ELECTRONIC STRUCTURE OF Al₂O₃:
VUV REFLECTIVITY MEASUREMENTS FROM ROOM TEMPERATURE TO 1100 °C

by

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B.S. Cornell University, Ithaca (1979)

Submitted to the Department of Materials Science and Engineering in Partial Fulfillment of the Requirements of the Degree of DOCTOR OF PHILOSOPHY at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

February 1985

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MAR 25 1985
ABSTRACT

Electronic Structure of Al₂O₃: VUV Reflectivity Measurements from Room Temperature to 1100 °C

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Submitted to the Department of Materials Science and Engineering on January 11, 1985 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

A Vacuum Ultraviolet (VUV) Spectrophotometer was built to measure the near normal incidence reflectivity and transmissivity from 6 to 15 eV of samples heated without contamination from room temperature to 1100 °C. The relative energy resolution is 0.01 eV while the absolute resolution is 0.1 eV. The temperature dependence of the electronic structure of single crystal Al₂O₃ was studied.

Room temperature measurements on oriented samples show three main features: an 8.8 eV absorption edge corresponding to transitions from the O 2p bands in the top of the valence band to the Al 3s bands in the bottom of the conduction band, a 9 eV peak which is attributed to exciton formation, and a 13 eV peak that is due to transitions to the Al 3p bands in the conduction band. The 13 eV peak shows orientation dependent features that have not been reported previously; for E perpendicular to the crystallographic c axis a shoulder at 12 eV and a peak at 13.1 eV are observed, while for E parallel to the c axis a doublet peak is observed at 12.9 and 12.3 eV. These features have been interpreted in terms of the available room temperature electronic structure models. Even though these measurements did not identify the direct or indirect nature of the minimum band gap of the material, the 8.8 eV edge is assigned to the room temperature optical direct band gap of the material.

With increasing temperature the three features in the reflectivity broaden and shift to lower energies; the shifts were linear over the temperature range studied. The linear temperature dependence should hold up to 1500 °C where anharmonicity of the lattice vibrations becomes noticeable. The temperature dependence of the band gap is given by E (T), where β is the linear temperature coefficient of the band gap and E°(T=0K) is the T = 0 K apparent optical band gap of Al₂O₃.

\[ E_g(T) = E_g^0(T=0K) - \beta T \]

\[ \beta = 1.1 \times 10^{-3} \text{ eV/K} +/\ 1 \times 10^{-4} \]

\[ E_g^0(T=0K) = 9.1 \text{ eV} +/\ 0.25 \]
The lattice stabilization energy ($\Delta$) represents the difference between the optical and thermal band gap energies and arises due to the difference between the time scales of electronic excitations ($10^{13}$ Hz) and the concomitant response of the lattice ($10^{15}$ Hz) to the excited carriers. $\Delta$ leads to a decrease in the carrier creation energy for thermal excitation processes. $\Delta$ was not determined in this work, and no reasonable estimates exist in the literature.

In previous attempts to analyze the high temperature intrinsic electronic conductivity of $\text{Al}_2\text{O}_3$, the conductivity was used with assumed models for the carrier mobility to determine the band gap energy. With the knowledge of the high temperature electronic structure presented in this work, a different and more fruitful approach can be pursued. The character of electrons and holes, whether they are large or small polarons, determines their mobility. Information on the character and mobility of carriers in $\text{Al}_2\text{O}_3$ is scant at best; electrons have mobilities on the order of 1 to $100 \text{ cm}^2/\text{V sec}$ and appear to form large polarons, while the mobility of holes has yet to be observed. Therefore, it seems reasonable to use the results of conductivity measurements, with our knowledge of the high temperature electronic structure, to derive information about the electron and hole mobilities. This analysis suggests that the holes in $\text{Al}_2\text{O}_3$ form small polarons with a thermally activated mobility.

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Acknowledgements

I am indebted to Prof. R. L. Coble for his guidance and support throughout this research project. In addition he taught me a creative approach to formulating research problems. The guidance of Dr. Hans Jenssen was instrumental in my becoming an experienced spectroscopist. I would also like to acknowledge Prof. R. Raj of Cornell for my first exposure to research.

The aid of Pat Kearney in teaching me the way around the lab was essential and I thank him.

I would like to dedicate this thesis to my parents who have supplied me with an education and an outlook that made this document possible. Their support and assistance throughout my life is gratefully acknowledged and appreciated.

The students in the department were a major asset both to my education and the quality of life during my tenure. I would like to thank Todd Gattuso, Art Keigler and Patti Morris for their assistance in preparation of this document. In addition to these three people I owe my thanks to Yet Min-Chiang, Alexana Roshko, Jeff Gambino, Brint Corb, Joe Dynys and many others for the technical and non-technical discussions we
had over the years, and the friendships we have built.

I gratefully acknowledge the support of the Department of Energy through contract number DE-AC02-76-ER02390 for making this research possible.
Chapter 1

Introduction

Aluminum Oxide (Al\textsubscript{2}O\textsubscript{3}) is an important ceramic material in both its single crystalline and polycrystalline forms for structural and electronic applications. Traditionally used for its high temperature structural abilities or as a high temperature and room temperature insulator, it is acquiring new importance in electronic applications as a chip carrier module, a thin film insulator, a single crystal substrate material for SOI (silicon on insulator) integrated circuits, and as an optical material in opto-electronic devices. Its major applications worldwide are as a polycrystalline ceramic and as a prototypical ceramic for fundamental ceramics research. The ceramics research has focused on understanding the high temperature defect structure, diffusion, sintering and creep behavior of Al\textsubscript{2}O\textsubscript{3}; the defect formation energies, specific defects, their charges and mobilities are fundamental to all of these processes.

Al\textsubscript{2}O\textsubscript{3} is a complex material; it is not an ideal isotropic model system. Anisotropic due to its hexagonal crystal structure, with 10 atoms per rhombohedral unit cell, Al\textsubscript{2}O\textsubscript{3} defies simple modeling. It is a highly ionic, highly insulating material, characterized by a large electronic band gap, where many properties are controlled by trace impurity atoms.
Considerable research on Al₂O₃ in the past 20 years has been focused on elucidating mass and charge transport in the material. The charged nature of all atoms and defects controls their transport properties, hence many studies have addressed the intrinsic and extrinsic defect structures.

Conductivity has been the major scientific tool used to understand the defect chemistry of Al₂O₃. Various diffusion experiments, and mass transport experiments such as grain boundary grooving, sintering and creep, have also been used to explore Al₂O₃'s fundamental defect chemistry. Surprisingly, the fundamental intrinsic disorder type (Schottky or Frenkel) is still controversial. The data collected from different laboratories have been inconsistent and inconclusive. These measurements are too nonspecific: parameters measured depend on intrinsic and extrinsic parameters of the sample, and on both ionic and electronic defects. Without fundamentally characterizing the samples it has been impossible to develop a coherent picture of the basic nature of Al₂O₃ and the processes that control its behavior.

Toward this goal, I explore the fundamental properties of Al₂O₃ necessary to separate the superimposed processes observed in conductivity data. Electronic and ionic contributions to the conductivity can be separated in a conductivity experiment by a transference number experiment. Al₂O₃ is a mixed conductor at high temperatures. Concentrating on the electronic conductivity, one wants to determine the number of electronic carriers, identify their intrinsic or extrinsic origins, and measure their mobilities in specific carrier bands. Determination of the electronic structure of Al₂O₃ is required for such analysis. Significant progress toward such is presented in this thesis, which experimentally identifies the temperature dependence of the
electronic structure of Al$_2$O$_3$, from 25 °C to 1100 °C.
Chapter 2

Literature Review

In this chapter the literature will be reviewed to develop an understanding of the electronic structure of $\text{Al}_2\text{O}_3$ at high temperature. In the first section the physical properties of $\text{Al}_2\text{O}_3$ will be reviewed. Then the experimental information that gives insight into the high temperature electronic properties will be presented. In the third section a more detailed discussion of electronic structure and optical properties is pursued. First, the room temperature electronic structure is discussed by considering the electronic structure models and the available optical measurements. Next, the temperature dependence of electronic structure is presented, consisting of the temperature dependent electronic structure theories and the available temperature dependent optical measurements.

2.1 Physical Properties

$\alpha\text{Al}_2\text{O}_3$ is a hard (9 on the moh scale), clear crystal, with exceptional high temperature mechanical and electrical properties. Large high quality single crystals of $\alpha\text{Al}_2\text{O}_3$ can be grown by a variety of techniques such as Verneuil, Czochralski$^1$, Edge-Defined-Film-Growth$^2$, and
the Heat-Exchanger-Method\textsuperscript{3} in a large variety of shapes and sizes. There are three major phases of $\text{Al}_2\text{O}_3$: the $\alpha$ phase is the thermodynamically stable phase at all temperatures, the $\gamma$ phase is a thermodynamically unstable intermediate cubic phase\textsuperscript{4} formed through the dehydration of hydrated aluminas, and the amorphous phase can be formed by the low temperature oxidation of aluminum metal. $\text{Al}_2\text{O}_3$ is an ionic material with a Pauling ionicity of 56\%. Effective charge calculations show a large charge transfer between Al and O atoms suggesting an even larger degree of ionicity. The band gap is large and the lattice point defect concentration is low, making $\text{Al}_2\text{O}_3$ a 'good' insulator. Its melting point is 2051 °C, while its Debye temperature has been variously reported to be 1050 K\textsuperscript{5}, 935 K\textsuperscript{6} or 695 K\textsuperscript{7}. The index of refraction and dielectric constant at room temperature are respectively 1.7604 and 9.3 perpendicular to the c axis and 1.7686 and 11.5 parallel to the c axis.

The $\alpha$ phase consists of a hexagonal close packed, AB oxygen stacking sequence, with two-thirds of the octahedral voids filled by aluminum atoms. The presence of three aluminum layers — in sequence $\alpha$, $\beta$, $\gamma$ — leads to a unit cell with twelve layers in the sequence $A \alpha B \beta A \gamma B \alpha A \beta B \gamma$. Along the octahedral sites parallel to the c axis there are two aluminum atoms followed by a void. The fact that only 2/3 of the octahedral sites are occupied allows aluminum-aluminum repulsion to distort the ideal octahedral ($O_h$ point group) coordination of the aluminum. Each oxygen ion is in distorted tetrahedral coordination with Al atoms. These coordination clusters can be seen in figure 2.1. The space group of $\text{Al}_2\text{O}_3$ is $D_{3d}^6$ or $R\overline{3}c$.\textsuperscript{8} With two different Al-O bond lengths of 0.186 nm and 0.197 nm.\textsuperscript{9} The fundamental unit cell is rhombohedral, containing two formula units (10 atoms). The hexagonal cell, containing 30 atoms has lattice parameters $a =$
0.475 \text{ nm} \text{ and } c = 1.299 \text{ nm}.

The structural changes associated with changes in temperature are: thermal expansion of the lattice, changes in the distortion of the atomic coordination of the atoms and increasing atomic vibration as demonstrated by the Debye Waller factors. Thermal expansion of Al$_2$O$_3$ varies with temperature, and at 1100 °C is $8.84 \times 10^{-6} / \text{oC}$ perpendicular to the c axis, and $7.96 \times 10^{-6} / \text{oC}$ parallel to the c axis.\textsuperscript{10} There have been two diffraction studies performed to determine the structural changes occurring with temperature. High temperature x-ray diffraction results to 1900 °C\textsuperscript{11} showed the changes in the crystal lattice at high temperature, and concentrated on the specific changes occurring for each interatomic distance. The Al-O bond lengths were reported to change from 0.1971 and 0.1852 nm at room temperature to 0.2024 and 0.1880 nm at 1900 °C. In other words the difference between the two Al-O bond lengths increases with temperature. The oxygen sub-lattice moves toward a more perfect hexagonal order with temperature, but the Al sub-lattice distortion increases with increasing temperature. At 1900 °C the distortion of the octahedral coordination of the Al has increased, with an increase in the Al-Al distance. The Debye-Waller factors, which represent the magnitude of thermal vibrations, were 0.33 nm$^2$ at room temperature and 2.25 nm$^2$ at 1900 °C. The Debye Waller factor $B = 8\pi^2 u^2$, where $u$ equals the rms thermal displacement, so these correspond to atomic vibrations of 0.0064 nm at room temperature and 0.0168 nm at 1900 °C.

The structural changes to 2000 °C were studied by Aldebert\textsuperscript{12} using neutron diffraction. The Debye-Waller factors measured are shown in figure 2.2. These are linear up to 1500 °C. The departure from linearity above this temperature is attributed to the onset of anharmonic atomic
vibrations. This implies there are three regimes: below the Debye temperature higher energy phonon modes are excited, above 750 °C thermal energy increases the amplitude of the modes present, and above 1500 °C lattice vibrations become anharmonic. This region of anharmonicity is associated with the approach to melting, although the corundum crystal structure is maintained up to the melting point. Aldebert also observed an increasing difference between the two Al-O bond lengths, and the increasing distortion of the Al Octahedral coordination.

2.2 High Temperature Electronic Properties

In this section various results from the ceramics literature will be cited that give insight into the electronic properties of Al₂O₃: the conductivity, the mobility of carriers, the energy for optical creation of carriers, and the difference between optically and thermally created carriers.

2.2.1 Conductivity Results

There have been numerous studies done on the conductivity of Al₂O₃ both in nominally pure or intentionally doped, single and polycrystalline samples. Most conductivity results reported in the 60's and early 70's were due to surface and gas conduction, not the conductivity of the sample. It became obvious that higher purity and better characterized
samples were needed to successfully model the defect chemistry. Kroger has studied the conductivity and defect chemistry of Al₂O₃ extensively, using many different dopants, and has reported a large quantity of data on well characterized samples. This has served to advance the modeling of Al₂O₃, has shown the dopant activity of hydrogen in Al₂O₃ and has measured the lowest electronic conductivity at the compensation point yet reported. Still even with Kroger’s extensive study we lack a comprehensive understanding of the conductivity and defect structure of Al₂O₃; for example, different experiments still suggest different fundamental disorder mechanisms. The temperature dependence of the electronic carrier creation energy $E_g(T)$ is an important factor necessary for the modeling of the conductivity behavior of Al₂O₃, but up to now such information has been lacking.

Al₂O₃ is a mixed ionic-electronic conductor whose behavior can be understood from the conduction mechanism plot of Kitazawa (see figure 2.3). Using a technique to avoid spurious conduction, and performing ionic transference numbers experiments, three regions of conductivity were identified. By looking at the variation of conductivity with $pO_2$ at constant temperature, (see figure 2.4) one can see the V shape of the curves corresponding to transitions from n to ionic to p type conduction. At low temperatures (T<1400 °C) the observed conductivity was predominantly ionic and independent of $pO_2$. At higher temperatures and low $pO_2$, the sample was an n type electronic conductor, while at high $pO_2$ the sample is a p type (hole) conductor.

Kroger has observed conductivities lower than those reported by Kitazawa and with a different transference number behavior, and therefore contests Kitazawa's conduction mechanism results. Kroger has used a
different conductivity technique to extract a band gap or electronic carrier creation energy from conductivity measurements. The $V$ shaped $\sigma$ vs $P_{02}$ curves taken under non-equilibrium conditions, where new atomic defects are not created show the compensation point of the material at the base of the $V$, where equal numbers of electrons and holes are present in the sample. Kroger used an acceptor dominated sample and 'titrated' with hydrogen, which acts as a donor. The conductivities due to ions, electrons and protons, and the transferences were measured, allowing the identification of $\sigma$ due to $e', h', V_{Al^{''''}}$, and $Al^{'''}_i$. The data was then analyzed, incorporating the mobilities of the various defects, permitting the extraction of the equilibrium constants $K$ for the mass action relations that then yield the carrier creation energies and defect formation energies. If the electronic carrier creation energy is known, and used in the calculation, then the mobilities can be determined.

It is useful to further analyze the theory behind these non-equilibrium titration experiments, because they show the relationship between $E_g$ and $\beta$ (the temperature coefficient of the gap) and the defect structure and models of the material. The electronic and hole conductivities are given by:

$$\sigma_e = N[e] q \mu_e \quad \text{and} \quad \sigma_h = N[h] q \mu_h.$$

Here $N$ is the number of $Al_2O_3$ molecules per $cm^3$, $[e]$ and $[h]$ are the concentration of electrons and holes per molecule, $q$ is the electron charge and $\mu$ is the appropriate mobility. At the compensation point,

$$\sigma_e \sigma_h = q^2 N_i \mu_e \mu_h \quad 0 \rightarrow e' + h' \quad K_i.$$
\( \sigma e \sigma_h \) gives one the mass action relation equilibrium constant for creation of intrinsic electronic carriers. Assuming large polarons this has the form

\[ K_i = C T^3 e^{-\frac{E_g}{kT}}. \]

Now \( E_g = E_g^0 (T=0 K) - \beta T \)

therefore \( K_i = C T^3 \frac{e^\beta/k}{e^{E_g^0/kT}} \)

or \( K_i \sim C \frac{e^\beta/k}{e^{-\left(E_g^0+\Delta\right)/kT}} \).

The linear model of \( E_g (T) \) is confirmed for \( Al_{2}O_{3} \) in this work. This analysis leads to values of \( 10 \pm 2.1 \) eV and \( 11 \pm 1 \) eV for \( E_g^{opt} (T=0 K) \) and a value of \( 0.65 \pm 2.1 \) eV for \( \Delta \), the difference between the optical and thermal gaps. The large number of assumptions used in these calculations raises doubt about the validity of these specific numbers. For example, the assumption that both carriers are large polarons is not well established but strongly affects the interpretation. But, the analysis is instructive in showing the role of the temperature dependence of the electronic structure in defect chemistry.

To summarize Kroger's reported values of the band gap of \( Al_{2}O_{3} \) for modelling conductivity data, the optical band gap, \( E_g^0 \), was 10.35 eV and the thermal gap energy, \( E_g^t \), was 9.7 eV Both of these energies correspond to a temperature of 0 K.

2.2.2 Mobility Measurements

The mobilities of electronic carriers in \( Al_{2}O_{3} \) have been measured in
Hall effect and photoconductivity experiments. In semiconductors, the mobility is related to the curvature of the 'band' through the effective mass. In a large band gap material, the mobility is also affected by carrier type, i.e. whether the carrier is a polaron or a band electron. The mobility serves as a good indicator of carrier type. Additionally, the mobility is required to estimate the conductivity.

Hughes\(^\text{16}\) measured transient photoconductivity in Union Carbide sapphire, inducing free carriers with low energy x-rays from 100 to 300 K. The mobility measured was 3 cm\(^2\)/V sec, was independent of temperature and assigned to conduction band electrons. He reported that the hole mobilities were not observed and therefore were much lower. He notes that this may be a trap-modulated mobility, appropriate to photoconductivity at these low temperatures, and is not indicative of the intrinsic carrier mobility. A large polaron without trapping would exhibit mobilities on the order of 15 to 100 cm\(^2\)/V sec due to optical phonon scattering. Dasgupta\(^\text{17}\) measured the Hall mobility of sapphire from 500 to 900 K and observed electron mobilities, increasing with increasing temperature, of 0.1 to 5 cm\(^2\)/V sec. Dasgupta considered that hole mobility may have also contributed to the results but concluded that the majority carriers were electrons. His carriers were not optically created and may have originated from impurity states. At these temperatures the mobility should also correspond to a trap-modulated or impurity scattered mobility, with traps being more efficient than phonons for scattering. Green\(^\text{18, 19}\) studied the Hall mobility of optically created carriers at temperatures up to 1000 K, and observed a mobility of 100 cm\(^2\)/V sec which was assigned to electron mobility; hole mobility was not observed. At high temperatures he concludes that phonon scattering is dominant and that the results represent
the intrinsic carrier mobility.

