3D samples respectively. Nearly $\frac{1}{4}$ of the impurity band is filled for the Q3B sample and $\frac{3}{4}$ of the band is filled for the R3E sample. Therefore, it is concluded that the center of the impurity band of $V_O^\bullet$ which is coordinated with Ca^{2+} is located at 0.3 eV above the valence band edge, and the half width of the band is less than 0.1 eV. As a reference, a Gaussian fit for the three points(Q3B, Q3C, R3E) shows the center at 0.32eV and the standard deviation of 0.07 eV.

For the Q3D sample, $f = 0.89$, which is smaller than unity. This is interpreted that the approximation for the occupation ratio by equation 6.26 is not complete, and it also suggests that there is another impurity band above the first one with the lowest energy. The second band from the valence band seems to be due to oxygen vacancies coordinated with Pb^{2+} , which might overlap the first one. It is expected that the bands with two electrons will be located at much higher energy.

It should be noted that the thermal energy at 300 K is only 0.026 eV, which is small enough not to affect the above discussion. The number of electrons excited from the valence band, which will be the same as p in the valence band, is estimated to be the order of 10^{13} cm^{-3} , while the number of electrons localized at the impurity band is of the order of 10^{20} cm^{-3} .

CHAPTER VII

Conclusion

Effects of oxygen vacancies on the magnetic and the electrical properties of calcium substituted yttrium iron garnet were investigated. The $\text{Ca}_{0.20}\text{YIG}$ samples which are thin films with thicknesses of about $5\text{ }\mu\text{m}$ were grown on GGG substrate in this laboratory. The study was done by annealing the samples in nitrogen atmosphere in a temperature range between 600°C and 1000°C , and in oxygen atmosphere in a temperature range between 1000°C and 1200°C . The important results of this research are described in the following sections.

7.1 Magnetic Properties

Annealing the samples at or under 800°C in N_2 did not change the magnetization from 4 K to the Curie temperature within experimental error. However, a dramatic change in the magnetization was observed by annealing the samples between 900°C and 1000°C . A decrease of lattice constant was also observed with the above annealing conditions and a linear relationship between the change in $4\pi M$ and the change in

the lattice constant was found. The ratio is

$$\frac{\Delta(4\pi M)}{\Delta a} = (1.78 \pm 0.03) \times 10^4 G/\text{\AA}.$$

The decrease in the magnetization was explained with a proposed model for the localized ferromagnetic superexchange, in which the oxygen vacancies with one localized electron, $V_{\dot{O}}$ mediate the exchange interaction. With this model, the ratio of the change in the lattice constant to the change in the total concentration of different kinds of oxygen vacancies was calculated,

$$\frac{\Delta a}{\Delta[V_{O,total}]} = -0.50 \text{\AA}/fmu = -1.18 \times 10^{-22} \text{\AA}cm^3,$$

where the estimated errors in the above constants are about 2 %.

A model of microscopic molecular field theory, based on the Heisenberg Hamiltonian, was proposed to explain the temperature dependence of the magnetization. The attempt to correlate the exchange integrals, J_{ad} , J_{dd} and J_{aa} with the change in the lattice constant quantitatively was not successful, but it was shown qualitatively that the change in the lattice constant invokes the change in the overlap of wavefunctions and hence the change in the exchange integrals. It was also explained clearly that the inverted spins due to the localized ferromagnetic superexchange show an anomaly in the magnetization at low temperatures for the as-grown samples and for the samples annealed in O_2 atmosphere, but the anomaly is completely hidden by other effects in the nitrogen annealed samples at or above $960^\circ C$.

The rapid decrease of magnetization following the increase of temperature from 4 K, which was observed in the samples annealed in N_2 at or above $960^\circ C$, was explained as an identification of Fe^{3+} ions at the d -site which have two missing a - d linkages. The large amount of these Fe^{3+} ions up to 0.4 fmu in the sample annealed

at 1000°C led to the conclusion that vacancies of iron ions of the order of 0.1 *fmu* exist in these samples.

The samples annealed in O_2 at 1000°C did not show any change in the magnetization and the lattice constant within experimental error, which supports the above interpretation for the nitrogen annealing that all the changes discussed above are due to the creation of oxygen vacancies. The samples which were annealed at 1100°C and 1200°C showed only a slight decrease in the magnetization and barely any change in the lattice constant. However, the shape of the $4\pi M$ vs T curve remained the same and the Curie temperature barely changed, which is interpreted as a site change or a diffusion of Fe^{3+} ions from d -site to a -site.

7.2 Electrical Properties

I-V characteristics of the samples with different annealing conditions were measured in the temperature range of $140 \sim 300\text{K}$. From the I-V characteristic, the signal from the surface layer was separated from that of the bulk using the two layer model. It was found that the surface layer showed trap-free-square law at high applied voltages above the trap filled limit, which is around 20 V. The voltage drop at the surface layer with low applied voltages changes from about 50 % at 150 K to 90 % at 300K, which is more than enough to mask the bulk properities. With high applied voltages, it is still an order of 10 %, which is also temperature dependent.

