This dissertation has been
microfilmed exactly as received 65-13,910

KELLY, Paul James, 1934-
STUDIES OF THE ELECTRICAL ENERGY STORAGE
AND LOSS MECHANISMS IN ALUMINUM OXIDE.

Carleton University, Ph.D., 1965
Engineering, electrical

University Microfilms, Inc., Ann Arbor, Michigan

STUDIES OF THE ELECTRICAL ENERGY STORAGE
AND LOSS MECHANISMS IN ALUMINUM OXIDE

by

PAUL JAMES KELLY, B.Sc., M.Sc.

A thesis submitted to the Faculty of
Graduate Studies in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Carleton University

Ottawa, Ontario

June, 1965

The undersigned hereby recommend to the Faculty of
Graduate Studies acceptance of this thesis, submitted by
Paul James Kelly, B.Sc., M.Sc., in partial fulfilment of
the requirements for the degree of Doctor of Philosophy.

.....*E. P. Hughes*.....
Chairman, Department of Physics

.....*W. H. Gosh*.....
.....*M. J. Saulis*.....
Supervisor

.....*J. M. Simpson*.....
External Examiner

To my wife

ABSTRACT

The ac electrical conductivity of dense sintered Al_2O_3 and MgO-doped Al_2O_3 specimens was determined by 3-terminal, guarded, measurements at various temperatures in the range 20°C to 1020°C and for frequencies of the applied field in the range 10^2 to 10^5 cps. It was found that Ohm's law was valid for temperatures greater than about 200°C , while at lower temperatures the conductivity depended slightly on the applied voltage, between 1 and 100 volts. The results indicate that the ac response is a complex function of the porosity in the case of the 6N Al_2O_3 specimens and of the separate spinel phase in the case of MgO-doped Al_2O_3 specimens. The frequency dependence of the results could not be readily interpreted. The dielectric constants and losses of the specimens were determined with an accuracy of 3.4% for $\tan \delta \geq 0.1$. Results obtained with fired Pt paste electrodes and bonded Pt foil electrodes agree within experimental error. Two terminal results on a 6N Al_2O_3 specimen indicate the presence of a high conductivity surface effect.

Thermal glow curves were obtained from the same specimens after irradiation with 5×10^5 R of Co^{60} γ -rays. A new method of glow curve analysis was used to analyze the curves. In general, it is shown that second order theory provides a better fit to the experimental curves than first order theory, which proved consistent with the results of decay studies. Emission studies in the wavelength region 3000 Å to 6000 Å indicate that the operative luminous centers are at 3.7 eV in the 6N Al_2O_3 and at 2.4 eV and 3.4 eV, in the MgO-doped Al_2O_3 specimens. The results of luminescence studies are interpreted as the thermal release of electrons from traps filled by γ -irradiation. Characteristic

trap depths are derived from glow curve analysis. The method of analysis proposed shows that the thermal trap depth energy, E , is related to the temperature, T^* , at which the intensity is a maximum and the temperature, T' , at which the intensity first reaches one half of its maximum value, by the relation

$$E = \alpha \frac{k T^* T'}{T^* - T'}$$

where k = Boltzmann constant

and $\alpha = 1.46$ for first order theory and $\alpha = 1.70$ for second order theory: provided $E/kT > 17$ the relation is valid to $\pm 5\%$ for first or second order theory.

ACKNOWLEDGEMENTS

I wish to thank my supervisor, Dr. M. J. Laubitz, for his direction throughout this work. I wish to express my appreciation to Dr. J. Hart for suggesting the electrical conductivity studies of alumina.

I also thank Dr. P. J. Hickson for the considerable length of time donated to writing, testing, and running computer programs. I am indebted to Dr. F. Lipsett for the use of his grating monochromator as well as for many stimulating discussions.

I thank the members of staff whose frequent discussions and criticism have helped greatly in the development of this project. Their willingness to discuss ideas involved in this work was highly appreciated.

Mr. A. Raffler and Mr. K. Hafner contributed a great deal to the construction of the high temperature cell and thermoluminescence apparatus.

I wish to thank Mr. P. Donovan for polishing the alumina specimens and Mr. W. Shields for every co-operation with the use of the N.R.C. specimen fabrication facilities.

I am grateful to the National Research Council for the granting of their scholarships.