2.2.3 Photoconductivity Measurements

Photoconductivity is a good technique to identify the energy required to optically create mobile electronic carriers that contribute to the observed conductivity. It has usually been used to study the carriers given off by color centers and other mid-gap states, but, if performed with higher energy optical excitation, it can serve to identify the energy at which true valence band to conduction band excitation occurs. In Al₂O₃, there has been some ambiguity in assigning the energy of band to band transitions to features in the optical spectra, specifically in differentiating the exciton peak observed in the optical spectra from the absorption edge. Kuznetsov²⁰ ²¹ studied the photoconductivity of sapphire from 7.4 to 9.9 eV at room temperature (see figure 2.5). Here one can see the onset of photoconductivity between 8 and 9 eV going to a peak at 9.25 eV. At 9.4 eV the photoconductivity increases very rapidly due to band to band transitions and the large joint density of states at the absorption edge. If one neglects the photoconductivity due to thermal dissociation of excitons, and projects the absorption edge photoconductivity back to observe its onset, one finds that the onset of band to band photoconductivity occurs at 9 eV.

2.2.4 An Electronic Defect Calculation

The atomistic techniques used to calculate point defect properties
in ceramics are generally crude calculations that consider point charges and electrostatic repulsion, their aim is to calculate the properties of atomic size defects. They do not operate on the correct scale to calculate electronic energy levels and states. But in the case of a material such as \( \text{Al}_2\text{O}_3 \) where a large electron-lattice interaction is present, it is instructive to review the results from an atomistic calculation for electronic 'defects'. The calculation of electronic states with atomistic techniques is an interesting hybrid. It serves to highlight many characteristics that might be ignored if the problem were considered to be one of electronic states existing outside the context of the dynamic atomic structure (as exists upon invoking the Born Oppenheimer approximation of a static lattice). Colbourn and Mackrodt have performed the necessary lattice calculation to determine the differences introduced by the lattice relaxation, and calculated the relative stability of large and small hole polarons. They found the large hole polaron state to be 0.4 eV more stable than the small hole polaron state.

They calculated the energy of electronic 'defects' by starting with experimentally determined electronic energies in their calculation and then determining the lattice contribution to the defect energy. The two electronic energies in the calculation are the optical band gap, \( E^o_g \), corresponding to the valence band to conduction band energy and the conduction band edge, \( E_c \), that is, the energy between the bottom of the conduction band and the vacuum level (see figure 2.6). They then define an optical ionization energy, \( E^o_i \), that is the sum of these:

\[
E^o_i = E^o_g + |E_c|.
\]

The optical ionization energy is experimentally determined. It can be decomposed into two components, an optical lattice term, \( E^o_L \), that
includes Madelung and short range contributions and the electronic polarization energy of the lattice due to electron shell relaxation (the thermal version of this term, $E_L^t$ would also contain the relaxation energy due to ion core motion), and an effective ionization potential $e_{eff}^0$ corresponding to the reaction

$$O^2^- \rightarrow O^- + e_{vac}^-$$

Due to small differences in the final state, the effective ionization potential also has a thermal counterpart $e_{eff}^t$ that differs from the optical one by 0.5 $eV$ for $Al_2O_3$. These energies are related to the optical ionization energy by

$$E_i^0 = E_L^0 + e_{eff}^0$$

The lattice contribution is calculated, and the effective ionization potential is determined. Then the thermal band gap $E_g^t$ can be calculated:

$$E_g^t = E_i^t - E_c = E_L^t + e_{eff}^t - E_c$$

Using 9.5 $eV$ for the optical band gap, and 1 $eV$ for the conduction band edge, $E_L^0$ equal to 18.4 $eV$, and $E_L^t$ equal to 16.1 $eV$, then $e_{eff}^0$ is found to be -7.9 $eV$ and $e_{eff}^t$ is 8.4 $eV$. This leads to a thermal band gap of 6.7 $eV$, 2.8 $eV$ less than the optical gap energy.

These lattice calculations are done for a lattice at 0 K only, and therefore, if the optical band gap energy changes with temperature, then the thermal gap energy, using this non-temperature-dependent calculation, will also shift at the same rate, and be 2.8 $eV$ less than the high temperature optical gap. To summarize, Colbourn, assuming the optical band gap, $E_g^0$, is 9.5 $eV$, calculates a thermal band gap, $E_g^t$, of 6.7 $eV$ which corresponds to the activation energy for carrier creation $E_a^{crea}$ at 0 K.

2.2.5 Summary

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The conductivity results reveal the combined effects of carrier creation and carrier mobility, but it is difficult to separate these two effects. From the mobility measurements we see that the mobility of electrons has been studied, but the observation of hole mobility has been obscured by the electrons. The photoconductivity measurements give an indication of the room temperature mobile carrier creation energy. The calculation of polaron defect state energies demonstrates the importance of the lattice to the electronic structure at high temperature.
2.3 Electronic Structure and Optical Properties

Optical property measurements can probe a material's electronic structure, measuring the energy difference between allowed electronic energy levels while avoiding the additional factor of the electron mobility that is necessarily involved in any transport measurement. Still, the analysis and interpretation of optical measurements require that a basic model of the electronic structure is available. Here a review of the room temperature optical properties and electronic structure of Al₂O₃ is presented. This is then followed by a discussion of the effects of temperature on the electronic structure and the available temperature dependent optical measurements.

2.3.1 Electronic Structure Models

There are two distinct approaches used in modeling the electronic structure of solids: the band structure calculation of solid state physics and the atomic cluster molecular orbital calculation of solid state chemistry. All of these models are done for $T = 0$ K. There are no atomic vibrations allowed in the models. The bond lengths used in the calculations are those appropriate to the material at room temperature.

The band structure models can give the most complete description of the transport properties of a solid, while the molecular orbital perspective highlights bonding and real space structure. Band structure
models are most appropriate to covalent materials that exhibit delocalized electronic carriers as demonstrated by highly curved, free-electron-like bands. A cluster model is most appropriate to an ionic tightly bound material where the bands are flat and the electrons reside in a specific bond between atoms. Neither of these models can encompass the changes that occur in a situation where strong electron-lattice interaction leads to relaxation of the lattice. The cluster approach could model the before and after state well through a transition state calculation, but this has yet to be done for Al₂O₃.

2.3.1.1 Cluster Models

The atomic cluster, molecular orbital method for calculating electronic structure represents the solid by a small cluster of atoms of the same structure and symmetry elements as the bulk. The most popular cluster for Al₂O₃ uses seven atoms: an Al surrounded, in octahedral coordination, by six O's. The calculation is done in real space using a local perspective without invoking long range periodicity. The electrons are represented by the atomic orbitals when the atoms are at infinite separation. As the separation between the atoms decreases, the atomic orbitals interact in accord with the Pauli Exclusion Principle, forming bonding, nonbonding and antibonding orbitals. In approaching the limit of the infinite solid, the set of molecular orbitals would broaden continuously into the bands of band structure theory.

The localized or molecular nature of the electronic structure and ionic character of Al₂O₃ is demonstrated by the fact that the cluster
models can reproduce the major features of the electronic structure when compared to the band structure models. The method used for both cluster calculations on Al₂O₃ was the Self Consistent Field, X α Approximation, Scattered Wave Cluster method of Slater and Johnson.²⁴

Brower's²⁵ results for an Al₂O₃ cluster with D₃ symmetry is shown in figure 2.7. In the model \( \Gamma_1 \) is s like, \( \Gamma_2 \) is \( p_z \) like and \( \Gamma_3 \) is \( p_x, p_y \) like. The atomic character of the various groups of levels is shown. The top of the valence band is of \( e_u^0 2p \) character. The next available level is an Al 3s level at 8.75 eV followed by an Al 3p level at 9.4 eV. From this one would deduce a band gap of 8.75 eV from 0 2p to Al 3s levels. The cluster chosen for this study lacks the true coordination of the bulk; neither the Al or the O atoms have their full complement of first nearest neighbors. Therefore the levels of the valence and conduction bands are sparse and the bandwidths are too small. The valence band is only 1 eV wide and does not show the dual peak structure that is observed in the photoemission spectra (PES) of the valence band (see figure 2.8).²⁶ ²⁷

Tossell²⁸ has calculated the molecular orbitals for an AlO₆⁻⁹ cluster with \( O_h \) symmetry (see figure 2.9). He choose to ignore the distortion (\( D_{3d} \)) from octahedral symmetry present in sapphire to simplify the calculation. The low lying 0 2s levels are separated by 14 eV from a 4 eV wide valence band. The valence band consists of two groupings of levels: the top of the valence band is 0 2p like while the bottom of the valence band is a mixture of 0 states with Al 3s and Al 3p states. This agrees with the PES results that show a 17 eV separation and a 6 eV wide valence band. The successful characterization of the valence band is due to the large amount of 0 - 0 interaction in the cluster chosen. In
contrast, there is no Al – Al interaction in this cluster, leading one to expect a narrow conduction band in the model. There is an Al 3s level at 7.6 eV and Al 3p levels at 11 eV, in qualitative agreement with other models. This cluster model would suggest a 7.6 eV band gap between 0 2p and Al 3s levels.

2.3.1.2 Band Models

Band structure models of the electronic structure can give greater insight into the details of the electronic structure than cluster models. By considering the flatness of the bands one can gauge the degree of covalency or ionicity, or the localized or delocalized nature of the carriers. The density of states (DOS) that can be derived from the band structure can supply invaluable information on the detailed structure of the bands and permit the calculation of the joint density of states (JDOS) that should closely map the energy and intensity of possible transitions between the valence band and conduction band. There have been four band structure calculations performed on Al$_2$O$_3$ in the past 15 years. Douglas$^{29}$ performed the first calculation in 1970 using a simplified technique and got results that were not unreasonable, but the ad hoc nature of the calculation led to excessive band widths of 16 and 17 eV for the valence bands. Evarestov$^{30}$ used a semi-empirical method to calculate a band structure that did not surpass the knowledge that is derived from the cluster models and in addition led to a forbidden gap of about 36 eV. In 1982 Batra$^{31}$ published the results of his first principles calculation, and in 1983 Ciraci and Batra$^{32}$ published the results of a semi-empirical
calculation that also discussed much of the available spectroscopic data on \( \text{Al}_2\text{O}_3 \). These two calculations are both high quality, complementary calculations that, while still rudimentary in comparison to the state of the art in our understanding of \( \text{SiO}_2 \), signal a new stage in our understanding of \( \text{Al}_2\text{O}_3 \).

Batra performed a first principles LCAO (linear combination of atomic orbitals) extended tight binding method calculation on \( \text{Al}_2\text{O}_3 \) with an interest in understanding ionicity and bonding as they relate to oxidation of Al with reference to \( \text{SiO}_2 \). This calculation was not self consistent or iterated to determine the stability of the answers. Also, even though it is a first principles calculation, the exchange parameter \( q_e \) is an input variable that can change the values of \( E_g \) the band gap and \( B_e \) the bandwidths. The symmetries of the bands were not identified, so it is not possible to discuss optical transitions from individual bands.

The band diagrams for selected directions (see figure 2.10) and all directions in the Brillouin Zone (see figure 2.11) are shown. The calculated value of \( E_g \) is 8 eV, while the valence band is 6 eV wide. Caution is called for with respect to these numbers. The accepted value of \( q_e \) is 0.75, but with \( q_e = 1 \), the gap increases to 11 eV while \( B_e \) decreases to 5 eV. Batra states a value of \( q_e = 0.95 \), and \( E_g = 9.5 \) may be more appropriate, compensating for problems in the techniques of the calculation. The band gap is found to be direct, at the zone center.

The density of states from this calculation is shown in figure 2.12. The top frame shows the total DOS, while the lower frames show the decomposition of the DOS on to the constituent atomic orbitals. The lowest lying bands are 0 2s in character. The valence band shows a 2 peak character, the bottom 4 eV of the valence band is made up of hybridized Al
3s and O 2p bands, while the top 2 eV of the valence band is comprised of O 2p bands. The structure of the valence bands is in good agreement with PES results (see figure 2.8). There is a large density of states in the top of the valence band. The bottom of the conduction band consists of Al 3s states, while it is stated that the first major peak in the conduction band appears 4 eV above the conduction band edge, and would correspond to Al 3p states.

The other recent band structure calculation was done by Ciraci and Batra. This was a semi-empirical calculation that used the band gap, the photoelectric threshold energy, and broad features, such as bandwidths, from PES experiments. Only broad features, no specific structure, were used. This study was performed to interpret the available experimental spectral results and to supply more insight into surfaces of Al₂O₃ and the process of oxidation. The effects of effective charge on the atoms (i.e. covalency) and the inter-orbital matrix elements on the valence band widths and positions of the bands were investigated. Using these two variables, the band structure model was then fitted to the previously mentioned experimental data.

The band structure calculated is shown in figure 2.13. Ciraci found the energy gap between the valence band and conduction band to be indirect, with a value of 8.7 eV, the direct gap would occur at $\mathbf{\Gamma}$ with a value of 8.9 eV. The lowest lying bands are associated with O 2s states. The valence band itself is found to have 3 different regions. The lowest part of the valence band is due to hybridization of O and Al 3s states, followed with hybridized O 2p and Al 3p states. Both of these regions, which were assigned as O-Al bands by Batra, demonstrate the covalency present in Al₂O₃ and the bands are non-flat. The top of the valence band
is predominantly of O 2p character, and the bands are very flat, demonstrating their ionic nature. The bottom of the conduction band is of Al 3s character, followed at higher energy by bands of Al 3p character.

In figure 2.14 the total and orbital DOS are shown. The valence band width calculated is 12 eV, larger than Batra found. A larger degree of covalency, in accord with the larger band width, can be seen by the greater degree of hybridization O contributes in the conduction band in this calculation. Upon comparing the valence band to the PES results of Balzarotti (see figure 2.8a) one sees that the widths agree, while the interpretation of 3 regions in the valence band would explain the low energy shoulder observed in PES. But in recent work of Tasker, the excessive width and shoulder in Balzoratti's spectra are attributed to experimental error.

To study the defect states in Al$_2$O$_3$, Ciraci calculated the states introduced by the dangling bonds formed on a (0001) surface. The band structure including surface states is shown in figure 2.15. Here we can see one mid-gap band and 2 bands that introduce states below the band edge. Ciraci suggests that the features observed near the band edge and normally attributed to exciton formation may actually arise from these surface state bands.

2.3.1.3 Franck-Condon Effect

The electronic structure models discussed previously only consider a static lattice, the effects of lattice relaxation and atomic vibrations are outside their scope. When the lattice changes configuration, the
position of the electronic energy levels will shift. A qualitative model for this is given by the Franck Condon Principle.

The Franck Condon Principle was first developed to explain the large differences between absorption energies and emission energies observed for F centers (anion vacancies) in alkali halide crystals. In the case of alkali halides, F center absorption may occur at 2 eV while emission occurs at 1 eV. The difference between these energies, 1 eV, is called the Stokes shift and represents the effect of lattice relaxation on the electronic energy levels. If we consider the relaxation to consist of breathing mode displacements for example, then these can be parameterized by a configuration coordinate $x$ that represents the radial displacements. Now referring to figure 2.16 which shows the energy of the ground and excited states as a function of the configuration coordinate $x$, we see the total energy minimum for the ground state occurring at $x_0$ while for the excited state it occurs at $x_1$. A transition that is fast relative to the lattice, such as an optical transition, will occur vertically requiring $E_a$. The lattice will then relax with the emission of phonons to its new equilibrium position at $x_1$, where the emission energy will be given by $E_e$. The difference between these energies is the Stokes shift, and for F centers in $\text{Al}_2\text{O}_3$ it is on the order of 3.1 eV.$^{34}$

2.3.1.4 Polarons

In ionic materials, with locally defined electronic structures, the interaction between the electrons and the lattice becomes very important. The charge carriers, electrons or holes, can be dressed by phonons, or
lattice relaxation fields, whereby the energy of the carrier is reduced and a polaron is created. Both electron and hole polarons can be created. Large polarons are formed where there is a weak electron lattice interaction and the relaxation field is spread over a large area in the lattice (see figure 2.17), leading to small displacements of the atoms. In this case the energy of the polaron is independent of its position relative to the nearest lattice atoms. A small polaron occurs in the case of strong electron-lattice coupling, and leads to a particle effectively self-trapped in its own lattice field. The electron's energy depends on its position, so it tends to reside near an atom. Large polarons can move in an applied field, but their effective mass is larger than the band effective mass . A small polaron can move only by a thermally activated hopping process similar to that of an atomic defect.

The strength of the electron-lattice interaction determines whether polarons should be considered in the strong interaction limit appropriate for small polarons, or in the weak limit for large polarons. The Frohlich polaron coupling constant , determines these two limits. It is a dimensionless measure of the lattice deformation or stabilization energy.

\[
\alpha/2 = \frac{2\pi}{2\pi} \left( \frac{2m*\omega_0}{\hbar} \right)^{1/2} \frac{e^2}{4\hbar\omega_0} x(e_\infty^{-1} - e_0^{-1})
\]

For \( \alpha \ll 1 \) we are in the large polaron limit, while for \( \alpha \gg 10 \) we are in the small polaron limit. \( \alpha \) for \( \text{Al}_2\text{O}_3 \) was calculated by Hughes to
be 2.7, while Kroger calculated a value of 3.1. These were calculated without regard to the differences between the optical phonon frequency $\omega_o$ most effective for lattice deformation around holes or electrons. Holes and electrons can have distinct values of $\alpha$ that determine their respective character. The measured carrier mobility is a good indicator of polaron type; mobilities below 0.3 cm$^2$/V sec are associated with small polarons. The polaron rest mass is given by

$$m^{**} = m^* (1 + \alpha/6) \quad \alpha < 1$$

or for $\alpha > 1 = m^* (1 - 0.0008\alpha^2)/(1 - (1/6)\alpha + 0.0034\alpha^2)$. This leads to a value of $m^{**}$ of 1.75 $m^*$ for Al$_2$O$_3$.

Due to the sparsity of experimental data on the mobility of electrons and holes in Al$_2$O$_3$, it is useful to refer to the theoretical polaron mobility models for conductivity calculations. The mobility of polarons is strongly controlled by the vibrational frequency $\omega_o$ of the optical phonon branch that most strongly couples to the carrier. This frequency is also the one that should be used to determine the Debye temperature $\Theta_D$. Reported values of the Debye temperature vary from 695 K to 1000 K depending on the reference. The 'best' value may be 695 K because it was calculated from an experimental phonon spectra for Al$_2$O$_3$\textsuperscript{37}. But this value is much lower than the other values quoted, and less than that for MgO. For large polarons, the mobility is determined by the fundamental equation given below.
\[
\mu_{1p} = 4 \frac{q}{3 \pi^{1/2}} \frac{e^{\theta/T} - 1}{m \alpha_0} \quad \text{[T<\Theta]}
\]
\[
\mu_{1p} = 4 \frac{q}{3 \pi^{1/2}} \frac{e^{\theta/T}}{m \alpha_0} \quad \text{[T>\Theta]}
\]

From this one can see that uncertainty in \( \Theta \) or \( \omega_0 \) can change the calculated mobilities by an order of magnitude. The small polaron mobility is not determined by a fundamental equation and is of the form:

\[
\mu_{sp} = \mu_{sp}^0 \frac{T^{3/2}}{e^{\epsilon h/kT}}
\]

where \( \epsilon_h \) is the activation energy for hopping of the polaron.

2.3.2 Optical Properties at Room Temperature

Over the years there have been many optical studies of single crystal sapphire (Al\(_2\)O\(_3\)) performed to better understand its applications as an optical window or a geological material. Most researchers studied only the absorption edge, the complexity of VUV measurements restricting higher energy analysis. Only in the past 15 years have measurements become available over a considerable energy range. The measurement of the reflectivity or absorptivity of a solid is among the most direct means of measuring the energy difference between allowed electron energy states. Therefore the optical spectra allow one to profile the electronic structure of the valence and conduction bands with ease. The room
temperature optical spectra in the energy range appropriate to an intrinsic electronic structure study will be reviewed.