The Ca:YIG samples were identified as p -type measuring the sign of thermopower. A huge change in the resistivity, at room temperature, from the order $10^3 \Omega\text{cm}$ to the order $10^{10} \Omega\text{cm}$ was observed by the annealing in nitrogen atmosphere, which is generally interpreted as a compensation of the acceptors by V_{O} .

The temperature dependence of the resistivity of the bulk in the temperature range between 200 K and 300 K favors the ionized impurity scattering as the dominant scattering mechanism of charge carriers. Assuming ionized impurity scattering, the equation $\rho = A^{-1}T^{-3} \exp\{(E_F - E_v)/kT\}$ was used to fit the data so that the position of the Fermi level from the valence band edge and the constant A were obtained. Since the constant A depends on the effective mass of a hole and the mobility at a constant temperature, it was compared for different annealing conditions.

From the analysis, it was found that the mobility increases from that of the as-grown sample by a factor of 3 with the annealing in O_2 at 1000°C. It was also found that the annealing in N_2 at 600°C and 800°C increases the mobility. The above change is interpreted as a decrease in the number of scattering centers, which means a better charge compensation than in the as-grown sample. A decrease in the mobility from that of the sample annealed in O_2 was observed in the samples annealed in N_2 at or above 900°C and a correlation between the mobility and $[V_O]$ was observed in these samples.

Based on the close relationship between the mobility and $[V_O]$, it was assumed that V_O 's are the major scattering centers. From the analysis following this assumption, the mobilities of the samples were estimated to lie within a range of $20 \sim 80 \text{ cm}^2/\text{Vsec}$, and the effective mass of a hole at the valence band edge was estimated as $m_h^* \approx 0.1 m_e$. These values of mobility are much higher than those reported for n -type YIG, which is an order of $0.1 \text{ cm}^2/\text{Vsec}$. The high mobility and the low effective mass of the hole suggest that the valence band of YIG might be the broad oxygen $2p$ band rather than the highly localized narrow $3d$ band of iron ions.

From the high temperature data of Larson, *et al*^[17], the mobility due to the acoustic lattice scattering was estimated to be $500 \text{ cm}^2/\text{Vsec}$ at 300 K, using the

effective mass $m_h^* \approx 0.1 m_e$, which is not in contradiction to the above analysis. The transition temperature from the ionized impurity scattering to the acoustic lattice scattering as a dominant scattering mechanism was estimated to be about 600 K for the as-grown sample.

7.3 Charge Compensation and Impurity Band

From the linear relationship between $\Delta(4\pi M)$ and Δa , it was found that the total amount of oxygen vacancies for the as-grown samples is larger than half of the Ca^{2+} concentrations. From the above observation, it was concluded that the oxygen vacancies, $V_O^{\bullet\bullet}$ and $V_O^\bullet$ are the major charge compensators for Ca-substituted YIG.

For the different annealing conditions, the content of the singly charged oxygen vacancies was obtained by the analysis of magnetic properties and the position of the Fermi level was obtained by the analysis of electrical conduction. Combining the above results, an impurity band of $V_O^{\bullet\bullet}$, coordinated with Ca^{2+} , which can localize single electrons was located. The center of the impurity band lies at about 0.3 eV above the valence band edge, and the half width of the band is about 0.1 eV. It was also discussed that the above impurity band is not the only one, because oxygen vacancies can be coordinated with different ions at the dodecahedral site and it may also have different coordination with d -site or a -site. The oxygen vacancy bands with double electrons will be located at much higher energies.

It was discussed that the Ca^{2+} or the Pb^{2+} ions cannot behave as acceptor ions for themselves. Experimental results of this research show that oxygen vacancies associated with those off-valency impurity ions, to compensate the charges of those ions, form impurity bands close to the valence band edge and the electrons excited by

thermal energy from the valence band to one of these impurity bands leave holes in the valence band. This is the proposed picture for the conduction in *p*-type YIG. The Fermi energy is located inside the impurity band, which corresponds to the amount of localized electrons at the oxygen vacancies. For the samples in this experiment, the estimated density of holes at the valence band is on the order of 10^{13} cm^{-3} while the concentration of localized electrons at the oxygen vacancies is on the order of 10^{20} cm^{-3} .