TABLE OF CONTENTS

ABSTRACT	iii
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vi
LIST OF ILLUSTRATIONS	viii
LIST OF TABLES	xi
SECTION I PURPOSE OF THE PRESENT STUDIES	1
1:1 Introduction	1
1:2 General Considerations	1
1:3 Review of Previous Work	3
SECTION II ELECTRICAL CONDUCTIVITY MEASUREMENTS	18
2:1 Introduction	18
2:2 Apparatus and Specimens for Electrical Conductivity Measurements	20
2:3 Experimental Procedure	51
2:4 Results	59
2:5 Discussion of Results	71
SECTION III THERMOLUMINESCENCE IN ALUMINUM OXIDE	84
3:1 Introduction	84
3:2 A Model for Thermoluminescence in Aluminum Oxide	84
3:3 The Analysis of Glow Curves	87
3:4 Purpose of the Study of Thermoluminescence in Al_2O_3	94
3:5 The Apparatus and Specimens Used for Luminescence Studies	95
3:6 Experimental Procedure	100
3:7 Results	102
3:8 Discussion of Results	112
3:9 Proposed Model for Thermoluminescence in Aluminum Oxide	139
SECTION IV CONCLUSIONS	146
REFERENCES	148
APPENDIX II-1 Two terminal measurements	151
APPENDIX II-2 Calibration of the G.R. 1650 capacitance bridge	161
APPENDIX II-3 Tabulated results of 3-terminal electrical conductivity measurements	166
APPENDIX II-4 An estimate of the accuracy of conductivity measurements	183
APPENDIX II-5 Summary of additional 3-terminal measurements with specimen C4A (1.0% MgO) using pure platinum electrodes	187
APPENDIX III-1 Error in the trap depth energy (equation 3.7) due to overlap effects	188
APPENDIX III-2 The error in the predicted first order decay time constant due to an error in the temperature	189

APPENDIX III-3	Tabulated results of decay studies	190
APPENDIX III-4	Program for interpolation	194
APPENDIX III-5	Calculation of the number of luminous centers and an estimate of the number of traps	196
APPENDIX III-6	A calculation of the error in the trap depth energy; (a) due to errors in analysis and (b) due to experimental errors	198
APPENDIX III-7	Derivation of the Randall and Wilkins' Relation	201
APPENDIX III-8	Summary of Emission Data	202
VITA		203

LIST OF ILLUSTRATIONS

Figure 1.1.	A typical plot of the electrical conductivity of Al_2O_3 , pre-1960	5
Figure 1.2.	Simple Wilson semiconductor model	7
Figure 2.1.	Electrode geometry for a disk specimen	19
Figure 2.2.	Heater elements and radiation screens	21
Figure 2.3.	Experimental set-up for electrical conductivity measurements	22
Figure 2.4.	A typical firing cycle used for sample preparation	24
Figure 2.5.	Schematic illustration of the 3-terminal cell used from measuring electrical conductivity	25
Figure 2.6.	Rubber mold assembly	36
Figure 2.7.	A specimen and its equivalent 3-terminal representation	46
Figure 2.8.	The basic bridge circuit	47
Figure 2.9.	The absolute accuracy of Tan δ readings with the G.R. 1650-A Capacitance measuring assembly	50
Figure 2.10.	Schematic illustration of the experimental set-up for electrical conductivity studies	52
Figure 2.11.	A modified version of the 3-terminal cell	58
Figure 2.12.	Summary of electrical conductivity results	61
Figure 2.14.	A comparison of the electrical conductivity results of MgO doped Al_2O_3 specimens	63
Figure 2.15.	The dielectric constant of pure Al_2O_3 and MgO doped Al_2O_3 specimens as a function of frequency at selected temperatures	64
Figure 2.16.	The dielectric constant of pure Al_2O_3 and MgO doped Al_2O_3 specimens as a function of temperature at selected frequencies	65
Figure 2.17.	The typical behaviour of the dielectric loss factor as a function of frequency at various temperatures	67
Figure 2.18.	The typical behaviour of the dielectric loss factor as a function of temperature	68