Loh\textsuperscript{38} studied the reflectance, at a 45 degree angle of incidence, of natural surfaces of \ce{Al2O3} doped with \ce{Cr} (ruby). The measurements were performed at room temperature, covering 6 to 14 eV and were taken point by point. The sample was cut to present a basal plane surface, so the spectra corresponds to \( E \) perpendicular to the \( c \) axis. Apparent in his spectra (see figure 2.18) is a peak at 9.1 eV, an edge starting at 10 eV followed by a shoulder at 10.6 eV, and a smaller peak at 12 eV followed by a larger peak at 13.2 eV. The sample was \ce{Cr} doped, yet conspicuously absent is the 7 eV \ce{Cr} charge transfer peak.\textsuperscript{39} His spectra show prominent features and structure, but the sharp absorption edge at 10 eV and the shallow slope in \( R \) below the 9 eV peak are not in agreement with most literature results. In addition, the intensity of the exciton peak is lower than in other work, and may have been due to experimental problems such as surface contamination of optics or sample. He did not perform Kramers Kronig analysis of his data, but interpreted his data to show an exciton peak at 9.1 eV, and a 10 eV band gap.

The most comprehensive work was done by Arakawa and Williams\textsuperscript{40} studying anodized films on aluminum and single crystal \ce{Al2O3} oriented with the \( c \) axis lying in the plane of the surface. They do note the polarization of their spectrometer but do not mention the sample orientation in the machine. They measured oblique incidence reflectance and transmission of corundum at room temperature from 8 to 28.5 eV. They analyzed their data using Kramers Kronig analysis, calculating the index of refraction \( n + ik \), the dielectric constant \( \varepsilon \) and the energy loss functions. Their reflectivities for corundum are shown in figure 2.19,
where one can see an edge, a peak at 9.5 eV, a shoulder at 11.6 eV and peaks at 13, 16.5 and 20.5 eV. In figure 2.20 the dielectric constant shows a shoulder at 9 eV. They choose to assign this to a separate peak corresponding to an exciton, or bound electron pair, occurring below the onset of band to band transitions at 9.9 eV. The higher energy peaks correspond to peaks in the joint density of states. In addition they identified the plasma energy for collective oscillations of the valence electrons as lying at 25.8 eV. Beyond these three assignments of features in the spectra they were unable to identify any other peaks or attribute optical features to the electronic structure. One interesting result they found, which demonstrates the relationship between physical and electronic structure, was that in the anodized disordered films, the exciton appeared 1.1 eV lower in energy at 8.4 eV, and the onset of band to band transitions they considered to occur 0.5 eV lower at 9.4 eV. Other features in the spectra did not shift from film to crystal.

Rubloff in unpublished work\textsuperscript{41} measured the reflectivity of Al\textsubscript{2}O\textsubscript{3} from 8.3 to 27.5 eV from 90 K to 400 K and for light polarized parallel and perpendicular to the c axis. The temperature dependent results will be discussed in section 2.4.4. They show (see figure 2.21) an exciton peak at 9.2 eV, and an absorption edge at 10 eV. The spectra do not go to low energy so it is not possible to determine if the absorption edge starts at 10 eV or if the exciton is superimposed on an edge. Arakawa had a similar problem in deconvoluting the exciton and the edge. The orientation dependent features of their spectra are pronounced. For E parallel to c, there is a broad peak centered at 12.8 eV, while for E perpendicular to c the peak is at 13.2 eV with a slight shoulder at 12.3 eV.

Abramov\textsuperscript{42} in a paper on electronic structure and optical properties
measured transmission and reflectance from 4.2 to 20 eV from 4.2 to 295 K on a sample cut to present a basal plane. Their reflectivity (see figure 2.22) shows an exciton peak at 9 eV, a small shoulder at 10.4 eV, another small peak at 11.7 eV, and a major peak at 12.8 eV. From the steepness of the absorption edge their exciton peak seems to be superimposed on the absorption edge. They say an absorption edge starts at 8.5 eV. The exciton is at 9.25 eV at room temperature, and the optical band gap is less than 9.5 eV. They measured photoconductivity, and from this they determine an energy gap of 9.25 eV. The exciton peak is superimposed on the edge with a halfwidth of 0.6 eV and a low binding energy (less than 0.1 eV). It was more intense for $E$ perpendicular to $c$ which agrees with Rubloff's spectra. They also reported that the highest joint density of states occurs at 13 eV.

2.3.2.1 Summary

Even in the most recent work the identification of the 9 eV peak as arising from excitons is not definitively reported. Disagreement persists as to whether the reflectance observed arises from an exciton peak below the onset of band to band transitions, or whether it is an exciton peak superimposed on the absorption edge of band to band transitions. Investigators agree upon energy positions of major features, but the relative shape of the reported reflectivities varies. Due to the lack of electronic structure models, the investigators did not attribute the reflectivities to different transitions. The exciton peak has been observed from 8.8 to 9.2 eV. Two groups observed a small shoulder at
~10.5 eV. For $E$ perpendicular to $c$, a shoulder is seen between 11.6 and 12.3 eV, and a major peak at 12.8 to 13.2 eV. For $E$ parallel to $c$, a broad peak is observed at 12.8 eV.

2.3.3 Temperature Dependent Electronic Structure Theories

In the past 30 years there have been many attempts to treat the electron-phonon problem so as to understand, from a fundamental point of view, the cause of temperature and pressure induced shifts of electron energy levels in solids. This is a very complex problem which at this point can address the shifts observed in most semiconductors, but for each new material of technological interest the theory has needed to be reformulated. Beyond the complexity of the calculations, it does not seem that all the necessary terms have even been determined to allow an understanding of the electron-phonon problem and the temperature induced shifts in solids.

All of the theories separate the temperature induced shift in the band gap into two terms.

\[
\frac{dE}{dT} = \frac{dE}{P} + \frac{dE}{dV} + \frac{dE}{dT \text{ ther. exp.}}
\]

The temperature induced shift is separated into a term at constant volume that is due to the electron-phonon interaction, and a second term due to the effect of lattice dilatation that accompanies thermal expansion.
Fundamental Models

In the fundamental models of the temperature dependence of electronic structure there have been two approaches taken: the physical approach considers the effect of phonons on the electronic states, while the chemical-thermodynamic approach considers the effect of the electrons on the phonons. The review here is after Cohen.\(^{43}\)

The first work in the physical approach was done by Radkowsky\(^{44}\) with the aim of understanding the shifts observed in insulators. This was the only work aimed specifically at ionic materials. He viewed the problem as resulting from the uncertainty principle: \(\Delta E/\Delta t = h/2\pi\). The electrons are interacting with phonons, undergoing transitions between states that leads to energy level broadening and a decrease in the band gap. This theory has not met with success and is no longer used.

The Fan Self-Energy theory developed independently by Fan\(^{45}\) and Muto and Oyama\(^{46}\) considers the effect of the electron's emission and absorption of phonons on the electron's self-energy. This is an effect that is added on to the temperature independent band structure and leads to energy level shifts. Their model predicts an exponential shift of the band gap below the Debye temperature \(\Theta_D\), while above \(\Theta_D\) the shift is linear because the number of phonons is proportional to \(2\pi kT/h\omega\). This model served to reasonably explain results observed in Si and Ge. Yet it has limited success with other materials because it requires a detailed knowledge of the electron-phonon coupling constants which are usually not known.

The Brooks-Yu Debye Waller theory developed independently by Antoncik\(^{47}\) and Brooks and S. C. Yu in unpublished work\(^{48}\) takes a different
point of view on the problem. Here they calculate temperature dependent band structures by modifying the crystal potential with structure factors or Debye Waller terms that represent the vibration and shift of the atoms with temperature. As the temperature increases the atomic potentials become shallower and more spread out, leading to spreading and shifting of bands. In this theory, there are three distinct temperature regimes. For temperatures far below the Debye temperature, the band gap shifts quadratically with temperature. For temperatures above the Debye temperature, the shift is linear, becoming exponential for temperatures far above the Debye temperature. Because the Brooks-Yu theory only requires modification of the potentials used in a standard band structure calculation, it has seen much application in Group IV, III-V, and II-VI semiconductors. This theory can supply results for some systems that are accurate to within \pm 30\%.

Even though the Brooks-Yu theory has seen the greatest use in calculating temperature dependent shifts, there is the belief that these two theories discuss two different terms that act in opposition. The reason for the success of the Brooks-Yu theory even when the self energy terms are ignored, lies in the uncertainties in the atomic potentials and Debye Waller factors used. These uncertainties are sufficient to cover up the self-energy contributions, but in certain cases, ignoring self-energy terms leads to incorrect results. The HgTe and CdTe alloys show an increasing band gap with temperature but the Brooks-Yu theory predicts a decreasing band gap. A study by Guenzer showed that the neglect of Fan self-energy terms might explain the HgTe case. Allen and Heine succeeded in uniting the two previous models into one coherent model for the shift, demonstrating the uniqueness and complementarity of the two
theories. This theory may be the correct unified theory for the temperature dependent shifts of the electronic structure observed in semiconductors, but because of the difficulty in determining the electron-phonon coupling constants it has not seen much application. Allen and Cardona performed the unified calculation for Si and Ge in 1981, and corrected it in 1983. They found that the self-energy terms could reduce the temperature coefficients by a factor of two.

The chemical thermodynamic approach to this problem is one that considers the effect of electrons on the phonons of the solid. The first work in this area was done by Thurmond\textsuperscript{51} followed recently by Heine.\textsuperscript{52} Various electronic structure features are identified in terms of their thermodynamic variables, the Fermi energy corresponds to the chemical potential of the carriers, the band gap corresponds to the Gibbs Free Energy for creation of electron-hole pairs, and therefore, the enthalpy and entropy due to carrier creation can be calculated and considered as a function of temperature. The major advantage of this method is that it considers the effects of thermal expansion, and self-energy and Debye Waller factors simultaneously without the need to explicitly consider them. The only thing that must be determined is the softening of the phonon modes due to the creation of electron hole pairs. This arises because excitation of an electron corresponds to breaking one or more bonds in the material, as the electron goes from a bonding valence band orbital to an anti-bonding conduction band orbital. The thermodynamic approach has met success in Si and Ge, and should also be able to explain the anomalous results observed in HgTe, because in that case the gap increases due to mode stiffening. When an electron enters the conduction band it enters a bonding orbital, in distinction to the other
semiconductors. This point may be the fundamental consideration that determines the sign of the temperature coefficient in any material. Still, due to the difficulty of determining the electron's role in mode softening, this method has not met wide acceptance.

Empirical Models

Due to the computational complexity of the fundamental theories, they are not readily applicable. Two empirical models have been advanced that are basically curve fitting models and do not contradict the fundamental models. The first by Varshni\(^{53}\) gives a quadratic dependence to \(E_g\) below the Debye temperature, and a linear dependence above the Debye temperature. It requires two parameters \(\alpha\) and \(\beta\), which are not derivable from experimental data. His equation is:

\[
E_g = E_0 - \frac{\alpha T^2}{(T+\beta)}.
\]

Ravindra\(^{54}\) simplified Varshni's equation removing the parameters and replacing them with \(\Theta_D\).

\[
E_g = E_0 - \left( (2.25\times10^{-5}\Theta_D) - 4.275\times10^{-3} \right) T^2 / (5(T+5\Theta_D-113))
\]

From the functional dependency of these models, one can see that they only consider the Debye Waller term. They have been applied by the authors to Si, Ge, SiC, GaAs, InP and InAs with reasonable results.

Linear Models

Most of the results presented in the literature use a simple linear
model for the temperature dependence of the band gap. This may be an assumed model or the data itself may be truly linear, a distinction that is important.

\[ E_g(T) = E_g^0 - \beta T \]

Here the linear temperature coefficient \( \beta \) is usually found to lie in the range of \( 10^{-4} \) to \( 10^{-3} \) eV/K and a positive value corresponds to a net decreasing band gap with temperature. The linear dependence should apply from theory for temperatures on the order of the Debye temperature.

2.3.4 Temperature Dependent Optical Properties

Temperature dependent optical measurements have been performed on \( \text{Al}_2\text{O}_3 \) over the years due to its use as an optical window material, and to develop an understanding of the processes that lead to temperature induced shifts of absorption edges. Most of these studies have been performed below the exciton peak and absorption edge due to the difficulties of high energy spectroscopy. Generally the transmittance limit of the material was measured. The transmittance limit is defined as the wavelength where \( T_x \) falls below some arbitrary value, usually between 0.1 and 5 percent. Because of the limited energy range covered, the specific character of the edge studied may not have been determined. In some cases the shift of what appears to be a chromium peak was studied and then reported as a result fundamental to sapphire. The choice of a cutoff value for \( T_x \) is arbitrary and can affect the calculated value of the temperature coefficient \( \beta \), while any experimental uncertainty or drift in the absolute magnitude of the temperature \( T \) between runs also introduces error in \( \beta \).
The first reported study on the temperature induced shift of the transparency of sapphire was done by Gilles in 1952. She measured the absorption coefficient of single crystal sapphire from 20 to 900 °C from 5.9 to 8 eV (see figure 2.23). These spectra do not go to high enough energy to determine the origins of the absorption studied, while at the same time a peak at 6.9 eV would seem to be attributable to Cr impurity. These spectra were analyzed by Harrop to explain observed conductivity results. He fit them to a power law expression and found noticeable second and third order terms, but then proceeded to use a linear model yielding a β value of $1.5 \times 10^{-3}$ eV/K. The data he extracted from Gilles data is plotted in figure 2.24 versus energy and shows noticeable nonlinearity. One of the complicating factors in using these measurements to determine β is the low lying peak at 6.9 eV that is discrete at low temperature while it is incorporated in the absorption edge at high temperatures.

Yakovlev in 1961 measured transmission up to 8 eV (140 nm) on samples heated from room temperature to 380 °C. The transmittance curves are shown in figure 2.25 along with the temperature coefficient they calculated for $T_r = 5\%$. From these one can see that the transmittance edge has not retained its shape with increasing temperature. The measured temperature coefficient for their transmittance cutoff and others chosen by this author give an idea of the scatter in the data.

$$\beta (T_r = 5\%) = 1.5 \times 10^{-3} \text{ eV/ K}$$

$$\beta (T_r = 20\%) = 1.4 \times 10^{-3} \text{ eV/ K for 85 °C<T<380 °C}$$

$$\beta (T_r = 20\%) = 2.0 \times 10^{-3} \text{ eV/ K for 20 °C<T<380 °C}$$

No attempt was made to explain the data since this was a short letter on an experimental problem of interest.
Another study, motivated by an interest in a suitable window material for high temperature photochemistry, by Laufer shows (see figure 2.26) the transmittance edge of sapphire, up to 8.75 eV (140 nm) moving to lower energy for temperatures from 20 °C to 175 °C. The value of $\beta$ calculated by this author for $T = 10$ % is $1.9 \times 10^{-3}$ eV/ K. The experiment covered a small temperature range. The authors specifically mention the importance of distinguishing peak broadening from peak shift. An attempt is made to explain their results on alkali halides in terms of trends in ion size and exciton transitions, but is not rigorously established. $\text{Al}_2\text{O}_3$ is said to be different, and no explanation is given.

In 1969 Hunter studied the temperature dependence of the transmittance limit of VUV window materials such as the fluorides, quartz and sapphire from 10 K to 373 K. A companion paper was published by Reilly explaining the observed shifts in terms of photoexcitation of excitons of reduced energy at thermally distorted regions of the lattice. Hunter refers to the fact that the value of $\beta$ is not well defined, and chooses the cut off wavelength, $\lambda_{co}$ to be at $0.1 < T < 0.5$. For all the materials they found a linear range for $\lambda$ above 20 °C, while at temperatures approaching 10 K, the slope changed and approached zero, i.e. the value of $\beta$ decreased to zero at low temperatures. LaF$_3$ was the only material studied that did not show a temperature induced shift. The lack of shift in this case was attributed to a large impurity content controlling the value of $\lambda_{co}$.

The results for sapphire were taken for a $\lambda_{co}$ of 142 nm at room temperature, corresponding to 8.75 eV. This is on the absorption edge and below the exciton peak. They do not show the actual $T_x$ edge measured for sapphire, but from the high temperature portion of the temperature shift
curve, a β value of $1.75 \times 10^{-3}$ eV/ K from 250 K to 373 K can be deduced. This value is in agreement with those measured previously, and the change of β with temperature is a new finding.

Rubloff$^{61}$ studied the reflectance of single crystal Al$_2$O$_3$ from 8.3 eV to 27.7 eV using synchrotron radiation and continuous scanning. Very detailed spectra were obtained showing reflectivities for E both parallel and perpendicular to the c axis, and for 'fused' Al$_2$O$_3$. In addition, temperature dependent curves were taken for E parallel to c at 90, 300, and 400 K. From this small amount of data this author has calculated peak center temperature coefficients for 3 features in the spectra, the 9 eV exciton peak, the 13 eV Al 3p peak and the 18 eV peak. These were calculated by measuring geometric peak centers at the half maximum for each of the temperature changes from 90 to 300 K and 300 to 400 K (see figure 2.27). Due to the lack of multiple runs over which to average, the results are only accurate to within a factor of two.

| TABLE 2.1 Calculated β Values from Rubloff's Data |
|----------------|-------------|
| eV/K            |             |
| 90 - 300 K      | 300 - 400 K |
| 9eV peak        | $-6 \times 10^{-4}$ | $-1.3 \times 10^{-3}$ |
| 13eV peak       | $6 \times 10^{-4}$ | $1.3 \times 10^{-3}$ |
| 18eV peak       | $6 \times 10^{-4}$ | $1.5 \times 10^{-3}$ |

Notice that β is larger above room temperature than below, in agreement with Hunter's findings. It is very unusual that the exciton peak appears to shift to higher energies with temperature, this may be due to the very small size of the exciton peak and its position at the beginning of the scans. Blum calculated the β value of Rubloff's exciton peak and reported a positive value of $5 \times 10^{-4}$ eV/K in contradiction to this author's analysis of the data.
Blum$^{62}$ measured the reflectivity of sapphire from 9 to 12.5 eV at 25 °C, 275 °C, and 450 °C (see figure 2.28). He reports a value of 1.4 x $10^{-4}$ eV/K for the rate of shift of his spectra with temperature and attributes it to a decrease in the band gap. He also analyzed a series of peaks on the high energy of the exciton peak, at 9.5, 9.9, and 10.1 eV and attributes them to the excited states of a Wannier type exciton. He stated that his data is consistent with a room temperature band gap of 10.3 eV for Al$_2$O$_3$.

2.3.5 Summary

From the literature results we can see that the room temperature optical properties of Al$_2$O$_3$ are generally agreed upon, but the position of the fundamental absorption edge is not well established. Some researchers have reported that the edge lies at 9 eV while others have reported a 10 eV edge. This disagreement may be due to the limited energy ranges studied. The assignment of the features in the optical spectra to electronic structure transitions has been retarded due to the lack of high quality electronic structure models. This has changed recently with the band structure calculations of Batra and Ciraci. The valence band is found to consist of two major sub-bands, of O 2p character at the top and of Al - O character in the bottom of the valence band. The conduction band consists of two major sub-bands, of Al 3s character in the bottom and Al 3p character at the top of the conduction band. The reported $T = 0$ K optical band gap of Al$_2$O$_3$ lies between 7.5 eV and 9.5 eV and is due to transitions from the O 2p sub-band in the top of the valence band to the Al 3s
sub-band in the bottom of the conduction band.

In terms of understanding the temperature dependence of the electronic structure, the field is still young. The theories of the temperature dependence are very complex and theorists are still struggling with the simpler cases of the covalent semiconductors. From experimental results we know that the band gap of Al₂O₃ decreases with increasing temperature. This has been modeled as a linear process with β values reported from $1.4 \times 10^{-4}$ to $2 \times 10^{-3}$ eV/K. None of the data has been of good enough quality, or over a large enough temperature range to determine if the true functional form of $E_g(T)$ is linear.