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Appendix A

PROGRAM FOR THE MICROSCOPIC MOLECULAR FIELD THEROY

```
C PROGRAM : MFIT3.FOR
C * Program to fit the 4piM vs T data of reduced samples.
C * MODE = 0 i.e. weight(I) = 1
C The program will ask you the tolerance for the iterations.
C A tolerance of 0.01 through 0.0001 is fine.
C * Reads the parameters for the molecular field calculations
C from a file named "*.PAR" and writes the results on the
C same file.
C The input files : filename.prn, filename.par
C The ouput files : filename.a.dat
C filename.b.dat
C filenames.dat, filename.par
C * To change the number of parameters, (1) change NPAR=3 to
C NPAR=5, for example, and (2) change the 3F10.5 to 5F10.5
C in the FORMAT on line 61(subroutine PRTPAR) and (3) add
C *** = A(4), xxx = A(5) in the DOUBLE PRECISION FUNCTION
C FUNC. *** and xxx are the correspondig variables
C with physical meanings, e.g. DJDD or FDVA and so on.
C (5) Make corresponding changes for assigning the initial
```

```

C      parameters to A(i) in the subroutine GETMFPAR.
C
C
C Main program for nonlinear least-square fitting
C
C      PARAMETER(NPAR=3)
C      PARAMETER(NLATT=11)
C      PARAMETER(NMX=50)
C
C      Variables to be used in the subroutine CURFIT
C      DOUBLE PRECISION X(NMX),Y(NMX),YFIT(NMX),SIGMAY(NMX)
C      DOUBLE PRECISION SIGMAA(NPAR),A(NPAR)
C      DOUBLE PRECISION FLAMDA,TOL1,TOL2,DELTAY
C      COMMON/DATA/ X,Y
C      REAL CHISQR
C
C      CHARACTER*10 FOLD
C
C      Variables to be used in the function FUNC (Molecular Field
C      Calculations)
C
C      DOUBLE PRECISION T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
C      COMMON/MOLA/ T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
C
C      DOUBLE PRECISION SDI(NMX),SAI(NMX),SDA(NMX),SDAA(NMX)
C      DOUBLE PRECISION SDV(NMX),SDVA(NMX),SAV(NMX),SAA(NMX)
C      DOUBLE PRECISION SDN(NMX),SAN(NMX),SD(NMX),SA(NMX),STOTAL(NMX)
C      COMMON/MOLB/SDI,SAI,SDA,SDAA,SDV,SDVA,SAV,SAA
C      *          ,SDN,SAN,SD,SA,STOTAL
C
C      DOUBLE PRECISION FI,F1,FDA,FDA,FDA,FDA,FDA,FDA,FDA,FDA
C      COMMON/MOLC/ FI,F1,FDA,FDA,FDA,FDA,FDA,FDA,FDA,FDA
C

```

```

EXTERNAL CURFIT,FUNC,FDERIV,FCHISQ,FCN
EXTERNAL OPENFILES,GETFITPAR,GETMFPAR,FREPT
EXTERNAL PRTPAR,PRT12,PRT13,PRT15

C
C
CALL OPENFILES(FOLD)
CALL RDDATA(NDATA,X,Y)
CALL GETMFPAR(A,FOLD)
CALL GETFITPAR(TOL1,TOL2,FLAMDA,DELTAY,SIGMAY,MODE,ITMAX)

C
CALL CURFIT(MODE,TOL1,TOL2,ITMAX,FLAMDA,NDATA,
*   X,Y,YFIT,SIGMAY,A,SIGMAA,CHISQR,NPASS)

C
C   *** final report to the screen and file #11
CALL FREPT(NPASS,CHISQR,A,SIGMAA)

C
C   *** raw data and calculated ones to file #12
CALL PRT12(NDATA,A,X,Y,YFIT)

C
C   *** average spins at various sites to file #13
CALL PRT13(NDATA,A,X)

C   *** parameters to file #15
CALL PRT15(FOLD,A)

C
CLOSE(10)
CLOSE(11)
CLOSE(12)
CLOSE(13)
END

C
C
C   ***** End of Main Program *****

```

```

C =====
C
C
C SUBROUTINE CURFIT
C
C     SUBROUTINE CURFIT(MODE,TOL1,TOL2,ITMAX,FLAMDA,NDATA,
C       *   X,Y,YFIT,SIGMAY,A,SIGMAA,CHISQR,NPASS)
C
C     PARAMETER(NPAR=3)
C     PARAMETER(NMX=50)
C
C     DOUBLE PRECISION X(NMX),Y(NMX),YFIT(NMX),SIGMAY(NMX)
C     DOUBLE PRECISION X1,A(NPAR),SIGMAA(NPAR)
C     DOUBLE PRECISION WEIGHT(NMX)
C     DOUBLE PRECISION ALPHA(NPAR,NPAR),B(NPAR)
C     DOUBLE PRECISION ARINV(NPAR,NPAR),ARRAY(NPAR,NPAR)
C     DOUBLE PRECISION DERIV(NPAR),BETA(NPAR),C(NPAR)
C     DOUBLE PRECISION FLAMDA,TOL1,TOL2
C     REAL CHISQR
C
C     COMMON/CF/WEIGHT
C     EXTERNAL FUNC,FDERIV,FCHISQ,PRTPAR,PRT13
C
C     NPASS=0
C     CHISQ=0.
C
C     IF(NPAR.GT.NDATA) RETURN
C     NFREE=NDATA-NPAR
C     IF(NFREE.LT.1) RETURN
C     IF(MODE.LT.-1.OR.MODE.GT.1)RETURN
C     DO 30 I=1,NDATA
C       IF (MODE.EQ.0) THEN
C         WEIGHT(I)=1.0