Figure 2.19.	Comparison of 2-terminal and 3-terminal ac electrical conductivity results obtained from one and the same specimen of 6N Al_2O_3 (C2A)	70
Figure 2.20.	Comparison of electrical conductivity measurements on a 1% MgO doped Al_2O_3 specimen using different types of electrodes	72
Figure 2.21.	The typical behaviour of dissipation factor results as a function of temperature	73
Figure 2.22.	The dissipation factor as a function of temperature at 10^5 cps resolved into two processes	75
Figure 2.23.	The dissipation factor of a pure Al_2O_3 specimen	78
Figure 3.1.	The model proposed for thermoluminescence in Al_2O_3 ..	85
Figure 3.2.	The application of saw-tooth annealing to theoretical first order glow curves	92
Figure 3.3.	(A) Typical heating rate used in thermoluminescence and emission studies. (B) Correction factors for emission apparatus (supplied by Dr. F. Lipsetz)	99
Figure 3.4.	Schematic illustration of the apparatus used for thermoluminescence studies	97
Figure 3.5.	Typical results from emission studies	104
Figure 3.6.	Basic optical system	101
Figure 3.7.	A typical glow curve obtained from a γ -irradiated 6N Al_2O_3 specimen (solid line)	106
Figure 3.8.	Typical glow curves obtained from γ -irradiated 6N Al_2O_3 specimens (solid lines)	107
Figure 3.9.	Typical glow curve from a 0.01% MgO doped Al_2O_3 specimen (solid line)	108
Figure 3.10.	Typical glow curve from a 0.1% MgO doped Al_2O_3 specimen (solid line)	109
Figure 3.11.	Typical glow curve from a 1.0% MgO doped Al_2O_3 specimen (solid line)	110
Figure 3.12.	Typical glow curves obtained from a Linde sapphire (A) and from specimens of Linde micropolishing Al_2O_3 sintered by N.R.C. (B)	111
Figure 3.14.	Energy level scheme for (A) 6N Al_2O_3 and (B) 0.1% MgO doped Al_2O_3	142

Figure II-1.	(A) Experimental arrangement for 2-terminal measurements. (B) The series and parallel representations of sample and cell	152
Figure II-2.	(A) Experimental arrangement for 2-terminal measurements of cell capacitance. (B) The series and parallel representations of spacers and cell	153
Figure II-3.	Equivalent circuit of the dissipation-factor standard	161
Figure II-4.	(A) Arrangement for the measurement of $C_d + C_g$. (B) Arrangement for the measurement of a constructed dissipation-factor standard.....	163
Figure III-1.	Illustration of the labelling system for interpolation program	194

- - - -

LIST OF TABLES

Table 2.1	Diffraction Pattern Data of Converted Cominco 6N Al_2O_3 Compared with Literature Values of Alpha Al_2O_3	32
Table 2.3	Impurity Content of Test Specimens (ppm)	34
Table 2.4	Summary of Sintering Data	39
Table 2.5	X-ray Diffraction Peak Data from a 1% MgO doped Al_2O_3 Specimen Compared with Literature Data for Al_2O_3 , MgO and Mg Al_2O_4	40
Table 2.6	Sample Dimensions at Room Temperature	43
Table 2.7	Dimensions of Platinum Foil Electrodes	57
Table 3.1	Specimens used for Thermoluminescence Studies	96
Table 3.3	Computed Results of the Exact Solutions of Equations 3.10 and 3.16 Expressed in Terms of the Parameter $\alpha = E(T^*-T')/kT^*T'$	116
	(A) 1st Order Theory	117
	(B) 2nd Order Theory	118
Table 3.4	First Order Glow Curve Parameters	124
Table 3.5	Second Order Glow Curve Parameters	125
Table II-1	Results of 2-terminal Measurements of the ac Conductivity of a Specimen of 6N Al_2O_3 (C2A)	157
	(A) With the sample in the cell	157
	(B) With the sample out; with 3 ruby spacers in	158
	(C) Derived parameters	159

- - SECTION I

PURPOSE OF THE PRESENT STUDIES

1:1 Introduction:

The electrical properties of Al_2O_3 are of interest for several reasons. For one thing Al_2O_3 is one of the most stable chemical compounds to a temperature of approximately 2000°C. For another, Al_2O_3 has a specific electrical conductivity of less than $10^{-10} \Omega^{-1} \text{cm}^{-1}$ at room temperature. Because of these properties, Al_2O_3 has been used as an electrical insulating material where ordinary organic insulators are unstable. The precise specific conductivity and the mechanisms of electrical conduction of Al_2O_3 are not completely known.