The role of the lattice in the electronic structure has not been seriously developed. This is a very important topic for materials such as Al₂O₃ where strong electron-phonon interaction gives rise to polarons and localized electron-lattice interactions.
FIGURE 2.1 Coordination clusters for Al₂O₃. Aluminum coordination octahedra and oxygen coordination tetrahedra are shown. The two sets of Al - O bond distances are distinguished by Ox1, Ox1' and Ox2, Ox2'. From reference 12.

FIGURE 2.2 Plots of refined thermal B factors as a function of temperature. Straight lines represent harmonic regions of thermal vibrations for Al and O. From reference 11.
FIGURE 2.3 Diagram of conduction mechanism in single crystal Al₂O₃. From reference 13.

FIGURE 2.4 Effect of O₂ partial pressure on conductivity of single crystal Al₂O₃. From reference 13.

FIGURE 2.5 Absorption (1) and photoconductivity (2) spectra of Al₂O₃ at 295 K. From reference 21.
FIGURE 2.6 Optical energy levels in Al₂O₃: the conduction band edge $E_c$, the optical band gap $E^o$ and the optical ionization energy $E_1^o$. From reference 22.

FIGURE 2.7 Molecular orbital energies for the Al₂O₃ cluster calculation of Brower. From reference 25.
FIGURE 2.8a X-ray photoemission spectra (PES) of the valence band of Al$_2$O$_3$. From Balzarotti, reference 26.

FIGURE 2.8b X-ray photoemission spectra (PES) of the valence band of Al$_2$O$_3$. From Kowalczyk, reference 27.

FIGURE 2.9 Molecular orbital energies for the AlO$_6$ cluster calculation of Tossell. From reference 28.
FIGURE 2.10 Band structure of Batra for a Al$_2$O$_3$ along two particular directions in the rhombohedral Brillouin zone. From reference 31.

FIGURE 2.11 Batra’s complete band structure of a Al$_2$O$_3$ along various directions in the rhombohedral Brillouin zone (shown as an inset). From reference 31.

FIGURE 2.12 Batra’s total and orbital densities of states for a Al$_2$O$_3$. The broken curve in the top panel shows the XPS results of Balzarotti. From reference 31.
FIGURE 2.13 Ciraci's band structure of $\alpha\text{Al}_2\text{O}_3$ along three directions in the Brillouin zone (shown as an inset). From reference 32.

FIGURE 2.14 Ciraci's total and orbital densities of states for $\alpha\text{Al}_2\text{O}_3$. From reference 32.

FIGURE 2.15 Band structure and density of states of the ideal $\alpha\text{Al}_2\text{O}_3$ (0001). $S_d$ and $S_p$ are the surface state bands. From reference 32.
Figure 2.16 Illustration of the Franck Condon Principle. The energy of the ground and excited states are shown as a function of the configuration coordinate x. The energy of the fast optical process is $E_a$ while the slow thermal process is shown as $E_e$.

Figure 2.17 Representation of the localized potential wells induced by electron-lattice interaction for (a) the large polaron-weak coupling limit and (b) the small polaron-strong coupling limit. From reference 18.
FIGURE 2.18
Reflectivity of Al₂O₃ with E perpendicular to the c axis.
From Loh, reference 38.

FIGURE 2.19
Transmittance (x) and reflectance at various angles of incidence of Al₂O₃.
From Arakawa, reference 40.

FIGURE 2.20
Dielectric constants of Al₂O₃. The dotted curves show Arakawa's separation of the exciton from the absorption edge. From reference 40.
FIGURE 2.21 Reflectance of $\text{Al}_2\text{O}_3$ for $\mathbf{E}$ parallel and perpendicular to the $c$ axis. From Rubloff, unpublished research.

FIGURE 2.22 Reflection (1) and absorption (2) spectra of $\text{Al}_2\text{O}_3$. The continuous curves were taken at 295 K and the dashed curves at 4.2 K. From Abramov, reference 42.
FIGURE 2.23 Temperature dependent transmissivities of Al₂O₃ from room temperature to 900 °C. From Gilles, reference 55.

FIGURE 2.24 Variation of an energy on the absorption edge with temperature using the results of Gilles as calculated by Harrop, reference 56.

FIGURE 2.25 Transmittance curves (a) of Al₂O₃ as a function of temperature from 20 to 380 °C, and the temperature dependence (b) of the Tₜ equals 0.05 point on the edge. From Yakovlev, reference 57.
FIGURE 2.26 Transmittance curves of Al₂O₃ as a function of temperature from 20 to 175 °C. From Laufer, reference 58.

FIGURE 2.27 Reflectivity of Al₂O₃ as a function of temperature from 90 K to 400 K. From Rubloff, unpublished research.

FIGURE 2.28 Reflectivity of Al₂O₃ as a function of temperature from 21 to 450 °C. From Blum, reference 62.
Chapter 3

Research Goals

In an attempt to improve our fundamental understanding of Al₂O₃, and as an aid in the analysis of conductivity results, the electronic structure as a function of temperature was studied. This work determines the temperature coefficient of the band gap, thereby allowing the determination of the electronic carrier concentration at any temperature. The major thrust of the work involved the development of a high temperature vacuum ultraviolet spectrophotometer to measure near normal incidence reflectivity from 7 to 15 eV on samples heated from room temperature to temperatures above 1000 °C.

Reflectivity measurements at room temperature were performed to confirm the available electronic structure models, and the observed spectral features assigned to fundamental electronic structure features. Experimental measurements of the temperature dependent shifts of electronic structure features, supply information, which at this time cannot be theoretically derived, on the temperature dependence of the electronic structure. From this a picture of the high temperature electronic structure can be developed, considering the role of the lattice on the creation energy of the electronic carriers and their mobilities.
Chapter 4

Experimental Apparatus and Procedures

The aim of this research has been to measure the near normal incidence reflectivity from 6 to 15 eV, in the Vacuum Ultraviolet (VUV) wavelength range from 210 nm to 82 nm, on oriented single crystal samples heated from room temperature to temperatures greater than 1000 °C. These are measurements that have never before been performed. They involved the design and construction of a custom high temperature vacuum ultraviolet spectrophotometer. New optical elements, optical geometries, advanced signal processing and heating techniques have been developed during this work. First the literature on VUV spectroscopy techniques and previous optical spectrometers will be reviewed. Then the design of the high temperature VUV spectrophotometer will be discussed, followed by its capabilities, resolution and accuracy.

4.1 Literature Review - Techniques of VUV Spectroscopy

Due to the increasing need to understand the bonding and electronic properties of solids, liquids, gases and molecules, in conjunction with the advent of high intensity tunable synchrotron sources, research in the
VUV has been growing in recent years.\textsuperscript{63} There are various texts on spectroscopy techniques for the VUV\textsuperscript{64} \textsuperscript{65} \textsuperscript{66} \textsuperscript{67} which cover the range of samples studied in the VUV. The most comprehensive work is that of Samson.

4.1.1 Light Sources

The two major sources for continuum VUV radiation appropriate to scanning, or continuous, reflectivity measurements are the synchrotron source and the glow discharge lamp used with flowing hydrogen gas. The synchrotron source generates continuum high intensity radiation from 0.01 nm to 200 nm (100,000 eV to 6 eV) using electrons accelerated in a circular orbit at speeds greater than 0.99 times the speed of light.\textsuperscript{68} The phenomena of UV and X ray radiation from a cyclotron was first noticed in the 1940's\textsuperscript{69} \textsuperscript{70} and has now lead to the construction of dedicated synchrotron light sources for materials science work at Brookhaven National Laboratory, Stanford University, the National Bureau of Standards, and DESY in Hamburg, Germany. The light is truly a continuum with no superimposed line spectra and only one broad hump in the spectrum related to the average energy of the electrons used to produce the radiation.

The other standard VUV source is the glow discharge lamp. For continuum radiation in the range of interest here hydrogen is the gas of choice. The gas flows through an insulating capillary, at a pressure on the order of 1 torr, where a high field of approximately 400 V/cm is applied. The gas molecules are ionized and collisions among ionized and ground state atoms lead to emission of radiation. The atoms are then
reaccelerated by the field until their energy is sufficient for a new radiation-producing collision. This leads to a dark-light banding of the glow discharge down the length of the capillary. Superimposed on the continuum are a large number of intense atomic hydrogen lines of approximately 0.01 nm intrinsic halfwidth, leading to rapid variation of intensity with wavelength (see figure 4.1). This dense structure is one of the major difficulties encountered in applying this lamp to continuum spectroscopy.

In addition, all radiation below 180 nm is strongly absorbed by air, so all optics must be in vacuum of less than $5 \times 10^{-5}$ torr. To work at wavelengths below 105 nm (11.8 eV), the LiF cutoff, there are no transparent window materials, so the measurements must be performed 'windowless'. This means the lamp at 1 torr must look directly into the system at $10^{-5}$ torr. Differential pumping of a special aperture mounted between the lamp and spectrometer is required, and high pumping speeds are required to attain the necessary high vacuum with such a substantial 'leak'.

4.1.2 Optical Elements

There are no transmissive optics such as lenses or prisms for use in the VUV below 105 nm. Reflection optics such as mirrors and gratings optimized for this region have reflectivities on the order of 30%. Coatings of MgF$_2$ on aluminum can have higher reflectivities but do not function below 115 nm. Gold, platinum and osmium are the preferred reflective coatings for gratings and mirrors. Optical design therefore
minimizes the number of reflective surfaces to retain intensity. Monochromators use concave focusing gratings that simultaneously disperse the light by wavelength and collect and focus it on the exit slit.

4.1.3 Monochromators

The most popular monochromator design for a small monochromator with resolution of a few tenths of a nanometer is based on the Seya-Namioka optical layout developed in 1952.\textsuperscript{71} 72 The design is simple; the entrance and exit slits are fixed on the Rowland circle of the grating and only the grating is rotated to scan wavelength. The gratings used in these monochromators are concave focusing gratings, to combine the collimating optics, the plane grating and the focusing optics all into one reflection from the grating. The major disadvantage of these gratings is that they are highly astigmatic. This is partially corrected by using holographic, aberration corrected gratings.\textsuperscript{73}

4.1.4 Detectors

There are various types of detectors for use in the VUV. They can be separated into photon counting detectors to measure single photon events and current measuring detectors for measuring the gross intensity of incident light. Only detectors suited to current measuring will be discussed here.

The most popular detector uses a sodium salicylate phosphor, to translate the VUV radiation into visible light which is then detected by a
photomultiplier tube (PMT) sensitive to visible light. The phosphor is mounted in the system, and emits blue light when struck by VUV photons. The blue light is then sent out of the system through a window or light pipe to the PMT. This detector is simple to make, but it is environmentally sensitive. Absorbed water and aging will change its response dramatically. In addition it decomposes at temperatures above 80 °C. Still, it is the detector of choice since the active electronic detector, the PMT, is sealed and the phosphor may be redeposited at will.

Another sealed detector utilizes a photomultiplier tube with a LiF window. In this case the photocathode of the detector responds directly to VUV photons. This is a very stable detector because it is never exposed to the system vaccum. But, because of the window, it does not function below 105 nm.

Nude vacuum photodiodes are an example of a detector where the actual detector signal is created in the system vacuum, not in a sealed detector tube. They are very simple, consisting of a cathode and anode with a voltage applied. They can be used with a phosphor (e.g. sodium salicylate) evaporated on them, whereby they are more water and age sensitive, or with the photons incident on metal. With no phosphor material their sensitivity is low at low energy but they are more environmentally durable.

Electron Multipliers can also be mounted directly in system vacuum, and are basically a photodiode with a 16 stage dynode chain to yield $10^6$ higher gain than a diode. Electron multipliers are used predominantly as ion or electron detectors, but they will respond to high energy photons. They are solar blind if used without a phosphor, i.e. they have no response at energies below the work function of the dynode materials.
Typically the dynode material is BeO on copper, and has no response beyond 350 nm.

Anyone who has used optical detectors such as PMT's will realize with horror the impact of having the detector mounted in the vacuum system and exposed to air regularly. A PMT would be ruined if brought to air, therefore the detector of choice is usually sodium salicylate with a PMT. For hostile applications electron multipliers with no phosphor have the advantages of high durability and high gain.

4.1.5 Optical Spectrometers

The design of VUV reflectometers require that each feature be chosen to best compensate for the difficulties of working in the VUV. The basic problems to overcome in a reflectometer lie in the light source, optics and detection techniques. Due to low reflectivity, the number of optical elements must be kept to a minimum. The superimposed line spectrum of a H₂ lamp, leads to a very dynamic lamp signal. Small errors in determining λ will lead to large errors in the calculated division \( R = \frac{r}{i} \) of the reflected r and incident i signals to determine the reflectivity R. Since the lamp operates on a flowing gas design, instabilities in gas pressure or flow lead to random fluctuation in light intensity. Optical surfaces and sample surfaces, detector phosphors or nude detectors age with time and vacuum cycling leading to changes in their response. Alignment of optics, sample and detectors is difficult due to the vacuum system and hard to ascertain due to lack of visible radiation. All of the spectrometers to be discussed perform normal
incidence reflectivity, and some also measure transmissivity and variable incidence angle reflectivity.

4.1.5.1 Room Temperature Spectrometers

The most successful reflectometer design was developed by Rubloff\textsuperscript{74} \textsuperscript{75} for near UV spectroscopy and then extended for use in the VUV to 36 eV with synchrotron radiation. It is a single beam apparatus, using one detector, and thereby avoiding the problems of matching or calibrating the optics and detector response of two dissimilar beam paths. The detector used is a PMT with a sodium salicylate coated light pipe. The light pipe rotates about an axis perpendicular to the light, alternately collecting the incident and reflected intensity 70 times a sec. The high speed of rotation removes temporal lamp instabilities, and approaches the simultaneous measurement of i and r of a dual beam system. In addition the on-off nature of the detector signal can be used for AC detection techniques. They quote an accuracy in the absolute value of R of +/- 3\%, and relative accuracy much better than that. They have taken very good data and reported no problems with their system. The single beam rotating light pipe design has become very popular for VUV spectroscopy.

A different approach, taken by two separate groups\textsuperscript{76} \textsuperscript{77} is a single beam single detector apparatus, where the light is incident on an ellipsoidal or toroidal focusing mirror. This mirror rotates, directing the light alternately from the detector to the sample. The reflected beam from the sample is incident on the detector. Sodium salicylate and visible PMTs were used to detect the VUV. Reported absolute accuracy was
+/- 3 %, and relative accuracy of +/- 0.2 %. Because of the existence of another reflecting surface, signal strengths are lower and system stability is reduced.

C. F. Dickinson\textsuperscript{78} used a pulsed H\textsubscript{2} lamp source to achieve greater intensity and, to compensate for the temporal instability of the source, they used a dual beam reflectometer. The incident signal was acquired by measuring fluorescence of sodium salicylate deposited on a nickel grid that obstructed part of the beam. The rest of the light traveled to the sample where the reflected beam hit sodium salicylate on the front of a fixed light pipe. The signal was measured by a second PMT. The detector could be placed in a no-sample position and the two detector systems cross calibrated. They mention problems of aging and contamination of the optics and sample.

4.1.5.2 Temperature Dependent Spectrometers

Various measurements have been made on the temperature dependence of the 'transparency limit' of Al\textsubscript{2}O\textsubscript{3} and other UV window materials over limited temperatures ranges.\textsuperscript{79 80 81} These were all performed with single beam spectrometers using one PMT with sodium salicylate phosphor. The highest temperatures reached were 110 °C, 180 °C and 300 °C, and no specific problems with the measurement were mentioned.

Blum\textsuperscript{82 83} measured the reflectivity of Al\textsubscript{2}O\textsubscript{3} from 9 to 12.5 ev from room temperature to 450 °C. He used a windowed H\textsubscript{2} lamp, Seya-Namioka monochromator, a single beam single detector system using a sodium salicylate rotating light pipe detector. He used a molybdenum heating
element in alumina insulation as a furnace to heat the sample. He mentions contamination of the sample surface, which may originate from the furnace. In addition the vacuum system contaminated the optics and the windowed lamp. The maximum temperature of 450 °C was limited by the black body radiation from the hot sample saturating the visible PMT.

4.1.6 Special Problems of High Temperature Spectroscopy

In high temperature VUV reflectivity measurements, there are additional problems to those associated solely with VUV spectroscopy. These problems are the heating method used, the effects of black body radiation on the signal acquisition, and the severe aging effects on the system; all are related to the high temperature of the sample. If a small furnace is used in vacuum to heat the sample, then there is substantial outgassing in the system. For heat flow to the sample to occur, the heating element must be at a higher temperature than the sample. There will be deposition from the heating elements onto the colder sample leading to changes in the reflectance of the sample in addition to unintentional doping of the sample. The other problems are caused by the heat load from the hot sample. Heating a sample of 2 cm² area, with no furnace, requires on the order of 30 watts to get above 1000 °C. Therefore anything exposed to the sample must be very durable, yet detectors and optics in the VUV are very sensitive to environmental damage. Assuming a clean sample that does not vaporize impurities, the sample still radiates all of its input heat into the spectrometer. This rules out the use of sodium salicylate or other phosphors because they are

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unstable, decomposing at low temperatures. The optical coatings on any surface exposed to the sample's black body radiation must be in contact with a good heat sink so that the coating does not heat up and de-adhere. Effects that occur more slowly than these catastrophic failures must also be taken into consideration. The characteristics of the optics will vary slowly with time, and must be regularly calibrated.

The effect of the sample's radiation on the signals detected are another concern. The black body radiation from the sample can be of $10^5$ greater intensity than the light from a H$_2$ source. Lock-in techniques become essential in this situation to recover the incident light signal from the background. The black body radiation can have two separate effects on the reflected light signal. If the detector responds to visible and IR radiation (i.e. it is not solar blind), then the black body radiation will be detected as an incident light signal. The normal way to avoid this problem is to use a monochromator to discriminate the light after the sample. If the incident radiation heats the detector, then its dark current will increase dramatically due to the greater ease of thermal electron emission from the cathode. For successful high temperature VUV spectroscopy all of these problems must be addressed.

4.1.7 Heating Methods

The various heating methods that have been used for optical measurements above room temperature can be separated into two types: indirect methods where the sample is heated by thermal contact and radiation from a furnace, and direct heating methods using light incident
upon the sample to heat it. Resistance furnaces using tungsten, molybdenum, or graphite elements, and alumina insulation have been used, but the outgassing and deposition on the sample are severe. Also the large thermal mass of the furnace requires that greater power be used to achieve the same temperature, thereby increasing the heat load on the system. The optical or direct heating methods have used both Xe arc lamp radiation and lasers of various sorts. Xe arc lamps have been used since the 1950's to grow high purity float zone or skull melted crystals. The major difficulty is collecting the light from the arc and concentrating it on the sample. CO$_2$ gas lasers operating at 10.6 microns are another optical heat source that has been used for high purity crystal growth. Being coherent and nondiverging the laser radiation is relatively simple to concentrate on the sample.

4.2 High Temperature Vacuum Ultraviolet Spectrophotometer

4.2.1 CO$_2$ Laser Heating Techniques

A CO$_2$ gas laser was chosen as the heat source for the high temperature reflectivity measurements. The output of the laser is at 10.6 microns in the infrared and coincides well with the natural absorption of Al$_2$O$_3$. The IR absorption of sapphire starts at 5.6 microns and, at 10.6 microns, it is decreasing with n the index of refraction ~ 1. Therefore
the incident laser radiation is totally absorbed, without a stray reflected beam being formed in the reflectometer. The laser is a Photon Sources, 400 watt, axial flow, continuous beam laser belonging to Dr. John Haggerty of the Ceramics Processing Research Lab at M.I.T. It is a non-tunable industrial welding laser. The laser was designed to operate from 125 watts to 450 watts, but by operating without nitrogen, the continuous power could be lowered to 9 watts. Using a rudimentary pulsing ability the minimum stable power was 1.5 watts. Power measurements were done with a battery operated power meter placed at the partially reflective rear mirror of the laser. Fluctuations in the meter were +/- 0.5 watts. The laser stability was much higher; power fluctuations were negligible. The laser beam was of high quality TEM_{00} mode above about 14 watts, but below this power the beam had a dumbbell power distribution.