```

```

ELSE IF (MODE.EQ.1) THEN
    WEIGHT(I)=1/SIGMAY(I)**2.
ELSE IF (MODE.EQ.-1) THEN
    IF (Y(I).EQ.0.0) THEN
        WEIGHT(I)=1.
    ELSE
        WEIGHT(I)=1./ABS(Y(I))
    END IF
END IF
30  CONTINUE
C
C    *** Main Loop ***
C
35  DO 42 J=1,NPAR
    BETA(J)=0.
    DO 40 K=1,J
        ALPHA(J,K)=0.
40    CONTINUE
42  CONTINUE
C
DO 50 I=1,NDATA
    X1=X(I)
    YFIT(I)=FUNC(I,X1,A)
    DO 48 J=1,NPAR
        DERIV(J)=FDERIV(I,J,X1,A)
        BETA(J)=BETA(J)+WEIGHT(I)*(Y(I)-YFIT(I))*DERIV(J)
        DO 46 K=1,J
            ALPHA(J,K)=ALPHA(J,K)+WEIGHT(I)*DERIV(J)*DERIV(K)
46    CONTINUE
48    CONTINUE
50  CONTINUE
DO 54 J=1,NPAR

```

```

        DO 52 K=1,J
            ALPHA(K,J)=ALPHA(J,K)
52      CONTINUE
54      CONTINUE
        CHISQ1=FCHISQ(Y,SIGMAY,NDATA,NFREE,MODE,YFIT)
C
C      *** Do it again with larger FLAMDA ***
C
70      NPASS=NPASS+1
C      *** Subroutine PRTPAR prints parameters on the screen
C      *** and into file #11.
        CALL PRTPAR(NPASS,A)
C      CALL PRT13(NDATA,A,X)
C
        IF (NPASS.GT.ITMAX) RETURN
        DO 65 I=1,NPAR
            B(I)=BETA(I)
65      CONTINUE
        DO 74 I=1,NPAR
            DO 72 J=1,NPAR
                ARRAY(I,J)=ALPHA(I,J)
72      CONTINUE
                ARRAY(I,I)=ARRAY(I,I)*(1.+FLAMDA)
74      CONTINUE
        CALL DLINRG(NPAR,ARRAY,NPAR,ARINV,NPAR)
        DO 75 J=1,NPAR
            B(J)=0.
            DO 73 K=1,NPAR
                B(J)=B(J)+BETA(K)*ARINV(J,K)
73      CONTINUE
            C(J)=A(J)+B(J)
75      CONTINUE

```

C IF CHI SQUARE INCREASED, INCREASE FLAMDA AND TRY AGAIN

C

DO 78 I=1,NDATA

X1=X(I)

YFIT(I)=FUNC(I,X1,C)

78 CONTINUE

CHISQR=FCHISQ(Y,SIGMAY,NDATA,NFREE,MODE,YFIT)

IF(CHISQ1.LT.CHISQR) THEN

FLAMDA=4.*FLAMDA

GOTO 70

ENDIF

C EVALUATE PARAMETERS AND UNCERTAINTIES

DO 100 J=1,NPAR

A(J)=C(J)

SIGMAA(J)=SQRT(1.0/ALPHA(J,J))

100 CONTINUE

FLAMDA=FLAMDA/4.

C TEST CONVERGENCE TO CHI SQUARE TOLERANCE

IF ((CHISQ1-CHISQR)/CHISQR.GT.TOL1.OR.CHISQR.GT.TOL2) GOTO 35

RETURN

END

C

C =====

C

DOUBLE PRECISION FUNCTION FCHISQ(Y,SIGMAY,NDATA,NFREE,
* MODE,YFIT)

C

PARAMETER(NMX=50)

C

DOUBLE PRECISION Y(NMX),SIGMAY(NMX),YFIT(NMX)

DOUBLE PRECISION CHISQ,WEIGHT(NMX)

COMMON/CF/WEIGHT

```

C
    CHISQ=0.
    FCHISQ=0.
C  ACCUMULATE CHI SQUARE
    DO 30 I=1,NDATA
        CHISQ=CHISQ+WEIGHT(I)*(Y(I)-YFIT(I))*(Y(I)-YFIT(I))
30  CONTINUE
C  DIVIDE BY NUMBER OF DEGREES OF FREEDOM
    FREE=NFREE
    FCHISQ=CHISQ/FREE
    RETURN
    END

C
C  =====
    DOUBLE PRECISION FUNCTION FDERIV(I,J,X,A)
C
    PARAMETER(NPAR=3)
C
    DOUBLE PRECISION X,A(NPAR),A1,FG,FL
    INTEGER I,J
C
    A1=A(J)
    A(J)=1.001*A1
    FG=FUNC(I,X,A)
    A(J)=.999*A1
    FL=FUNC(I,X,A)
    A(J)=A1
    FDERIV=(FG-FL)/(.002*A1)
    RETURN
    END

C
C  =====

```



```

C
DOUBLE PRECISION FUNCTION FUNC(I,X1,A)
C
C      Program to calculate the effect of Oxygen Vacancy
C      All the S's are vectors(1-dim)
C      1st order perturbations are considered.
C
PARAMETER(NPAR=3)
PARAMETER(NLATT=11)
PARAMETER(NMX=50)
C
DOUBLE PRECISION A(NPAR),MFMU,X1,X2(NMX),Y2(NMX)
COMMON/DATA/ X2,Y2
C
DOUBLE PRECISION T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
COMMON/MOLA/ T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
C
DOUBLE PRECISION SDI(NMX),SAI(NMX),SDA(NMX),SDAA(NMX)
DOUBLE PRECISION SDV(NMX),SDVA(NMX),SAV(NMX),SAA(NMX)
DOUBLE PRECISION SDN(NMX),SAN(NMX),SD(NMX),SA(NMX),STOTAL(NMX)
COMMON/MOLB/SDI,SAI,SDA,SDAA,SDV,SDVA,SAV,SAA
*      ,SDN,SAN,SD,SA,STOTAL
C
DOUBLE PRECISION FI,F1,FDA,FDAA,FDV,FDVA,FAV,FAA
COMMON/MOLC/ FI,F1,FDA,FDAA,FDV,FDVA,FAV,FAA
C
DOUBLE PRECISION FNORM,ERRREL
DOUBLE PRECISION XGUESS(NLATT),X(NLATT)
INTEGER ITMFMAX,I
C
EXTERNAL DNEQNF,FCN
C

```

```

C   *** Mfmu is the value of 4*pi*M for 1 bohr magneton per formula
C       UNIT of pure YIG ***
      MFMU = 491.863
C
C   The following exchange integrals have units of 1e-15 erg.
C
      T = X1
      JAD = -5.02 * A(1)
      JDD = -2.362 * A(2)
      JAA = -1.683 * A(3)
C
      ERRREL = 1.0D-2
      ITMFMAX = 100
      IF (I.EQ. 1) THEN
        XGUESS(1)= 2.5
        XGUESS(2)= -2.5
        XGUESS(3)= 2.5
        XGUESS(4)= -2.5
        XGUESS(5)= -2.499
        XGUESS(6) = 2.5
        XGUESS(7) = 2.5
        XGUESS(8) = 2.5
        XGUESS(9) = 2.5
        XGUESS(10) = -2.5
        XGUESS(11) = -2.5
      ELSE
        XGUESS(1) =SD(I-1)
        XGUESS(2) =SA(I-1)
        XGUESS(3)=SDN(I-1)
        XGUESS(4)=SAN(I-1)
        XGUESS(5) =SDI(I-1)
        XGUESS(6) = SDA(I-1)

```

```

        XGUESS(7) = SDAA(I-1)
        XGUESS(8) = SDV(I-1)
        XGUESS(9) = SDVA(I-1)
        XGUESS(10) = SAV(I-1)
        XGUESS(11) = SAA(I-1)
    END IF
    CALL DNEQNF(FCN,ERRREL,NLATT,ITMFMX,XGUESS,X,FNORM)
    SD(I) = X(1)
    SA(I) = X(2)
    SDN(I) = X(3)
    SAN(I) = X(4)
    SDI(I) = X(5)
    SDA(I) = X(6)
    SDAA(I) = X(7)
    SDV(I) = X(8)
    SDVA(I) = X(9)
    SAV(I) = X(10)
    SAA(I) = X(11)
C
    STOTAL(I) = (3.0-VFD)*SD(I)-0.2*FI*SDI(I) +(2.0-ASUB-VFA)*SA(I)
    FUNC = 2.0 * STOTAL(I) * MFMU
C
    WRITE(*,245) T,Y2(I),FUNC,SDAA(I)
245  FORMAT(5X,F7.0,1X,F10.2,1X,F10.2,2X,F10.2)
C
    RETURN
    END
C
C =====
C
C
    SUBROUTINE FCN(X,F,N)
C

```

```

C      This subroutine is used for DNEQNF
C
C      PARAMETER(NLATT=11)
C      DOUBLE PRECISION X(NLATT),F(NLATT),ARG(NLATT)
C
C      DOUBLE PRECISION CF
C      DOUBLE PRECISION T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
C      COMMON/MOLA/ T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
C
C      DOUBLE PRECISION FI,F1,FDA,FDAA,FDV,FDVA,FAV,FAA
C      COMMON/MOLC/ FI,F1,FDA,FDAA,FDV,FDVA,FAV,FAA
C
C      INTRINSIC TANH
C
C      The CF is 2*10*S/kT. 10 comes from the unit of J's(1e-15 erg)
C      and the unit of k(1e-16 erg/K).
C
C      CF = 2.0*10*2.5/(1.38062*T)
C
C      F(1)= X(1)- 1.0/(3.0-VFD)* ( 3.0-VFD-FI-FDA-FDAA-FDV-FDVA)*X(3)
C      *      +FI*X(5)+FDA*X(6)+FDAA*X(7)+FDV*X(8)+FDVA*X(9) )
C      F(2)= X(2)- 1.0/(2.0-ASUB-VFA)* ((2.0-ASUB-VFA-FAV-FAA)*X(4)
C      *      +FAV*X(10)+FAA*X(11) )
C
C      ARG(3)= CF*( JDD*4.0*X(1) + JAD*4.0*X(2) )
C      ARG(4)= CF*( JAD*6.0*X(1) + JAA*8.0*X(2) )
C      ARG(5)= CF*( JDD*4.0*X(1) + JI*X(2) + JAD*3.0*X(2) )
C
C      ARG(6)= CF*( JDD*4.0*X(1) + JAD*3.0*X(2) )
C      ARG(7)= CF*( JDD*4.0*X(1) + JAD*2.0*X(2) )
C      ARG(8)= CF*( (JDD*4.0+DJDD)*X(1) + JAD*3.0*X(2) )
C      ARG(9)= CF*( (JDD*4.0+DJDD)*X(1) + JAD*2.0*X(2) )