The beam line to deliver the laser radiation to the sample used water cooled silver overcoated Si wafer mirrors. The beam went through a water cooled copper aperture before entering the system, to protect the optics from being destroyed due to accidental misalignment. The widows into the system were ZnSe high power IR laser windows sealed for vacuum with indium wire welds. The laser beam geometry was designed so that the CO₂ beam intersected the plane of the VUV optics only at the sample, thereby minimizing danger to the delicate detectors and optics. Any overslash of the beam on the sample exited the system through a window into a water cooled aluminum beam dump.

To minimize the heat load in the spectrometer, only the sample was heated, the sample stand having minimal contact with the sample. Therefore the sample was mounted horizontally resting on three points of a sapphire tripod. Sapphire was chosen to minimize contamination of the
sample at high temperatures. The laser beam was incident on the top surface of the sapphire sample, the same surface where the VUV beam was incident. The beam diameter was the same as the wafer diameter. A nichrome heat shield surrounded the sample, with holes to allow access for the incident, reflected and transmitted VUV beams, the laser beam and the sample tripod stand. A shutter was used to obscure the detectors and optics from the black body radiation of the sample during heating up to temperature. It was opened for data taking. In addition the detectors had heatshields in front of them to reduce detector heating.

4.2.2 Vacuum Ultraviolet Spectrophotometer

The physical design of the spectrophotometer will now be discussed. The signal acquisition and processing will be covered in the next section. The design of the reflectometer VUV optics, the chamber and the monochromator was developed here at M.I.T. in conjunction with Acton Research Corporation of Acton MA. ARC did the detailed design and constructed the reflectometer chamber, optics and the monochromator (see figure 4.2). The vacuum system consisted of a 6 inch hydrocarbon oil diffusion pump, with a mechanical fore pump using low vapor pressure oil and a foreline trap. A liquid nitrogen trap was between the pumps and the system. Precautions were taken to minimize the back streaming of oil from the pumps into the system. Only hydrocarbon oils were used; the silicone oils form SiO₂ upon combustion by the VUV photons, destroying the optics. A flowing-gas glow-discharge source with a differential pumping aperture and separate mechanical pump allowed windowless operation.
These were made by VUV Associates. High purity hydrogen gas was used to create usable continuum radiation from 82.5 nm to 225 nm.

Due to the horizontal sample geometry of the sapphire sample stand, and the demands of the VUV optics, the monochromator was mounted with the monochromator slit horizontal, or in other words the plane containing all of the VUV radiation is vertical. In this manner the radiation is incident on the top surface of the sample. The monochromator is an ARC model VM-502 0.2 meter Seya-Namioka type monochromator, with a holographic aberration corrected grating with 1200 grooves per millimeter. The inherent resolution of this grating is 4 nanometers per millimeter of slit width. The grating was overcoated with osmium due to its high (30%) reflectivity below 105 nm. Bilateral adjustable slits and a synchronous motor drive were also used. A movable MgF₂ filter, with a cutoff at 115 nm (10.7 eV) was installed in the monochromator so that during low energy scans, the higher order radiation could be blocked. The high energy range is 7.5 to 15 eV while use of the filter allows the low energy scan to cover 6 to 9.5 eV.

The reflectometer itself is designed to use chopped light for the application of lock-in techniques, and uses a beam splitter to create a dual beam optical setup. The subminiature tuning fork chopper is installed on the exit slit of the monochromator, modulating the light at 400 hz. The light is then incident on an osmium coated focusing spherical mirror beam splitter. The mirror is used so that its spherical aberration takes the image of the slit and focuses it to a square spot. One half of the beamsplitter takes one end of the slit image and directs it upward to the incident intensity detector, focusing to a spot on the detector. The other half of the slit image is directed down to the sample, where it is a
square spot approximately 4 mm on a side. This is then reflected upward to the reflected detector, or alternatively the light can travel straight through the sample to a transmitted signal detector located below the stand. The optical path lengths are identical for both incident and reflected light. The beamsplitter is movable along the length of the slit to allow balancing the signal levels or for calibration purposes. The beamsplitter is removable without loss of alignment for cleaning or replacement.

The standard sample is a 1.12 cm diameter disk, polished on one side and typically 500 μm thick. It rests on the 3 points of the sapphire tripod sample stand. The sample stand is kinematically mounted in the reflectometer chamber, with micrometer adjustment from outside the system, to permit adjusting the sample's height and angle of tilt. Once installed, the sample is tilted with the lamp on until the light is incident on the reflection detector.

After extensive measurements on the various possible detectors for our high temperature measurements, nude metal electron multipliers were chosen. These have copper-beryllium oxide dynodes, are solar blind and have 16 stages of dynode amplification yielding a gain of $2 \times 10^6$ with 3000 volts applied. They are durable under incident IR radiation, and can be regenerated by heating in oxygen at 400 °C to remove contaminants. Their response is not matched, so a calibration procedure was required, which is discussed in the section 4.2.3.

Additional features of the reflectometer allow remote monitoring of the sample. A sapphire viewport window allows sighting on the edge of the sample for optical and IR pyrometry. An 11 pin electrical feed-through allows for thermocouple measurement and other electrical measurements on
the sample.

4.2.3 Data Acquisition and Signal Processing

Lock-in detection techniques were used to discriminate the VUV signals from the black body radiation of the sample, and to improve the signal to noise ratio. Scans of 100 nm were taken from 80 nm to 180 nm for the higher energies and from 130 nm to 230 nm for the lower energies in the spectral range. The data was acquired on a Hewlett Packard^92 87-XM computer using two computer controlled digital voltmeters, one for each lock-in amplifier, corresponding to the incident and reflected signals. A pulse shaft encoder was installed on the monochromator drive shaft to supply trigger pulses to the digital voltmeters, which were triggered simultaneously. To be able to accurately reproduce the highly dynamic H₂ lamp spectrum, so that the division of these rapidly varying signals would be flat, data points were taken every 1/2 angstrom, 2000 points to a scan. Since typical slit width of the monochromator was 100 or 500 microns leading to 4 to 20 angstrom resolution, a minimum of 8 points were used on each peak.

To reduce the thermal noise of the detectors and system, a 1 sec time constant was used in the lock-ins. Scans were taken at 4 nanometers per minute, so this time constant, or integration time, did not remove any meaningful information from the signals.

Due to the fact that this is a dual beam spectrometer with unmatched detectors that are not very stable in their response, some method of calibrating the system without a sample present and to
compensate for the detector behavior was needed. This was accomplished by taking a 'background' run with no sample and the 'reflected' light detector in the transmission position (below the sample stand). Two spectra files were acquired in this manner, one corresponding to $r_b$, the reflected path background, and $i_b$, the incident path background signal. The reflected detector would then be put in the reflected position (above the sample), a sample mounted and a sample run taken. The reflectivity $R$, referred to here as a four file background corrected reflectivity, would then be calculated by

$$R = \frac{r}{r_b} \times \frac{i_b}{i}.$$ 

Here each term, $(r/r_b)$ and $(i_b/i)$, compensates the appropriate path for its characteristic response. A comparison of the uncorrected two file background and a corrected four file background of the spectrophotometer is given in figure 4.3. In addition, a background run can also be taken after a sample run and the two background runs, i.e. the four files, can be used to calculate a four file background corrected reflectivity that corresponds to the spectrometer baseline, since no sample is present. These are used between every sample run to check: the state of the spectrophotometer, that no damage has occurred to the optics or detectors, or that the system gives a value of unity for the result with no sample present. The baseline value is one because the baseline is taken in the transmission position with no sample, hence no absorption is seen. This has been a very powerful method to compensate for many of the inherent problems of VUV spectroscopy.
4.3 Resolution and Accuracy

Any consideration of experimental work must consider the resolution and accuracy of the results. For this study of the temperature dependent VUV reflectivity of Al₂O₃, the parameters were: the wavelength \( \lambda \) or energy \( E \) at which a spectral feature is observed, the value of the reflectivity \( R \) at a certain energy, and the temperature \( T \) of the sample under study. Each of these will be discussed separately.

4.3.1 Energy \( E \)

The resolution in energy can be determined in two ways: by the slit width of the monochromator or by the spectral resolution of the overall system. The grating in the monochromator has an inherent resolution of 4 nanometers per millimeter of slit width. The higher energy scans (7.5 to 15 eV) were taken with 100 \( \mu \)m or 200 \( \mu \)m slits, while the lower energy scans (from 6.5 to 9.5 eV) were taken with 500 \( \mu \)m slit width. In figure 4.4 the variation of energy resolution with photon energy is shown for the 3 slit widths used. At all energies except the high energy limit of the scan the resolution is always below 0.1 eV, and at all energies it is below 0.14 eV.

The overall spectral resolution is worse than the slit resolution due to noise in the reflectivity remaining even after signal processing. The hydrogen lamp produces a very dynamic ( \( 10^3 \) ) signal with very sharp
features. Upon division these features can appear in the calculated reflectivity curves. The size of these lamp features is on the order of 0.1 eV. Therefore it is hard to attribute a feature of this size as arising from the sample or the system. For this work, only features on the order of 0.3 eV or larger were considered to be representative of the sample. The origin of a specific feature can be checked by comparison to the lamp spectra, and by observing the temperature dependence of the feature; sample features shift, while lamp features do not. The energy position of a feature, once it has been attributed to the sample, is known to within an absolute accuracy of +/- 0.1 eV as determined by the slit resolution. The relative accuracy in energy is higher than this, on the order of +/- 0.01 eV. This relative uncertainty is determined by the reproducibility of the grating position, which leads to a reproducibility of the monochromatized light wavelength of +/- 0.05 nm. It is the relative accuracy in energy that determines how accurately one can determine energy shifts between spectra, as one does in measuring the temperature induced shift of a feature.

4.3.2 Reflectivity R

The resolution in the measurement of the reflectivity R at a certain energy can be separated into two types of errors: systematic and random. Systematic errors lead to an offset of R from the true value for the sample. Random errors are unpredictable and lead to scatter in the data.
4.3.2.1 Systematic Errors

For a study of the temperature induced shifts of features in optical spectra only the relative reflectivity, not the absolute reflectivity, is used in analysis. Still, in the High Temperature Vacuum Ultraviolet Spectrophotometer, absolute reflectivity is calculated, using the four file background corrected method, so as to constrain a larger number of system variables. The magnitude of a spectral offset, if present, could be determined by measuring the value of $R$ for a reference standard. Due to the difficulties of establishing VUV reference standards, and the fact that such knowledge was not needed for this study, this was not done. Instead, to determine if an offset is present, one can compare the values measured in this study to those reported in the literature. Most measured reflectivities for sapphire, at the top of the 13 eV peak, are less than 0.2. Arakawa measured reflectivities up to 0.3 in a very carefully controlled study. Some spectra taken in this work had reflectivities below 0.25, but most reflectivities were in the range from 0.28 to 0.32 for the highest peak, in agreement with Arakawa's work. The other studies probably had low light collection efficiency leading to an offset of the measured $R$ values from the higher true values for the sample. The reflectivities measured in this work are of the correct order of magnitude so as to suggest that no fixed offset errors are present in the measurements.

Another systematic error is due to the changes in the spectrometer during the actual spectra acquisition. This is aging of the system caused by environmental exposure of the optics and detectors, and aging induced
by the heat load on the system. Therefore the system is not in an identical state from scan to scan, leading to tilts in the baseline and features appearing in the baseline due to the adsorbed gaseous species. Another source of baseline errors, and consequently reflectivity errors, is scan to scan instabilities in things such as gas flow in the lamp, or vacuum system leaks. In addition, during high temperature scans, the detectors and beamsplitter are exposed to the radiation of the sample, therefore, they age during the time of the run, causing shifts in the baseline as the run proceeds. As long as these cause only smooth shifts in the baseline, then the relative reflectivity is not adversely affected. The baseline shift observed in these measurements was on the order of +/- 5%. A more serious problem was observed in some runs where a notch would appear at 10.2 eV (124 nm). This was not sample dependent, appeared in some scans and not in others, and at times led to a depression or offset in R at energies below the notch. The notch would appear in the measured reflectivity as a feature approximately 0.4 eV wide and therefore precluded analysis of features in the area of the notch in spectra where it was present. Much work was done to determine the origin of the notch, but no explanation was found. The fact that the notch was a spectroscopy aberration was definitively established in temperature dependent runs where all spectral features would shift, but the notch stayed at the same energy. In addition the notch appeared in spectra taken on other materials.

4.3.2.2 Random Errors
Random errors in $R$ lead to fluctuations in the values of $R$ measured over a set of reflectivities. These can be due to small drifts in the zero of the lock-in amplifiers leading to division and multiplication errors in calculating $R$. Using the change in $R$ at 15 eV, this variation was found to be $+/- 0.03$ in $R$ or $+/- 12\%$.

4.3.2.3 Polarization

By varying the crystallographic orientation of the sample face, and relying on the inherent polarization of the light, orientation dependent spectra were taken. This allowed the differentiation of spectral features as arising from transitions parallel and perpendicular to the crystal's $c$ axis. The light, after being incident on the monochromator grating, is predominantly polarized with its electric vector $E$ parallel to the grating grooves. Then samples mounted on the sample stand with the $c$ axis in the surface plane of the sample and parallel with the grating grooves will show the transitions that occur parallel to the $c$ axis. The same sample with the $c$ axis perpendicular to the grating grooves, or a basal face sample with the $c$ axis as a sample face normal, will show the transitions that are permitted perpendicular to the $c$ axis. Because temperature broadens the features in the reflectivity, it was not considered essential to determine the exact polarization efficiency of the optical system. If this had been needed it could have been done by measuring the reflectivity of a sample as a function of the angle of incidence for two sample orientations.
4.3.2.4 Signal to Noise Ratio at High Temperature

At very high temperatures, random noise was also present in the calculated reflectivities. Lock-in amplifiers were used to establish a good signal to noise ratio for the spectrometer. Still, the best signal to noise improvement that can be achieved using lock-in techniques over the DC case is $10^5$, i.e., the noise can be $10^5$ larger than the signal and still be discriminated. Operating near this condition, the lock-ins are subject to overload and random noise appears in the output. This would appear as a band of noise on both sides of the average value of $R$ and could approach $\pm 20\%$ of $R$. To remove or average this noise, the calculated $R$ spectra would be smoothed by computer with a flat box smoothing function that encompassed the same number of data points as represent the slit determined resolution of the monochromator. Therefore no information from the sample was lost.

4.3.3 Temperature T

The temperature of the sample is the third parameter measured. The sample was heated with a laser beam with a gaussian power distribution, this coupled with the radiation heat loss lead to a radial temperature gradient. The VUV light reflected from the sample was only incident on a 4 mm by 4 mm square in the center of the 11 mm diameter sample, so the gradient in the part of the sample actually used for measurement is taken to be less than the uncertainty in the temperature. The temperature of the sample was determined indirectly by performing calibration runs with a
thermocouple to determine the temperature vs. laser power calibration curve and the temperature vs. optical pyrometer reading. The temperature of a sample of this geometry, a thin disc, contained in a cold wall furnace, and made of a material that is transparent in the visible, is very difficult to determine. Optical methods are not reliable because the sample is not a black body (emissivity $\varepsilon = 1$) or a grey body ($\varepsilon < 1$), instead the emissivity varies with temperature. The problem is not a normal radiation heat loss problem, because a volume emissivity as opposed to a surface emissivity must be used. In addition a sample of such low thermal mass is very sensitive to heat conduction losses, and may not be able to reach equilibrium with a thermocouple bead.

The temperature of the center region of the sample was calibrated by installing a 75 $\mu$m (.003 inch) Pt/Pt 10% Rh thermocouple in a 250 $\mu$m (.010 inch) groove in the back side of the sample and firing it in place with alumina cement. The thermocouple reading is accurate to +/- 0.5 °C, and in this configuration thermal contact with the sample was assured, and heat conduction through the thermocouple leads was minimal. This thermocouple temperature was then calibrated against the laser power as read on the laser power meter (accuracy +/- 0.5 watt) while other laser parameters such as current and gas mixture were noted. In figure 4.5 two sets of data are shown: one with the laser in a pulsed mode and one with the laser on continuously. The curve is not linear when plotted power (q) vs $T^4$ because the radiation is not normal radiation heat loss as mentioned earlier. A separate calibration was done to serve as a check on each sample used for spectra acquisition. The thermocouple temperature was used to calibrate the optical pyrometer reading of a microfocus optical pyrometer (see figure 4.6).
All factors that could change the heat loss from the sample were kept constant. The sample size, geometry, sample polish, the sample stand and heat shielding were kept constant. The setting of the laser power was carefully controlled, all variables kept constant, and the laser beam alignment on the sample checked regularly. With all of these precautions, reasonable and reproducible temperature were attained. A cross check on this was obtained from the reflectivities taken; reflectivities taken at 900 °C overlaid each other exactly. The accuracy of the temperature measurement was +/- 25 °C.

4.4 Conclusions

A high temperature vacuum ultraviolet spectrophotometer has been designed, built and used for optical measurements on $\text{Al}_2\text{O}_3$. It is a dual beam spectrophotometer capable of measuring polarization dependent absolute reflectance and transmittance on high temperature samples at near normal incidence. A focusing beamsplitter is used and a windowless source allows measurements in the range from 6.5 to 15 eV. Nude electron multipliers are used as solar blind detectors, and lock-in techniques are used to improve the signal to noise ratio. Spectra are acquired by computer, 2000 points per 100 nm, and to calculate the reflectivity a four file method is used that compensates for the variation in the base line of the spectrophotometer due to aging of the optics and detectors. The absolute resolution in energy is +/- 0.1 eV, while the relative energy resolution is +/- 0.01 eV. The system's ability to remove the highly
dynamic lamp signal from the calculated reflectivity dictated that only features over 0.3 eV wide were considered to arise from the sample. The reflectivity is accurate to within +/- 12%. Spectroscopy can be performed on samples up to 1100 °C, using a CO₂ laser to cleanly heat the sample without contamination. The accuracy in temperature measurement is +/- 25 °C.
FIGURE 4.1 H₂ Lamp spectrum. 100 μm slits, 0.4 nm resolution.

FIGURE 4.2 High Temperature Spectrophotometer. Monochromator and sample chamber built by Acton Research.
FIGURE 4.3a Two file baseline. \( R = \frac{r_b}{i_b} \).

FIGURE 4.3b Baseline of a four file background corrected reflectivity. Taken in transmission position with no sample, therefore \( T = 1 \). No offset is evident. Four file reflectivity calculated by \( R = \frac{r}{r_b} \frac{(r/r_b)}{(i_b/i)} \).
FIGURE 4.4 Absolute energy resolution versus energy for different slit widths.

FIGURE 4.5 Laser power versus thermocouple temperature calibration curve.
FIGURE 4.6 Optical pyrometer 'temperature' versus thermocouple temperature calibration curve.
Chapter 5

Experimental Results

Temperature dependent reflectivities were taken on samples of \( \text{Al}_2\text{O}_3 \) using the High Temperature Vacuum Ultraviolet Spectrophotometer. The spectra were taken from 83 nm to 210 nm, corresponding to energies from 15 eV to 6 eV. This energy range is covered in two scans, 80 to 180 nm and 130 to 230 nm. The samples were heated without contamination from room temperature up to 1100 °C. The reflectance or transmittance measured corresponds to the absolute value of the property measured within experimental limits. The reflectivity is accurate to +/- 12 %, the absolute accuracy in energy is +/- 0.1 eV, while the relative accuracy is +/- 0.01 eV, and the minimum width for a spectral feature to be attributable to the sample is 0.3 eV.