```

```

C
    ARG(10) = CF*( 5.0*JAD*X(1) + 8.0*JAA*X(2) )
    ARG(11) = CF*( 6.0*JAD*X(1) + 7.0*JAA*X(2) )
C
    DO 250 I=3,11
    F(I)= X(I) - 2.5*(1.2/TANH(1.2* ARG(I))-0.2/TANH(0.2*ARG(I)))
250  CONTINUE
    RETURN
    END
C =====
    SUBROUTINE OPENFILES(FOLD)
C
    Character*10 fold
    Character*11 fnew1,fnew2,FNEW3
C
    WRITE(5,311)
311  FORMAT(// ' Name of data file excluding ".prn" ? ', $)
    READ(*,321) FOLD
321  FORMAT(A10)
    FNEW1=FOLD// 'A'
    FNEW2=FOLD// 'B'
    FNEW3=FOLD// 'S'
C
C
    WRITE(5,331) FNEW1
331  FORMAT(/ ' * Interacting I/O will be recorded in ',A11, '.DAT')
    WRITE(5,333) FNEW2
333  FORMAT(' * The data and calculated values   in ',A11, '.DAT')
    WRITE(5,337) FNEW3
337  FORMAT(' * Values of the spins are written in ',A11, '.DAT')
C
    OPEN(10,FILE=FOLD,STATUS='OLD',DEFAULTFILE='.PRN')

```

```

      OPEN(11,FILE=FNEW1,STATUS='NEW')
      OPEN(12,FILE=FNEW2,STATUS='NEW')
      OPEN(13,FILE=FNEW3,STATUS='NEW')
C
      WRITE(11,*)
      WRITE(11,*) '                TRACE OF FITTING PROCEDURE'
      WRITE(11,*)
      WRITE(11,*) '      A(1)          through      A(NPAR) '
C
      RETURN
      END
C =====
      SUBROUTINE RDDATA(NDATA,X,Y)
C
      PARAMETER(NMX=50)
      DOUBLE PRECISION X(NMX),Y(NMX)
      INTEGER NDATA,I
C
      I = 0
371      I = I + 1
          READ(10,*,END=373) X(I),Y(I)
          GO TO 371
373      NDATA = I-1
C
      WRITE(*,381) NDATA
381      FORMAT(/ '*** The number of data points is now ',I3)
C
      RETURN
      END
C =====
      SUBROUTINE GETFITPAR(TOL1,TOL2,FLAMDA,DELTAY,SIGMAY,MODE,ITMAX)
C

```

```

PARAMETER(NMX=50)
DOUBLE PRECISION TOL1,TOL2,FLAMDA,DELTAY,SIGMAY(NMX)
INTEGER MODE,ITMAX
WRITE(5,711)
711  FORMAT(/ / ' Enter TOL1(a constant less than 0.1): TOL1 = ? ', $)
      READ(*,*) TOL1
      TOL2=1000000.
      FLAMDA=0.0010
      DELTAY=1.0
C
C  POSSIBLE MODES ARE -1,0,1
      MODE= 0
C  MAXIMUM NUMBER OF ITERATION
      ITMAX=100
C
      DO 713 I=1,NMX
        SIGMAY(I) = DELTAY
713  CONTINUE
C
      RETURN
      END
C  =====
      SUBROUTINE GETMFPAR(A,FOLD)
C
C      Assign the INITIAL VALUES OF PARAMETERS
C
      PARAMETER(NPAR=3)
      DOUBLE PRECISION A(NPAR),AF(11)
C
      CHARACTER*10 FOLD
      CHARACTER*10 DUMMY
C

```

```

DOUBLE PRECISION P1,P2
DOUBLE PRECISION T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
COMMON/MOLA/ T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
C
DOUBLE PRECISION FI,F1,FDA,FDAA,FDV,FDVA,FAV,FAA
COMMON/MOLC/ FI,F1,FDA,FDAA,FDV,FDVA,FAV,FAA
C
OPEN(15,FILE=FOLD,STATUS='OLD',DEFAULTFILE='.PAR')
DO 730 I=1,11
  READ(15,735) DUMMY,AF(I)
  WRITE(*,735) DUMMY,AF(I)
730  CONTINUE
735  FORMAT(5X,A10,F8.5)
      CLOSE(15)
C
DO 740 I=1,3
  A(I) = AF(I)
740  CONTINUE
C
DJDD = -2.362 * AF(4)
C
JI    = 5.02 * AF(5)
VO    = AF(6)
FDVA  = AF(7)
C    FDAA = AF(8)
CA    = AF(9)
ASUB  = AF(10)
VF    = AF(11)
C
VFD = VF/2.0
VFA = VF - VFD
VO2 = 0.5*CA - 0.5*VO + 1.5*ASUB + 1.5*VF