5.1 Room Temperature Results

The samples used in this study, unless otherwise noted, were single crystal \( \text{Al}_2\text{O}_3 \) grown by the Czochralski method by Union Carbide. They are high quality, optical grade crystals with no bubbles, striations or scattering centers. The dislocation density is typically \( 10^4/\text{cm}^2 \), and the
samples are loosely stated to be 99.99 % pure. The samples used for reflectivity measurements are polished on one side to a 1/4 micron finish with the back side of the wafer roughened to reduce reflection from this back side. The samples used are wafers with the c axis lying in the surface of the wafer and will be referred to here as 'c in plane'. By orienting the sample in the spectrophotometer, reflectivities both perpendicular and parallel to the c axis can be taken, due to the inherent polarization of the spectrophotometer. In addition spectra taken were compared to spectra of high purity (< 70 ppm cation impurities) laser float zone grown and zone refined sapphires produced by Morris.95

5.1.1 Reflectivity of Sapphire

Reflectivities taken at room temperature on a Union Carbide sapphire and a laser float zone sapphire are shown in figure 5.1. The laser float zone crystal had a natural basal face (c axis normal to the sample surface). The spectra were taken with the sample oriented in the spectrometer so that the predominate electric vector \( \mathbf{E} \) of the incident light is perpendicular to the c axis. The features observed are a 9 eV peak and a 13 eV peak that consists of a peak at 13 eV and a 12 eV shoulder. There is also a suggestion of a shoulder at 10.4 eV, but this has not been used in the analysis because this is the area of the 10.3 eV 'spectroscopy notch' (see section 4.3.2.1); therefore, confidence in this feature is low. One can see from these spectra that the features are identical for the two samples. This demonstrates that the reported results are intrinsic to \( \text{Al}_2\text{O}_3 \) and independent of sample origin or trace
impurity content. In addition, since the laser float grown crystal has a natural, as grown, basal face, the results are not controlled by dislocation density or polishing damage in the crystals used. The comparison of a basal face sample to a c in plane sample also supplies useful information on the polarization efficiency of the spectrometer. As can be seen from the Union Carbide spectra, the light is sufficiently polarized to excite only transitions perpendicular to the c axis, leading to results that are comparable to those from a true basal face.

In room temperature reflectivities taken on 7 samples of Union Carbide sapphire, the major features were an absorption edge below 9 eV, a 9 eV peak and a broad 13 eV peak. These features were common to all samples without regard to orientation, and were measured by determining the geometrical center of the peak. The variability of the peak positions for samples of one orientation, reported as the standard deviation $\sigma_{n-1}$ was $\pm 0.025$ eV for the 9 eV peak and $\pm 0.1$ eV for the 13 eV peak.

5.1.2 Orientation Dependent Features

In figure 5.2 room temperature reflectivities from UC c in plane sapphire are shown. Curve a was taken with $E$ perpendicular to the c axis while curve b corresponds to excitations parallel to the c axis. These show the orientation dependent features observed for sapphire. In curve a, for $E$ perpendicular to the c axis, there is superimposed on the broad peak a small peak at 13.1 eV and a shoulder at 12 eV. In curve b, for $E$ parallel to the c axis, the broad peak has two small peaks superimposed on it at 12.9 eV and 12.3 eV. Looking at curve b one can see that the
structure is more complicated than summarized here; there is a slight shoulder suggesting a third peak at higher energy in the 13 eV broad peak. Due to the emphasis on temperature dependent spectroscopy, these features are only noted in passing in this study. Such fine features will broaden and disappear with increasing temperature.

5.1.3 Transmissivity of Sapphire

Measuring the transmissivity of a sample is a useful technique to determine the energy of the absorption edge. In transmission a change in the absorption coefficient rapidly leads to a transition from high transmissivity (clear) to low transmissivity (opaque). In figure 5.3 the transmissivity $T_r$ of R plane (1102, 57.52 ° to the c axis) Union Carbide sapphire is shown. One can see $T_r$ decreasing slowly from 7.5 to 8.5 eV, and then a strong decrease in $T_r$ starts, leading to $T_r = 0.01$ at 8.8 eV. There is still some transmission present up to 9.5 eV, whereupon the sample is opaque. The absorption edge energy is determined by projecting the region of abrupt decrease in $T_r$, corresponding to the onset of the absorption process responsible for the edge, to $T_r = 0$. In this case this gives an absorption edge energy of 8.8 eV. The sample used here was 500 μm (0.020 inch) thick. The value of the absorption coefficient $\alpha$ could be determined by measuring $T_r$ for samples of varying thickness, but this was not done.
5.1.4 Other Forms of Al₂O₃

It is interesting to look at other forms of Al₂O₃ to see the effects of structural differences on the spectra and electronic structure. Reflectivities have been taken on amorphous or γ Al₂O₃ and polycrystalline alumina. The amorphous sample of Al₂O₃ was formed through a sol-gel process at low temperature (< 200 °C) and then dried at temperatures below 600 °C, therefore inhibiting the phase transformation to the α phase. It is believed, from x-ray diffraction measurements, to be amorphous with very small γ crystallites. In the reflectivity shown in figure 5.4, one can see that the absorption edge has shifted to 8 eV, and a peak is not observed above this edge. Also the center of the broad high energy peak which is at 12 eV, is shifted 1 eV from the crystalline case. Figure 5.5 shows a reflectivity taken from a sample of Lucalox, a polycrystalline Al₂O₃ that is doped with MgO so as to yield a fully dense translucent material. Here again one can see that the absorption edge has shifted to 8 eV, there is a peak at 9 eV, and the broad high energy peak is centered at 13 eV.

5.1.5 Other Materials

To confirm that the features observed in the reflectivities of Al₂O₃ correspond to unique characteristics of Al₂O₃, reflectivities taken with the spectrophotometer on other materials are shown. The reflectivity of single crystal MgO is shown in figure 5.6. Here one can see an absorption edge starting at 7.4 eV, increasing to a peak at 7.6 eV. There
is a series of peaks up to 11.5 eV, and then a single large peak at 13.5 eV. Figure 5.7 is the reflectivity of single crystal LiF. This shows a gradually increasing reflectivity up to a single peak at 12.7 eV, and a short broad peak at 14.2 eV. These examples demonstrate that the results on Al₂O₃ are unique to the material and not a function of the spectrometer.

5.2 High Temperature Results

Temperature dependent reflectivity measurements were taken on Union Carbide c in plane sapphire crystals at temperatures up to 1100 °C. These measurements were taken with the c axis parallel to the predominant polarization of the spectrometer. This orientation was chosen so that the 13 eV peak would have the doublet structure and broaden into a symmetrical peak, and the problem of having to measure the shift of an asymmetrical peak and shoulder as would occur for spectra taken perpendicular to the c axis, could be avoided. The samples were glowing red at temperatures above 800 °C, and at 1100 °C, the Lock-in amplifiers were operating very close to overload, which required substantial smoothing of the spectra. Spectra taken at room temperature on samples before and after heating showed no change in the reflectivity, demonstrating that the results are not controlled by changes in polishing damage or surface structure due to annealing.

Spectra taken at many temperatures are shown in figure 5.8, where they have been displaced in R to show the temperature dependent shifts.
All of these curves, with the exception of the 900 °C curve, were taken as one set in two major runs over two weeks. Therefore they are subject to low experimental uncertainty. From these spectra one can see the 8.8 eV absorption edge shifting to lower energy with increasing temperature, being below 8 eV at 1100 °C. The 9 eV peak broadens and decreases in intensity with increasing temperature. The 9 eV peak has shifted to approximately 8 eV at 1100 °C. The 10.5 eV shoulder, which lies in the area of the 'notch' and has been attributed to a spectroscopy aberration, is still observable at high temperature, and has not shifted in energy, reconfirming that it is a machine dependent feature. The 13 eV peak, which for this sample orientation has a doublet structure, broadens with increasing temperature and shifts to lower energy.

More detailed analysis is possible by looking at the unstacked reflectivities. In figure 5.9 a reflectivity taken at 300 °C is shown. The doublet structure of the 13 eV peak is still visible, but the peak has shifted to 12.7 eV. The 9 eV peak has shifted to 8.75 eV. At 700 °C (see figure 5.10) the 9 eV peak has broadened and shifted to 8.3 eV, while the 13 eV peak has shifted to 12.4 eV. At 900 °C (see figure 5.11) the 13 eV peak has shifted to 12.3 eV, the 9 eV peak to 8.2 eV, and the 9 eV peak has broadened and decreased in intensity. At 1100 °C (see figure 5.12) the 13 eV peak is at 12.2 eV, the 9 eV peak is at 7.9 eV. At this temperature the absorption edge is below 7.7 eV.

5.3 Calculated Results: The Temperature Coefficient B
The high temperature reflectivities were analyzed to extract a temperature shift coefficient for the three major spectral features. Due to the fact that no theoretical models predicted the explicit functional dependence of $E_{\text{feature}}(T)$, the data was analyzed to determine its functional dependence. For this analysis the energies of the peaks and edge were determined by two techniques. For the peaks, see figure 5.13, the geometrical center or center of mass of the peak was determined. This was done by drawing a line under the peak, determining the half maximum of the peak, and measuring the energy of the midpoint of the width of the peak at half maximum. To determine the energy of the absorption edge, a reproducible manner of determining a characteristic edge energy was needed. Geometrical methods did not yield a systematic edge energy. Instead an energy for the edge was determined from a closely controlled set of runs where the magnitude of $R$ was accurate within $\pm2.5\%$. In these the energy at which $R$ on the edge was 0.2 (see figure 5.14) was used as an edge energy. This was midway up the absorption edge.

The energy (eV) versus temperature (K) for the 3 features, the 13 eV peak, the 9 eV peak and the absorption edge from all of the temperature dependent spectra is given in figures 5.15 through 5.17. By measuring the peak position for the 13 and 9 eV peaks, the value of $\beta$ corresponds to shift rate of the peak center, and ignores the effect of peak broadening. This is most appropriate for determining the temperature shift of the average transition energy. In the case of the absorption edge, both broadening and shift are included in the calculated $\beta$, corresponding to the shift of the minimum transition energy. Due to the difficulty of reproducibly measuring the shift of the absorption edge, $\beta$ values for the edge were determined only up to 700 °C. But due to the fact that the $\beta$ of
the edge is similar to that of the peaks, and the three features shifted in unison, the result for the edge is stated to hold for the complete temperature range studied, up to 1100 °C.

The data shows a predominantly linear relationship over the complete temperature range. A linear regression fit of these data was performed to yield an equation of the form:

$$E_{\text{feature}}(T) = E_f(T=0K) - \beta T.$$ 

Here $E_f(T=0K)$ is the energy position of the feature at $T = 0$ K, while $\beta$ is the linear temperature coefficient of the feature. In the case of the edge calculation, $E_f(T=0K)$ is not a relevant number since the calculation was done with an arbitrary energy on the edge. The results are given below, along with the correlation coefficient of the data. The correlation coefficient in all cases was quite close to +/- 1, demonstrating that for a linear model the data was highly correlated; in all cases the probability that the data is uncorrelated is less than 1 % and in most cases less than 0.1 %.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Equation</th>
<th>c.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 eV peak</td>
<td>$E(T) = 13.18 - 7.3 \times 10^{-4} T$</td>
<td>-.93</td>
</tr>
<tr>
<td>9 eV peak</td>
<td>$E(T) = 9.32 - 9.9 \times 10^{-4} T$</td>
<td>-.98</td>
</tr>
<tr>
<td>abs. edge</td>
<td>$E(T) = 8.56 - 1.1 \times 10^{-3} T$</td>
<td>-.97</td>
</tr>
</tbody>
</table>

The standard deviations $\sigma_{n-1}$ of $\beta$ for the 3 features were determined by calculating the value of $\beta$ for each high temperature spectra relative to room temperature and then determining the standard deviation of these results. From these values a standard error can be determined,
which considers the number of data points $N$ used to determine $\beta$. 13 data points for the 13 eV peak, 14 data points for the 9 eV peak and 4 data points for the absorption edge were used. The standard error is defined as: standard error $= \frac{\sigma_{n-1}}{N^{1/2}}$. The values are given below.

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\sigma_{n-1}$ (eV/K)</th>
<th>Standard Error (eV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 eV peak</td>
<td>$1.5 \times 10^{-4}$</td>
<td>$4 \times 10^{-5}$</td>
</tr>
<tr>
<td>9 eV peak</td>
<td>$1.2 \times 10^{-4}$</td>
<td>$3 \times 10^{-5}$</td>
</tr>
<tr>
<td>abs. edge</td>
<td>$1.9 \times 10^{-4}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

To confirm the linear relationship between feature energy and temperature the data was fitted to a second order polynomial to determine the magnitude of the second order term. This was done for the 13 and 9 eV peaks:

13 eV peak: $E(T) = 12.93 - 7.4 \times 10^{-4} T + 6 \times 10^{-8} T^2$

9 eV peak: $E(T) = 9 - 8.7 \times 10^{-4} T - 7 \times 10^{-8} T^2$.

In each case the second order term is very small, there is no reason to believe that the relationship is second order. Additional support is given by considering the data from the one set of two major runs referred to earlier. These spectra were very closely controlled and in figure 5.18 we can see that the data fall on a straight line with the exception of one point. Additionally, figure 5.18 demonstrates that the 'spread' in the data is attributable to systematic errors arising from the peak measurement techniques used, not from actual variability of the properties of $\text{Al}_2\text{O}_3$. 

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From this one can conclude that the energy of the three features measured is linearly dependent on the temperature from 300 to 1400 °C. \( \beta \), the linear temperature coefficient for each feature is given in the table below.

| TABLE 5.3 $\beta$ (Temperature Coefficient) Values For $\text{Al}_2\text{O}_3$ |
|-----------------------------|------------------|-------------------|
| Absorption Edge            | $1.1 \times 10^{-3}$ eV / K | +/- $1 \times 10^{-4}$ |
| 9 eV Peak                  | $1.0 \times 10^{-3}$ eV / K | +/- $3 \times 10^{-5}$ |
| 13 eV Peak                 | $7 \times 10^{-4}$ eV / K | +/- $4 \times 10^{-5}$ |

5.4 Summary of Results

Reflectivities were measured of single crystal sapphire, with light polarized both parallel and perpendicular to the c axis, and on samples oriented with the c axis parallel to the predominant polarization of the spectrophotometer from room temperature to 1100 °C. The major features observed at room temperature are an absorption edge at 8.8 eV, a peak on the absorption edge at 9 eV, and a broad peak at 13 eV. The 13 eV peak shows orientation dependent features, for optical excitation parallel to the c axis there is a doublet peak, while with excitation perpendicular to the c axis, there is a higher energy peak, and a shoulder evident at lower energy. With increasing temperature all three features shift to lower energy. At 1100 °C the absorption edge has shifted to 7.6 eV, the 9 eV
peak decreased in intensity and has shifted to 7.9 eV, and the 13 eV peak shifted to 12.2 eV. The relationship between the energy of the features and temperature is found to be linear. The linear temperature coefficient $\beta$ for these three features are given in table 5.3. $\beta$ for the absorption edge is $1.1 \times 10^{-3}$ eV/K.
FIGURE 5.1a Reflectivity of laser float-zone grown sapphire: natural basal face, E perpendicular to the c axis, T equals 21 °C.

FIGURE 5.1b Reflectivity of Union Carbide sapphire: c in plane, E perpendicular to the c axis, T equals 21 °C.
FIGURE 5.2a Reflectivity of Al₂O₃: c in plane, E perpendicular to the c axis, T equals 21 °C.

FIGURE 5.2b Reflectivity of Al₂O₃: c in plane, E parallel to the c axis, T equals 21 °C.
FIGURE 5.3 Transmissivity of Al₂O₃: R plane, T equals 21 °C.

FIGURE 5.4 Reflectivity of gel-amorphous Al₂O₃: T equals 21 °C.
FIGURE 5.5 Reflectivity of Lucalox polycrystalline Al₂O₃: T equals 21 °C.

FIGURE 5.6 Reflectivity of single crystal MgO: T equals 21 °C.
FIGURE 5.7 Reflectivity of single crystal LiF: $T$ equals 21 °C.
FIGURE 5.8 Temperature dependent reflectivities of Al$_2$O$_3$: T (from bottom to top of figure) equals 21, 300, 500, 700, 900, and 1100 °C. Each division on R axis equals 0.01.
FIGURE 5.9 Reflectivity of Al₂O₃: c in plane, E parallel to the c axis, T equals 300 °C.

FIGURE 5.10 Reflectivity of Al₂O₃: c in plane, E parallel to the c axis, T equals 700 °C.
FIGURE 5.11 Reflectivity of Al$_2$O$_3$: c in plane, E parallel to the c axis, T equals 900 °C.

FIGURE 5.12 Reflectivity of Al$_2$O$_3$: c in plane, E parallel to the c axis, T equals 1100 °C.
FIGURE 5.13 Demonstration of the method used to determine the energy of peaks: peak energies are 12.9 and 9 eV, T equals 21 °C.

FIGURE 5.14 Demonstration of the method used to determine an arbitrary energy on the absorption to determine the temperature coefficient: at R equals 0.20, energy is 8.7 eV, T equals 21 °C.
FIGURE 5.15 Energy of the '13 eV' peak as a function of temperature.

FIGURE 5.16 Energy of the '9 eV' peak as a function of temperature.
FIGURE 5.17 Energy of the \( R = 0.20 \) point on the absorption edge as a function of temperature.

FIGURE 5.18 Energy of the '9 eV' peak as a function of temperature. This data is from a single closely controlled run; note the linearity of the results.
Chapter 6

Discussion

6.1 Introduction

In this chapter the measurements of the vacuum ultraviolet reflectivity of single crystal $\text{Al}_2\text{O}_3$ will be compared to the literature. Insight into the electronic structure and the changes of the electronic structure with temperature will be developed using the results of the temperature dependent reflectivity measurements. The aim is to understand the electronic structure at temperatures up to 1500 °C and then, considering the relationship between the electronic structure and the crystal lattice, to develop a picture of the electronic carriers that contribute to the observed electronic conductivity of $\text{Al}_2\text{O}_3$ at high temperature. Using this information, some conductivity results will be analyzed to extract information on carrier character and mobility.
6.2 Room Temperature Optical Spectra and Electronic Structure

6.2.1 Comparison of Optical Spectra to the Literature

The room temperature reflectivities taken in this study have shown orientation dependent features which have been demonstrated to be intrinsic features of the optical spectra of single crystal α-Al₂O₃. In spectra taken from 7 to 15 eV, these show a prominent absorption edge at 8.8 eV, leading into a peak at 9 eV. At 13 eV there is a broad peak which shows features dependent on the orientation of the sample, for E perpendicular to the c axis (figure 5.2a) there is a shoulder in the peak at 12 eV, while for E parallel to the c axis (figure 5.2b) there is a peak at 12.3 eV. These orientation dependent features have not been reported previously in the literature.

In the literature most reflectivities have been over a limited energy range and taken point by point, reducing our confidence in these results. Still, there is good agreement between the literature and the results reported here; the only discrepancies are attributable to shape changes of the reflectivity caused by systematic errors. Loh's results for E perpendicular to the c axis (figure 2.18) are in agreement with the 9 eV, 12 eV and 13 eV features, except that he shows a 12 eV peak, where a shoulder is found in this work. In addition he shows a prominent edge leading to a 10.6 eV shoulder that is not reproduced here, and below the 9
eV peak the reflectivity shows only a gradual decrease instead of an edge. This is probably caused by the chromium doping of his sample.

Arakawa (figure 2.20) does show a prominent edge below a 9.5 eV peak, a 11.6 eV shoulder and a 12.8 eV peak. Their results don't go to low enough energy to see the absorption edge below the 9 eV peak, but they hypothesize that it is there from transmission measurements, and they don't show the prominent edge at 10 eV that Loh observed. From the shoulder peak structure they observed, I believe their sample was oriented with E perpendicular to the c axis, in agreement with this work. Rubloff (figure 2.21) shows a 9.2 eV peak, an edge at 10 eV, and for E perpendicular to c, a peak at 13.2 eV and a shoulder at 12.3 eV. For E parallel to c, he shows a single broad peak at 12.8 eV, not showing the doublet peak observed in this work. He also does not extend his measurements to low enough energy to determine whether the absorption edge starts below the 9.2 eV peak. Abramov (figure 2.22) shows a peak at 9 eV, a small shoulder at 10.4 eV, a peak at 11.7 and a broad peak at 12.8 eV for a sample oriented with E perpendicular to c. He shows a doublet where this work shows a shoulder and peak. He shows a prominent absorption edge below the 9 eV peak.

All of these results are in agreement with the spectra taken in this study, or in cases where there is disagreement, some other spectra show features similar to those observed here.

6.2.2 Room Temperature Electronic Structure

Using the band structure and atomic cluster models of α-Al₂O₃
reviewed in section 2.3.1, it is now possible to interpret the observed optical spectra in terms of the room temperature electronic structure. Al₂O₃ is an ionic material with carriers localized in real space and retaining much of their atomic character and origin. This is a material where the formation of excitons, or localized electron hole pairs, is expected. The localized nature of the electronic structure also gives rise to the polaronic nature of the free carriers in Al₂O₃. The 9 eV peak observed in the reflectivity has previously been attributed to exciton formation. This seems plausible in this material; both MgO and SiO₂ have been identified as forming excitons. Still, in Al₂O₃ the 9 eV peak has yet to be definitively identified as arising from excitons; this would require high resolution low temperature (10 K) optical studies to document the hydrogenic levels of the excitons. A separate possible explanation was put forth by Ciraci that the excitons are due to surface state bands, which does not seem plausible due to the low density of such states, but does demonstrate that the spectral features are still open to interpretation. Pending future work to identify or refute the excitonic nature of the 9 eV peak, the 9 eV peak is attributed to exciton formation.

The existence of the 9 eV exciton peak has made identification of the absorption edge difficult. In addition most optical studies have not covered the full energy range from 7 to 15 eV, therefore omitting some of the structure present. Previously the spectra has been interpreted as showing an exciton peak below a 10 eV edge. If we compare the reflectivity of sapphire at room temperature and 900 °C (see figure 5.8) where the exciton peak has broadened and decreased in intensity (due to the difficulty of forming the exciton with such a high phonon density), we
can see that there is a large absorption edge still present. It has shifted to about 7.8 eV but is the same edge that at room temperature lies at 8.8 eV. Now the question arises whether, for this material, to expect the exciton to be formed below the fundamental band edge, as previously interpreted, or do the exciton states superimpose themselves on the edge? In both MgO$^{99}$ and SiO$_2$ $^{100}$ the exciton states are observed as a peak superimposed on the absorption edge. Therefore the observation of a large fundamental absorption edge below the exciton peak, which becomes fully exposed at high temperature, is reasonable.

Further confirmation of the existence of the fundamental absorption edge at 8.8 eV can be gained from looking at the transmissivity of Al$_2$O$_3$ (see figure 5.3). Here we see the transmissivity equal to 0.75 at low energy and then decreases to 0.01 between 8.5 and 8.8 eV. The edge position determined in this work is given as 8.8 eV $\pm$ 0.25 eV.

The absorption edge at 8.8 eV in Al$_2$O$_3$ at room temperature corresponds to the fundamental absorption edge of the material. It demonstrates the onset of valence band to conduction band transitions. In Al$_2$O$_3$ this absorption edge corresponds to transitions from the O 2p bands at the top of the valence band to Al 3s bands in the bottom of the conduction band. The intensity or height of the absorption is smaller than the higher energy features observed in the reflectivity due to the low density of states of the Al 3s bands. The 8.8 eV absorption edge corresponds to the band gap at room temperature in the material. Further confirmation of this interpretation is found by considering the photoconductivity results of Kuznetsov $^{101}$, who found the onset of room temperature photoconductivity to occur at 9 eV. The band gap measured in this work corresponds to an optical gap, since it was measured at
relatively low temperature (compared to $\theta_D$) and by optical means that do not allow the relaxation processes involved in a thermal gap process. In addition it is a direct gap because the low temperature does not supply the necessary phonons to permit optical measurement of the indirect transitions that change the $k$ of the electron. It is not possible to determine with these measurements whether the minimum fundamental gap in $\text{Al}_2\text{O}_3$ is indirect or direct; this would involve detailed analysis of the absorption edge shape which is beyond the scope of this work. It is possible to conclude that the optical direct gap of $\text{Al}_2\text{O}_3$ is at 8.8 eV at room temperature. The accuracy of this number is low (+/- 0.25 eV), due to uncertainty in separating the exciton peak from the edge. Calculating the dielectric constant or index of refraction using Kramers Kronig analysis would more accurately determine the band gap, but was not performed in this work.

The third major feature observed in the reflectivity is the broad 13 eV peak which shows orientation dependent features. The 13 eV peak is the most intense peak observed in this energy range. Batra in his band structure calculation found the peak in the conduction band density of states to lie 4 eV above the conduction band edge, arising from Al 3p bands. With a band gap of 8.8 eV, the Al 3p bands should lie at 12.8 eV, corresponding to excitations from the top of the valence band (0 2p) to the Al 3p states in the conduction band. Other transitions from lower lying states in the valence band are also occurring at 13 eV, but the peak in the joint density of states is dominated by transitions from the 0 2p bands to the Al 3p bands due to the high density of states of the 0 2p sub-band, giving rise to the 13 eV peak.
6.2.2.1 Summary

Through the use of the electronic structure models for α-Al₂O₃, the measured reflectivity spectra at room temperature have been interpreted. The 9 eV peak is attributed to exciton formation, though no definitive evidence is presented at the present time to substantiate the assignment. The fundamental absorption edge lies at 8.8 eV, and corresponds to transitions from the O 2p states at the top of the valence band to the Al 3s states at the bottom of the conduction band. The optical direct gap of Al₂O₃ is 8.8 eV at room temperature, even though no statement is made as to the direct or indirect nature of the minimum band gap in the material. The 13 eV peak observed corresponds to transitions to the Al 3p states in the conduction band.

6.3 Temperature Dependent Optical Spectra and the High Temperature Electronic Structure

6.3.1 Optical Results

Optical reflectivities taken from room temperature to 1100 °C, from 7 to 15 eV on single crystal α-Al₂O₃ showed the following changes with temperature. The detailed shape of peaks changed, for example small shoulders were lost, due to the effects of phonon broadening on the
electronic states. The peak centers, or centers of mass, shifted to lower energies with increasing temperature. This corresponds to the shift of the bands leading to a decrease in the band to band energy gap. The basic peaks also broadened, corresponding to spreading of the bands. Measuring the temperature coefficient of the peak center, as was done for the 13 and 9 eV peaks, determines the temperature coefficient for peak shift, while the temperature coefficient of the absorption edge combines both band shift and spreading. For the band gap the minimum transition energy is of interest and both band spreading and shift should be considered. The measured results, taken on many samples showed a very linear relationship between the temperature and the energy of a spectral feature. The temperature coefficients determined in this work are given in table 5.3. The absorption edge temperature coefficient is $1.1 \times 10^{-3}$ eV/K.

To compare to the literature the absorption edge shift coefficient will be used since the edge shift is what was measured in previous experiments. The work of Gilles, as analyzed by Harrop, was over the largest temperature range, and yielded a value of $1.5 \times 10^{-3}$ eV/K. This is the value of $\beta$ that has been referenced in the conductivity literature for Al$_2$O$_3$. The results, when plotted as energy versus temperature (see figure 2.24) show a nonlinear relationship. With more samples and improved statistics, one could determine if this is in disagreement with the present finding of a linear relationship, but this is not possible. The value reported seems reasonable, even though high, but the actual spectra from which the data was extracted are cause for concern. The existence of the Cr peak in the area where the data was taken, and the associated gross change in the absorption edge shape may explain the nonlinearity and the magnitude of the result.
The rest of the data discussed here was analyzed by this author to extract values of \( \beta \) for comparison. This was instructive, because it demonstrates the variability in \( \beta \)'s calculated from one set of data and the importance of error bars in these data. The data of Yakovlev was taken over a small temperature range, as was all the subsequent data, and had noticeable absorption edge shape changes. These lead to a wide range of values from \( 1.4 \) to \( 2 \times 10^{-3} \) eV/K for \( \beta \). Laufer's data suggests a value of \( 1.9 \times 10^{-3} \) eV/K. Hunter and Rubloff each suggest \( 1.75 \times 10^{-3} \) eV/K and \( 1.3 \times 10^{-3} \) eV/K, and report that the value of \( \beta \) decreases below room temperature. The latter value is quite close to the value of \( 1.1 \times 10^{-3} \) eV/K measured in this work. Blum determined a value of \( 1.4 \times 10^{-4} \) eV/K which is very low, but he was working over a very limited energy range and therefore it is hard to determine what feature was shifting.

Most of these values are of the same order as the results reported here. The values of \( \beta \) extracted from the literature are taken from very few runs, and do not have good statistical qualities. Also the variability of the results due to arbitrary analysis decisions has been demonstrated. One advantage of the present work has been that the analysis of both peak center shift and absorption edge shift has demonstrated the internal consistency of the measurements. One would expect the absorption edge shift to be larger than a peak center shift which ignores broadening. The calculated literature values give confidence in the order of magnitude of the effect while the superior statistics of the present work give confidence in the reported values.

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6.3.2 Temperature Dependent Electronic Structure Models

It is useful to review the findings of the work on the temperature dependence of electronic structure to develop an idea of what effects control the electronic structure at high temperatures. Only band structure techniques have addressed the problem, considering it in terms of the interaction of electrons and phonons. This work was done mostly for the covalent semiconductors which show delocalized electron and phonon states as opposed to the bond oriented electrons and localized lattice distortions of Al₂O₃. Therefore they are unable to address the gross and localized lattice effects that, for example, lead to polarons. The interaction of the lattice and the electronic structure in determining the high temperature electronic properties will be discussed in section 6.4. Due to the complexity of electron-phonon calculations, they have never been attempted for Al₂O₃.

The band structure models yield three basic terms that determine \( E(T) \). The first is the effect on the electronic structure of the thermal expansion of the lattice; this will tend to increase the band gap by decreasing the band width of the valence and conduction bands. The other two terms produce effects that are larger than that of thermal expansion. The Debye-Waller term leads to band broadening. It is proportional to \( T^2 \) below the Debye temperature, linear above this temperature, and exponential far above it. The electron self-energy terms lead to band shift. They are exponential below the Debye temperature and linear above it. It is plausible that the 3 terms can superimpose to give a linear behavior to \( E(T) \) as has been found in this work from below the Debye
temperature to above it.

The thermodynamic approach to the problem demonstrates the importance of local effects that are not well treated in a covalent case. Here the effects of bond breakage, corresponding to excitation of an electron from the valence band (bonding orbitals) to the conduction band (anti-bonding orbitals), change the phonon properties of the system thereby effecting the electronic energy levels. The effect of this process will be of greater importance in materials with localized electronic structures.

The atomic cluster molecular-orbital approach seems more appropriate to localized materials such as \( \text{Al}_2\text{O}_3 \), even though no work has been done using this method to study the temperature dependence of the electronic structure. Because the cluster models allow the creation of a localized electronic structure without the requirements of translational periodicity and averaged structure, they can allow the localized electronic orbitals to relax in the excited states. This electronic relaxation is a noticeable portion of the electronic energy. In addition, by changing the bond lengths in the cluster the effects of thermal expansion and atomic vibrations can be introduced directly from experimental data. Thermal expansion increases the bond lengths, but, in the time frame of the electronic excitation, atomic vibrations can lead to a decrease in the instantaneous bond length, leading to a thermally reduced band gap energy. With information about the atomic relaxation that accompanies the formation of polarons, the relaxation energy gained due to polaron formation could be calculated directly.

The fact that bond length is a useful method for qualitatively interpreting the temperature induced changes in optical spectra and
electronic structure can be confirmed by considering the effects of bond length changes on samples at room temperature. Other forms of \( \text{Al}_2\text{O}_3 \) which have varying bond lengths relative to single crystal \( \alpha \text{Al}_2\text{O}_3 \) are fine grained polycrystalline \( \alpha \text{Al}_2\text{O}_3 \), amorphous or \( \gamma \) crystallite sol-gel derived \( \text{Al}_2\text{O}_3 \), and anodized films of \( \text{Al}_2\text{O}_3 \). The strained bonds present in these materials will lead to band spreading and, if the average bond length is different from single crystal \( \alpha \text{Al}_2\text{O}_3 \), shift of the band centers. This effect has been observed in this work for polycrystalline lucalox (see figure 5.5) and the sol-gel \( \text{Al}_2\text{O}_3 \) (see figure 5.6), which show absorption edges at about 8 eV.

It is useful to apply the empirical model of Ravindra to the case of \( \text{Al}_2\text{O}_3 \). This is a model with no fundamental basis; it is a curve fitting model which only depends on the Debye temperature and is essentially linear with temperature. Calculating the decrease of the band gap with temperature up to 1500 °C, for a \( \theta_D \) of 695 K, the gap decreases 1.33 eV while for \( \theta_D \) equal to 1000 K, the decrease is 1.53 eV. Experimentally from this work the gap is predicted to decrease 1.65 eV over 1500 K. So, Ravindra's model underestimates the shift, but then it is the only predictive model available and is not grossly inadequate. The fact that such a naive model can predict the temperature dependence of the band gap suggests that the complexity of the electron-phonon modeling is not essential to understand the effect, and that the simplicity of the localized cluster approach which considers bond length changes may be more appropriate.

6.3.3 High Temperature Electronic Structure of \( \alpha \text{Al}_2\text{O}_3 \)
From the temperature dependent optical measurements we determine the temperature coefficient of three electronic structure features. The absorption edge shift demonstrates the broadening and shift of the O 2p and Al 3s bands and determines the minimum transition energy for valence band to conduction band transitions. It gives the temperature dependence of the band gap. The shift of the 9 eV peak demonstrates the temperature coefficient of the average energy of the exciton state. The shift rate of the 13 eV peak demonstrates the rate of shift, without broadening, for the O 2p and Al 3p bands.

It is now of interest to determine the band gap energy as a function of temperature. The data was linear over the total temperature range measured; no change of mode was observed near the Debye temperature. The next fundamental change in the lattice properties of Al₂O₃ has been observed to be the onset of anharmonic lattice vibrations around 1500 °C, so there is no reason to expect a change in the temperature coefficient up to these temperatures. Therefore one can confidently use the β value of 1.1 x 10⁻³ ev/K as the temperature coefficient of the band gap energy up to 1500 °C. The room temperature gap determined in this work was 8.8 eV. To determine the 0 K value of the gap we can use β to project back to 0 K. This gives a value of 9.1 eV. As Hunter found, the β value is linear above room temperature, but decreases to zero below room temperature. Therefore the application of a constant β to determine E₄(T=0K) may be incorrect. But with the emphasis of this work on the high temperature conductivity of sapphire, the error would be small, and, more importantly, the linearly extrapolated T = 0 K band gap is the one that would be determined in a high temperature conductivity.
measurements. In this work the linearly extrapolated $T = 0 \text{ K}$ band gap will be referred to as the apparent $T = 0 \text{ K}$ band gap. Combining this information, with energy in eV and temperature in K yields:

$$E_g [T(K)] = 9.1 \text{ eV} - 1.1 \times 10^{-3} T$$

while

$$E_g [0 \text{ K}] = 9.1 \text{ eV}$$
$$E_g [273 \text{ K}] = 8.8 \text{ eV}$$
$$E_g [1500 \text{ K}] = 7.15 \text{ eV}.$$

This is the minimum optical energy gap of the electronic structure and, since it was experimentally measured, automatically accounts for thermal expansion, Debye-Waller effects and the electron's self-energy. It is an optical band gap because of the high frequency of optical measurements; no effects of lattice relaxation, which may reduce the gap energy, can be seen. From these measurements, it is not possible to determine if the minimum band gap is direct or indirect, but if it is indirect, then at high temperatures, with the large numbers of phonons present, the optically measured gap will be equivalent to the indirect gap.

6.4 The Role of High Temperature Electronic Structure and Lattice Properties in Determining Electronic Carrier Character and Creation Energy

Up to this point the temperature dependence of the optical band gap
has been determined, producing a value for the \( T = 0 \) K optical band gap and the linear temperature coefficient of the band gap. The carriers that are created optically are free band electrons created in a static lattice, which can then undergo lattice relaxation forming polarons. For the application of these results to understand high temperature conductivity, the thermal band gap and the properties of the carriers with their lattice relaxation fields must be considered. This is because the time scale of the carrier creation in a thermal process will be that of the lattice, and the energy required to create the resulting polaronic carrier will be the thermal gap energy. In other words it is not the band structure that determines the properties of the carriers at high temperature, but the interaction of the electronic structure with the lattice that determines the carrier creation energy, the carrier character and the carrier mobility.

6.4.1 Polaronic Nature of The Electronic Carriers

The first major effect the lattice has on the electronic structure is in determining the character and mobility of the carriers: whether they are band electrons or, with strong electron-lattice interaction, polarons. The polaron coupling constant \( \alpha \) equals 2.7, suggesting that sapphire is a material that forms large or small polarons. Kroger for many years has been suggesting that the carriers are polarons, while Colbourn calculated the relative stability of small and large hole polarons. The idea of polaron formation in sapphire is accepted in the literature.
The carrier mobility is another good indicator of the polaronic nature of the carriers, but we have such information only for electrons in sapphire. For electrons the measured mobilities lie in the range of 0.1 to 100 cm$^2$/V sec suggesting that the electrons are large polarons. The hole may be a small polaron with a thermally activated hopping mobility. These results are very similar to those found in amorphous and crystalline SiO$_2$ where the holes are small polarons with a mobility of $10^{-5}$ cm$^2$/V sec while electrons are large polarons with a mobility of 20 cm$^2$/V sec. We have no information from the band structure calculations on the effective masses $m^*$ of the carriers, but from naive band curvature arguments electrons in the bottom of the conduction band have $m^* < m_e^*$, while for holes in the top of the valence band $m^* > m_e^*$ due to the very flat bands. The polaron effective mass $m^{**} = 1.75 m_e^*$. In the rest of this work the band effective mass will be taken to be $m_e^*$.

6.4.2 Thermal versus Optical Band Gaps

The other major effect of the lattice on the high temperature electronic properties is the reduction of the carrier creation energy due to lattice stabilization of the carrier. This is embodied in the difference between the thermal and optical band gap energies. In covalent materials which do not form polarons, the optical gap corresponds to direct or vertical transitions in the band structure, while the thermal gap corresponds to phonon-assisted indirect transitions. In ionic materials any assumed equivalence of optical and direct gaps, and thermal and indirect gaps is not correct. In materials with localized electronic
structures, the optical gap corresponds to the energy to create the band electron, while the thermal gap is the energy required to create the polaron directly. If we define \( \Delta \) (analogous to the Stokes Shift) to be the difference between the optical and thermal gap energies, then \( \Delta \) is the lattice stabilization energy imparted by the lattice to the band carrier, forming the polaron. The Franck Condon Model then allows us to show the relationship between optical and thermal gaps, and lattice relaxation and \( \Delta \) as in figure 6.1. In the fast optical process, \( E_0^o \) is required to create the band electron, which then relaxes to the polaron, while in the slow thermal case, the lattice relaxes during the time period of the excitation requiring only \( E_t^g \) to create the polaron directly. From experimental data Kroger estimated \( \Delta \) for Al\(_2\)O\(_3\) to be 0.65 eV +/- 2.1 eV while Colbourn theoretically calculated the value of 2.8 eV.