```



```

C
      P1 = (ASUB+VFA)/2.0
      P2 = V02/12.0
C
      FI = V0
C
      FDVA = 3 * 6*P1*P2*(1-P1-P2)**2
      FDAA = (ASUB+VFA)*(8*P1*(1.0-P1)**7 *2 + 6*P1*(1-P1)**5)*0.5
C
      0.5 in the above formula is included to avoid double counting.
C
      FDV = V02 - FDVA
      IF (FDV.LT.0) THEN
        FDV = 0
      END IF
C
      FDA = 6.0*(ASUB+VFA) - 2.0*FDAA - FDVA
      FAV = V02 + V0 + 4.0*VFD
      FAA = (2.0-ASUB-VFA) * 8.0*P1*(1.0-P1)**7
      WRITE(*,750) FDA,FDAA,FDV
      WRITE(*,760) FDVA,FAV,FAA
750  FORMAT(/,5X,'FDA =',F8.4,3X,'FDAA =',F8.4,3X,'FDV =',F8.4)
760  FORMAT(5X, 'FDVA =',F8.4,3X,'FAV =',F8.4,3X,'FAA =',F8.4)
C
      RETURN
      END
C  =====
      SUBROUTINE PRTPAR(NPASS,A)
C
      PARAMETER(NPAR=3)
      DOUBLE PRECISION A(NPAR)
      WRITE(5,61) NPASS,(A(I),I=1,NPAR)

```

```

        WRITE(11,61) NPASS,(A(I),I=1,NPAR)
C        WRITE(5,62)  (A(I),I=6,NPAR)
C        WRITE(11,62) (A(I),I=6,NPAR)

61      FORMAT(1X,I3,3F10.5)
C 62      FORMAT(4X,5E15.6)

        RETURN
        END

C =====
        SUBROUTINE FREPT(NPASS,CHISQR,A,SIGMAA)
C
        PARAMETER(NPAR=3)
        INTEGER NPASS
        DOUBLE PRECISION A(NPAR),SIGMAA(NPAR)
        REAL CHISQR
C
        PRINT 600, NPASS
        WRITE(11,600) NPASS
600      FORMAT(6X,'LOOPING STOPPED AFTER ',I2,' ITERATIONS')
        PRINT 610, CHISQR
        WRITE(11,610) CHISQR
610      FORMAT(/ 6X,'FINAL CHI SQUARE PER DEGREE OF FREEDOM =',E12.5 /)
C
C      * Write parameters and their errors on the screen and file #11.
        DO 620 I=1,NPAR
        WRITE(5,630)  I,A(I),I,SIGMAA(I)
        WRITE(11,630) I,A(I),I,SIGMAA(I)
620      CONTINUE
630      FORMAT('  A(',I2,')=',F10.6, '      SIGMAA(',I2,')=',E12.5)
C
        RETURN
        END

```

```

C =====
  SUBROUTINE PRT12(NDATA,A,X,Y,YFIT)
C
  PARAMETER(NPAR=3)
  PARAMETER(NMX=50)
  DOUBLE PRECISION A(NPAR),X(NMX),Y(NMX),YFIT(NMX)
  INTEGER NDATA
C
  WRITE(12,815)
815  FORMAT(/ 9x,'T',3x,'Measured',2x,'CALCULATED')
  DO 820 I=1,NDATA
    WRITE(12,825) X(I),Y(I),YFIT(I)
820  CONTINUE
825  FORMAT(2X,F10.1,F10.2,F10.2)
  RETURN
  END
C =====
  SUBROUTINE PRT13(NDATA,A,X)
C
  PARAMETER(NPAR=3)
  PARAMETER(NMX=50)
  INTEGER NDATA
  DOUBLE PRECISION A(NPAR),X(NMX)
C
  DOUBLE PRECISION T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
  COMMON/MOLA/ T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
C
  DOUBLE PRECISION SDI(NMX),SAI(NMX),SDA(NMX),SDAA(NMX)
  DOUBLE PRECISION SDV(NMX),SDVA(NMX),SAV(NMX),SAA(NMX)
  DOUBLE PRECISION SDN(NMX),SAN(NMX),SD(NMX),SA(NMX),STOTAL(NMX)
  COMMON/MOLB/SDI,SAI,SDA,SDAA,SDV,SDVA,SAV,SAA
  *          ,SDN,SAN,SD,SA,STOTAL

```

C

```
DOUBLE PRECISION FI,F1,FDA,FDAA,FDV,FDVA,FAV,FAA
COMMON/MOLC/ FI,F1,FDA,FDAA,FDV,FDVA,FAV,FAA
```

C

```
WRITE(13,810) -JAD/5.02,-JDD/2.362,-JAA/1.683
WRITE(13,811) -DJDD/2.362,-DJAA/1.683,JI/5.02
810  FORMAT(4X,'JAD=',F8.5,1X,'JDD=',F8.5,1X,'JAA=',F8.5)
811  FORMAT(6X,'DJDD=',F8.5,1X,'DJAA=',F8.5,1X,'JI=',F8.5)
```

C

```
WRITE(13,812) VO,VO2,ASUB,VF
812  FORMAT(8X,'VO=',F8.5,2X,'VO2=',F8.5,2X,'Asub=',F8.5,
*      2X,'VF=',F8.5)
WRITE(13,814) FDVA,FDV,FDAA,FDA
814  FORMAT(8X,'FDVA=',F8.5,2X,'FDV=',F8.5,3X,'FDAA=',F8.5
*      ,2X,'FDA=',F8.5 )
WRITE(13,815)
815  FORMAT(/ 6X,'temp',8X,'SDN',5X,'SAN',5X,'SDI'
*      ,5X,'SDA',4X,'SDAA',4X,'SDV ',4X,'SDVA',5X,'SAV',5X,'SAA')
```

C

```
DO 820 I=1,NDATA
WRITE(13,825) X(I),SDN(I),SAN(I)
*      ,SDI(I),SDA(I),SDAA(I),SDV(I),SDVA(I),SAV(I),SAA(I)
820  CONTINUE
825  FORMAT(4X,F7.2,2F8.4,2X,2F8.4,1X,4F8.4,1X,F8.4)
RETURN
END
```

C

```
C =====
SUBROUTINE PRT15(FOLD,A)
```

C

```
C This subroutine makes a file of parameters.
```

C

```

PARAMETER(NPAR=3)
CHARACTER*10 FOLD
CHARACTER*10 B(11)

```

C

```

DOUBLE PRECISION AF(11),A(NPAR)
DOUBLE PRECISION T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA
COMMON/MOLA/ T,JAD,JDD,JAA,DJDD,JI,VO,VO2,CA,ASUB,VF,VFD,VFA

```

C

```

DOUBLE PRECISION FI,F1,FDA,FDAA,FDV,FDVA,FAV,FAA
COMMON/MOLC/ FI,F1,FDA,FDAA,FDV,FDVA,FAV,FAA

```

C

```

OPEN(15,FILE=FOLD,STATUS='NEW',DEFAULTFILE='.PAR')

```

```

  B(1) = 'Jad'

```

```

  B(2) = 'Jdd'

```

```

  B(3) = 'Jaa'

```

```

  B(4) = 'DJdd'

```

```

  B(5) = 'JI'

```

```

  B(6) = 'Vo'

```

```

  B(7) = 'FDVA'

```

```

  B(8) = 'FDAA'

```

```

  B(9) = 'Ca'

```

```

  B(10) = 'Asub'

```

```

  B(11) = 'VF'

```

```

  AF(1) = JAD /(-5.02 )

```

```

  AF(2) = JDD /(-2.362)

```

```

  AF(3) = JAA /(-1.683)

```

```

  AF(4) = DJDD/(-2.362)

```

```

  AF(5) = JI  / 5.02

```

```

  AF(6) = VO

```

```

  AF(7) = FDVA

```

```

  AF(8) = FDAA

```

```

  AF(9) = CA

```

```
        AF(10) = ASUB
        AF(11) = VF
    DO 850 I=1,11
        WRITE(15,855) B(I),AF(I)
850    CONTINUE
855    FORMAT(5X,A10,F8.5)
        CLOSE(15)
C
        RETURN
    END
C
C =====
```

Appendix B

SAMPLE DATA FILES FOR PROGRAM MFIT3.FOR.

E3D.PRN

4	2037.2
6	2037.1
8	2027.0
11	2009.1
15	1971.6
20	1959.6
30	1898.2
40	1842.2
50	1784.9
60	1730.3
80	1631.2
100	1543.2
150	1372.9
202	1231.1
250	1098.5
295	976.8
350	817.1

400	689.0
450	536.0
490	317.7
495	257.2
500	198.9
503	156.7
506	92.0

E3D.PAR

Jad	1.03078
Jdd	1.14415
Jaa	0.75308
DJdd	-0.20000
JI	1.70621
Vo	0.15900
FDVA	0.40000
FDAA	0.09730
Ca	0.25000
Asub	0.11000
VF	0.14000

E3DA.DAT

TRACE OF FITTING PROCEDURE

	A(1)	through	A(NPAR)
1	1.02662	1.13332	0.74528
2	1.03054	1.14387	0.75240
3	1.03054	1.14387	0.75240

LOOPING STOPPED AFTER 3 ITERATIONS

FINAL CHI SQUARE PER DEGREE OF FREEDOM = 0.24874E+03

A(1)= 1.030785 SIGMAA(1)= 0.36968E-04
A(2)= 1.144153 SIGMAA(2)= 0.12139E-03
A(3)= 0.753083 SIGMAA(3)= 0.14058E-03

E3DB.DAT

T	Measured	CALCULATED
4.0	2037.20	2025.82
6.0	2037.10	2024.27
8.0	2027.00	2019.94
11.0	2009.10	2007.96
15.0	1971.60	1985.26
20.0	1959.60	1952.60
30.0	1898.20	1887.25
40.0	1842.20	1827.57
50.0	1784.90	1773.78
60.0	1730.30	1724.92
80.0	1631.20	1638.13
100.0	1543.20	1561.12
150.0	1372.90	1391.82
202.0	1231.10	1236.03
250.0	1098.50	1103.24
295.0	976.80	983.33
350.0	817.10	833.93
400.0	689.00	684.42
450.0	536.00	501.00
490.0	317.70	283.87

495.0	257.20	243.74
500.0	198.90	195.55
503.0	156.70	159.87
506.0	92.00	113.52