In an attempt to determine the true thermal carrier creation energy, which encompasses both \( \beta \) and \( \Delta \), it is useful to consider Colbourn's calculation of \( \Delta \) for Al\(_2\)O\(_3\). In Colbourn's \( T = 0 \) K calculation, the causes of \( \Delta \) are electron shell relaxation after excitation for large polarons, and additionally, atom core motion for the small polaron. Therefore one can see that this calculation is very different from the temperature dependent electronic structure calculations. It serves to demonstrate the differences between the causes of \( \beta \), which are the averaged thermal bond length changes leading to increased orbital overlap and energy level shifts and \( \Delta \) which is due to localized lattice relaxation around the carrier, after excitation, leading to an overall reduction in the thermal carrier creation energy. Colbourn found that \( \Delta \) was 2.8 eV for band to band transitions, and 1.2 eV for optical versus thermal excitation of Ti\(^{3+}\) to Ti\(^{4+}\). In the paper they compared their value of a thermal gap.
(9.5 - 2.8 = 6.7 eV) to a value of 6.5 to 7 eV computed by Kroger as the gap of Al₂O₃ at 1600 K, and stated that there was agreement. This was in error, because what they compared was E₉ₒ(T=0K) - Δ to E₉ₒ(T=0K) - βT - Δ; they neglected the β term. Instead, considering both β and Δ, the high temperature carrier creation energy is given by E₉ₜ(T) = E₉ₒ(T=0K) - βT - Δ. Therefore using their value of Δ, and the value of E₉ₒ(T=0K) and β from this work, E₉ₜ(T=1500K) = 4.35 eV. This value of the carrier creation energy will be evaluated in the next section.

6.5 Intrinsic Electronic Conductivity in Al₂O₃

How can the temperature dependence of the electronic structure of Al₂O₃ be used to understand alumina's high temperature electronic conductivity? First the role of E₉(T) in controlling σ will be determined to illustrate the roles of E₉(T=0K), β and Δ. Then the other terms that are controlling - the mobility (μ) terms - will be discussed. Finally the σ data and the E₉(T) values will be used to extract information on the mobility of electronic carriers in Al₂O₃.

6.5.1 Factors That Control Conductivity

6.5.1.1 Carrier Concentration
To determine the role of \( E_g(T) \), consider the electronic conductivity \( \sigma_{elec}(T) \) from 1400 to 1600 °C, where \( \sigma_{elec} = n\mu_e + p\mu_h \).

It is easier to consider the product, \( \sigma_e \sigma_h \).

\[
\sigma_e \sigma_h = n^2 p^2 \mu_e \mu_h
\]

\[
= \mu_e \mu_h q^2 N_c N_v e^{-E_g/kT}
\]

where setting \( m^* = m^* = m_e \)

then \( N_c N_v = (2\pi m_e k/\hbar^2)^3 T^3 \)

and putting in

\[
E_g(T) = E_g^0(T=0K) - \beta T - \gamma T^2 - \Delta
\]

one arrives at

\[
\frac{(\sigma_e \sigma_h)}{T^3} = \frac{\mu_e \mu_h q^2 (2\pi m_e k/\hbar^2)^3}{e^\beta/k e^{\gamma T/k} e^{-(E_g - \Delta)/kT}}
\]

Plotting this function as \( \log(\sigma_e \sigma_h/T^3) \) versus \( 1/T \) one can extract useful information about the carrier creation energy. The first thing to note is that the activation energy for carrier creation, as given by the slope of the curve, is \( E_{g}^t(T=0K) \) the thermal band gap at zero K, or \( E_{g}^o(T=0K) - \Delta \) the zero K optical gap minus \( \Delta \).

The effect of the nonlinear term \( \gamma \) in the temperature dependence of the band gap is considered next. The only way that an Arrenhius plot of the conductivity can have noticeable curvature is due to a nonlinear term. The linear \( \beta \) term factors out front as a temperature independent term. The \( \gamma \) term does give a temperature dependent exponential term, but in the case of Al2O3 this term is too small to give noticeable curvature. Using the results of the nonlinear analysis of the 9 eV peak, the change in \( \gamma T^2 \) from 1400 to 1600 °C is only 0.04 eV, much too small in comparison to the experimental inaccuracies to be observed as curvature. Therefore
due to the insignificant $T^2$ component of $E_g(T)$, one can say that the conductivity should plot as a straight line in this type of analysis. As stated earlier, the nonlinear analysis of $E_g(T)$ is rejected, and only a linear dependence is found for $E_g(T)$.

The true effect of $E_g(T)$ is due to the $\beta$ term and is not observed in the slope (or $E_a^{crea}$) of the conductivity plot but instead in the pre-exponential term. $E_\beta/k$ equals $3.5 \times 10^5$, a large factor and very sensitive to the value of $\beta$. $\beta$'s role, in the pre-exponential, is similar to that of the carrier mobility terms. A one third change in the value of $\beta$ used leads to 2 orders of magnitude change in the value of the exponential factor, making extraction of meaningful mobility information very difficult.

Good values for $E_0^g(T=0K)$ and $\beta$ are presented in this work. The value of $\Lambda$ is not confirmed; it is calculated to be 2.8 eV, and estimated to be .65 eV. Values are lacking for the effective masses but that should have only a small effect. The only modeling assumptions employed up to this point are in the use of semiconductor theory, which is well accepted, to determine the number of carriers created. There has been no need to make any choices between competing models.

6.5.1.2 Carrier Mobility

There is a lot of controversy about $\mu_e$ and $\mu_h$. Measured values of $\mu$ for electrons suggest large polarons but no information exists to determine whether holes are large polarons or small polarons. Since we lack hard experimental evidence of the mobility of electronic carriers, it
seems fruitful to use data and \( E_g(T) \) data to elucidate the carrier mobilities.

To extract information on mobility we must invoke models, which are not necessarily well-founded, for the polaron mobilities. In the case of the holes, the models for small and large polaron mobility show very different functional dependencies, while for the electrons, the large polaron model does not demonstrate the observed temperature dependence. The large polaron mobility is given by a fundamental equation that depends on \( \Theta_D \), \( \omega_o \), \( m^* \), and \( a \). The first two constants are not well-known and strongly affect \( \mu \), while the third is unknown and the last is at least agreed upon. For the small polaron mobility, no fundamental equation exists, only a phenomenological type equation that fits to data, and depends on the fitted value of \( \mu_{sp}^o \) and \( E_{hop} \). We can assume a large polaron model for electrons, and then we can derive the parameters for hole mobility.

In summary, the high temperature electronic conductivity is controlled by carrier concentration and mobility terms. The carrier concentration terms are controlled by \( E_g^0 \), \( \beta \), \( \Delta \), \( m_e^* \) and \( m_h^* \). The mobility terms are controlled by \( \Theta_D \), \( \omega_o \), \( a \), \( \mu_e \), \( \mu_h \), \( m_e^* \), and \( m_h^* \). Most of these parameters are not well-known at the present time but progress is being made.

6.5.2 Calculation of \( \sigma_e^{mg} \)

Using the available information, an attempt will be made to calculated \( \sigma \) from 1400 to 1600 °C in Al\(_2\)O\(_3\) to compare to the data of
Kroger on nonequilibrium titration measurements of Ti doped sapphire titrated with hydrogen. These measurements showed the conductivity minimum, or compensation point, as a function of temperature from 1400 to 1600 °C (see figure 6.2). The compensation point can then be plotted versus 1/T to give the total activation energy for conductivity (see figure 6.3). Since data and a model exist for $\mu_e$, the electronic conductivity with the Fermi energy at mid-gap $\sigma_e^{mg}$ will be calculated. This may not correspond to $\sigma$ at the compensation point if $\mu_e$ does not equal $\mu_h$. In other words, at the compensation point, the Fermi energy is not necessarily mid-gap.

For the calculation of the carrier concentration, both $\Delta = 0$ eV and $\Delta = 2.8$ eV are used. These correspond to thermal gaps of 7.15 eV and 4.35 eV at 1500 °C. For the electron mobility values of $\Theta_D$ of 695 K and 1000 K, with the related values of $\omega_o$, are used. With this spread in the Debye temperature, the calculated mobilities were 12.1 or 1.6 cm$^2$/V sec at 1500 °C, in the same range as the experimental values. The values of $\sigma_e^{mg}$ for this range of input parameters are given below.

<table>
<thead>
<tr>
<th>$\Theta_D$ (K)</th>
<th>$\sigma_e^{mg}$ ((\Omega \text{cm})^{-1})</th>
<th>$\Delta = 0$ eV</th>
<th>$\Delta = 2.8$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400°C</td>
<td>8x10^{-9} 1x10^{-9} 1x10^{-4} 1x10^{-5}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500°C</td>
<td>5x10^{-8} 7x10^{-9} 4x10^{-4} 5x10^{-5}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1600°C</td>
<td>3x10^{-7} 4x10^{-8} 1x10^{-3} 2x10^{-4}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.5.2.1 Evaluation of $\Delta$

Comparing the calculated values of $\sigma_e^{mg}$ computed using $\Delta = 2.8$ eV to the measured values of Kroger ($\sigma_{\text{min}}((\Omega\text{cm})^{-1}) = 5 \times 10^{-12}$ (1400°C), $2 \times 10^{-10}$ (1600°C)), one sees that the calculated values are 7 or 8 orders of magnitude too high. If we make an extreme case calculation where $\mu_h = 0$, then the creation energy for electrons will be $E_g$, and the Fermi energy will lie at the top of the valence band. In this case, with $\Delta = 2.8$ eV, the calculated values decrease to $10^{-11}$ to $10^{-10}$ (Ωcm)$^{-1}$, which are still larger than the measured values. The assumption that $\mu_h = 0$ is obviously extreme, but even then the $\sigma$ values cannot be brought into agreement. Therefore it seems that the value of 2.8 eV for $\Delta$, the difference between the optical and thermal gap energies, is too large, and it cannot be used to fit the available data. From now on in this work $\Delta$ will be assumed to be zero for lack of any reasonable estimate.

6.5.2.2 Derivation of $\mu_h/\mu_e$

The $\sigma_{\text{min}}$ measured by Kroger is determined by the condition $\sigma_e = \sigma_h$. This will correspond to $\sigma_e^{mg}$ only if $\mu_e = \mu_h$. If $\mu_h < \mu_e$ then $E_F < E_g/2$, i.e., a larger number of low mobility holes must be created to balance the (higher) electron conductivity. By comparing the $\sigma_e^{mg}$ values to $\sigma_{\text{min}}$, the value of the conductivity at the compensation point, we can see that they do not agree. Depending on the choice of $\theta_D$, there are 2 to 3 orders of magnitude of disagreement. The value of $\sigma_e^{mg}$ is too high, therefore the hole mobilities must be lower than the electron mobilities, as is
expected from the literature. The degree of Fermi level lowering is directly controlled by the ratio of the hole and electron mobilities, and is manifested by the difference between $\sigma_e^{mg}$ and $\sigma_{\text{min}}$. The mobility ratio and amount of Fermi level lowering are given by the following:

$$\frac{\mu_h}{\mu_e} = \left(\frac{\sigma_e}{\sigma_e^{mg}}\right)^2$$

$$(E_g/2) - E_F\ = \ -.5kT \ln \left(\frac{\mu_h}{\mu_e}\right).$$

For $\Theta_D = 695 \text{ K}$, the mobility ratios at the three temperatures are on the order of $10^{-7}$ while for $\Theta_D = 1000 \text{ K}$, they are on the order of $10^{-5}$. Since these calculations are admittedly crude, and the value of $10^{-5}$ seems more reasonable, the results for $\Theta_D = 1000 \text{ K}$ (assumed) will be shown.

| TABLE 6.2 Calculated Mobility Ratios and Fermi Energy Lowering |
|-----------------|---------|---------|---------|
| Temp°C          | 1400    | 1500    | 1600    |
| $\mu_h/\mu_e$   | $1.8 \times 10^{-5}$ | $3 \times 10^{-5}$ | $4.7 \times 10^{-5}$ |
| $E_g/2 - E_F^{(eV)}$ | .788   | .796   | .805   |

These mobility ratios, even considering the inaccuracies in the calculations, strongly suggest that the holes are small polarons with a thermally activated mobility. This is in agreement with information from the literature. In addition the degree of the Fermi level shift, on the order of one volt, is consistent with one's feeling that in the large band gap ionic materials, it is very difficult to shift the Fermi level far
from mid-gap. Upon evaluating $\mu_h(T)$ one can derive the activation energy for hopping which is 1.4 eV. This is obviously just the difference between the 10.5 eV activation energy Kroger observed in his measurements and the 9.1 eV $T = 0$ K band gap of $\text{Al}_2\text{O}_3$. Therefore the added slope observed in the conductivity measurements is the activation energy for hopping of the holes.

A check on this result may be gotten by deriving the mobility product contained in the intercept of Kroger's data using no assumed values of $E_g$. Assuming that the electrons fit a large polaron model, and that the holes a small polaron model, we can plot the data according to the following:

$$\alpha_{\text{min}}/T^{1/2} = 1540(\mu_{sp}^{0} \mu_{1p}^{0}) \times e^{- (E_g + E_h)/2kT}.$$  

The intercept of the log versus $1/T$ curve gives a mobility product which can be used, with a suitable $\mu_e$ values, to derive values of $\mu_h$. These are found to be .4 and 3 cm$^2$/V sec. There is a contradiction here, as these values do not support the previously derived mobility ratios, and are on the borderline of small to large polaron mobilities.

6.5.2.3 Summary

These calculations have been performed to serve as an overview of our understanding of the electronic conductivity of $\text{Al}_2\text{O}_3$. They have not been expected to provide exact numbers for the mobilities of carriers but
instead to determine plausible conclusions. Knowledge of many of the fundamental parameters is lacking, making further numerical analysis more difficult. More information is needed about the mobility of the electronic carriers. The calculation does serve to show a reasonable approach to evaluate conductivity results. This is: to use the carrier concentration and conductivity, both reasonably well founded at present, to derive information on the carrier mobility. More information is required to definitively understand conductivity, but the knowledge of $\beta$ and $E_g (T=0K)$ allows us to know the carrier concentration and increases our understanding of electronic conductivity in this material.
FIGURE 6.1 Relationship between optical band gap $E_g$, thermal band gap $E_g^t$, and lattice stabilization $\Delta$ energies.

FIGURE 6.2 Electronic conductivity versus partial pressure of H$_2$ showing the electronic and ionic compensation points. From Kroger, reference 104.

FIGURE 6.3 Compensation point conductivity plotted versus $1/T$ to give the activation energy for conductivity. From Kroger, reference 104.
Chapter 7

Conclusions

A High Temperature Vacuum Ultraviolet Spectrophotometer has been built that is capable of measuring the reflectance and transmittance of samples from 6 eV to 15 eV (210 nm to 85 nm) in the VUV on samples heated without contamination from room temperature up to 1100 °C. The temperature dependence of the electronic structure of single crystal Al₂O₃ has been studied with this facility.

7.1 Reflectivity Measurements at Room Temperature

At room temperature, the reflectivity shows three main features: a 9 eV exciton peak, superimposed on a 9 eV absorption edge, and, at higher energy, a 13 eV peak. The 13 eV peak shows features that depend on the orientation of the sample. A doublet peak appears for light incident parallel to the c axis, while a peak and a shoulder are observed for light perpendicular to the c axis. The absorption edge is due to transitions to the Al 3s sub-band of the conduction band, while the main peak at 13 eV corresponds to transitions to the Al 3p sub-band of the conduction band. The valence band has a lower lying Al-O sub-band, with the top of the
valence band being of 0 2p character. Transmission measurements show the absorption edge to lie at 8.8 eV at room temperature. This corresponds to a direct (8.8 eV) band gap at room temperature. This measurement provides no information about the nature (direct or indirect) of the minimum band gap of the material. These results are in agreement with band structure and atomic cluster models of the T = 0 K electronic structure of Al₂O₃.

7.2 Temperature Dependent Reflectivity Measurements

With increasing temperature the features in the reflectivity shift to lower energies. These shifts are due to spreading of the electronic energy level bands and shifts of the band centers. This may be explained either from the electron-phonon interaction, or as arising from the superimposed effects of thermal expansion and atomic vibrations on the instantaneous bond lengths in the material. It was found that the different sub-bands have different temperature dependencies. Over the temperature range studied, (25 °C to 1100 °C), the shift was found to be linear with temperature, second order terms were negligible. The experimentally determined values of the linear temperature coefficient β, expressed in eV/K are:

\[ \beta \ (\text{Al} \ 3s \ \text{abs. edge}) = 1.1 \times 10^{-3} \ \text{eV/K} \quad +/\ - \ 1 \times 10^{-4} \]
\[ \beta \ (9 \ \text{eV Exciton Peak}) = 1.0 \times 10^{-3} \ \text{eV/K} \quad +/\ - \ 3 \times 10^{-5} \]
\[ \beta \ (13 \ \text{eV Al}3p \ \text{Peak}) = 7 \times 10^{-4} \ \text{eV/K} \quad +/\ - \ 4 \times 10^{-5} \]
7.3 High Temperature Electronic Structure

To understand the high temperature electronic structure of $\text{Al}_2\text{O}_3$, the role of the lattice in determining the properties of the electronic carriers must be considered. The interaction of the lattice with the electronic carriers can lower their creation energy and affect their mobility. Mobility measurements and the value of the polaron coupling constant point to the formation of polarons which are electronic carriers surrounded by a stabilizing field due to lattice relaxation. The degree of electron-phonon coupling determines whether large polarons with a band type mobility or small polarons with a thermally activated mobility are formed. The lattice stabilization imparted to the carrier also determines the difference ($\Delta$) between the energies of the optical gap and the thermal gap. The energies reported in this work correspond to optical energies that create carriers without lattice relaxation. In an attempt to determine the thermal band gap energy a theoretically calculated (2.8 eV) value of $\Delta$ was used in an analysis of conductivity measurements. This led to conductivities orders of magnitude larger than observed in $\text{Al}_2\text{O}_3$. No reasonable values exist for $\Delta$.

The room temperature band gap extrapolated to $T = 0$ K, using the measured temperature coefficients, gives 9.1 eV for the $T = 0$ K apparent optical band gap of $\text{Al}_2\text{O}_3$. Ignoring the contribution of $\Delta$, this is the carrier creation energy that will appear in the exponential factor of high
temperature conductivity equations. The carrier creation energy at 1500 °C is 7.15 eV, as determined by extrapolation from these measurements.

7.4 Implications for Conductivity

Intrinsic electronic conductivity in Al₂O₃ is controlled by the carrier concentration and the carrier mobility. Previously, theoretical models for the carrier mobility, which assume the carrier type (large or small polaron) and the scattering mechanism (thermal or impurity), were used with conductivity measurements to determine the carrier creation energy. Electron mobilities have been deduced from a small number of mobility measurements, but the mobility of holes has yet to be observed. Due to the large number of carrier mobility models and the lack of experimental data, it is misguided to analyze conductivity measurements in Al₂O₃ assuming a specific mobility model and thereby to deduce the carrier creation energy. From the present work we know the contribution of the carrier creation energy (the band gap) to the activation energy for electronic conductivity, and the value of the band gap temperature dependence β which due to its linear character appears in the pre-exponential term of the conductivity equation. Therefore, this information has been used with the conductivity results of Kroger to derive insight into the electron and hole mobility terms. The mobility of electrons is found to be much higher than hole mobilities, in agreement with mobility measurements. We tentatively conclude that the electrons form large polarons with a band-type mobility while the holes form small
polarons with a thermally-activated mobility. This could be confirmed by high temperature mobility measurements.
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103. The author acknowledges helpful discussions with R. M. Cannon (Berkeley), D. Monroe (M.I.T.) and H. L. Tuller (M.I.T.).


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