It must be borne in mind that any discussion of the theoretical aspects of electrical conduction when applied to a system like Al_2O_3 will be complicated by the very nature of the system as well as by the many conflicting reports of electrical conductivity measurements by various workers on rather low purity Al_2O_3 . Consequently in attempting to discuss the reasons for: the choice of system investigated, the choice of method and the choice of added impurity, an arbitrary limit has been set on the discussion of previous work. Except for those results of previous work which can be directly compared with the results of the present studies, only the common features of previous work will be discussed.

1:2 General Considerations:

Interest in the precise measurement of the specific electrical conductivity of Al_2O_3 is due to the many discrepancies in previously reported measurements. Some of the discrepancies can be attributed to the lack of knowledge concerning the system Al_2O_3 .

Al_2O_3 has a close-packed hexagonal structure with a c/a ratio = 1.366.¹ The specific gravity of single crystal Al_2O_3 (sapphire) is 3.986 and its melting point is approximately 2040°C. The static dielectric constant is about 10.0 and the index of refraction is roughly 2.0. The electrical conductivity is generally a function of heat treatment of the sample. There have been no reports of Hall Effect measurements.

The optical properties have been reported by a number of authors.^{2,3,4} From absorption studies the optical band gap of Al_2O_3 is between 8 ev and 9 ev. Irradiation with X-rays or U.V. light leads to new absorption bands which can be completely bleached by heating to high enough temperatures. There have been no reports of photoconductivity, but there has been a report of the observation of Kramer's effect.⁵ Characteristic glow curves observed from γ -irradiated Al_2O_3 have been related to lattice defects and impurities.⁶

Oxide semi-conductors, such as Al_2O_3 , differ from the elemental semi-conductors, Si and Ge, in several respects. The most important is the high melting point which increases the difficulty of obtaining specimens of high purity. A related effect is the high concentration of defects frozen into specimens fabricated at high temperatures. The formation of an oxygen vacancy, for example, is a source of two electrons having an activation energy less than that required to raise an electron to the conduction band in the stoichiometric material. Thus, the transport properties of Al_2O_3 are altered by departures from stoichiometry just as they are by the presence of impurities.

The phenomenon of electrical conduction in oxides has a strong theoretical foundation only for those which fall into either of the

two categories: ionic or covalent bonded crystals. Unfortunately, the bond type of Al_2O_3 is not known precisely.

If the covalent contribution to bonding is small as is the case for the alkali-halides, a quantitative estimate of its effect can be made. When, however, this is not the case, then it is usual to use certain criteria of covalency. For example: since the optical and static dielectric constants of covalent bonded crystals are almost equal whereas the static dielectric constant of highly ionic crystals is considerably greater than the optical dielectric constant then the values for sapphire (quoted previously) are highly indicative of a major ionic contribution to the total bonding.

On the other hand, the low solubility of Al_2O_3 in polar solvents such as water is taken as evidence for a considerable covalent contribution to the Al-O bond.

The application of Pauling's criteria⁷ to Al_2O_3 indicates that the total bonding is roughly sixty-five percent ionic and thirty-five percent covalent. Thus on the basis of bonding alone, it is possible to have both ionic and electronic contributions to the total conductivity. As far as the electronic processes are concerned, they are described by semi-conductor models whether the bonding is ionic or covalent. Basically ionic conduction is a diffusion like process where mass transport accompanies charge transport with the application of an electric field while electronic conduction does not involve mass transport.

1:3 Review of Previous Work:

A review of the work on electrical conductivity of Al_2O_3 previous to 1960 has been given by Cohen⁸ and by Kelly.⁹ Work previous to 1960 dealt for the most part with Al_2O_3 specimens of less

than 99.5% (2N5) Al_2O_3 content. The typical behaviour of electrical conductivity is shown in Figure 1.1 where the one common feature of the results has been stressed, this being the straight line behaviour in certain temperature intervals when the log of the conductivity, σ , is plotted against the reciprocal absolute temperature. The conductivity in these temperature intervals is given by:

$$\sigma = A \exp(-E/kT)$$

however, the reported values of the electrical conductivity, σ , in this equation have varied by 5 to 6 orders of magnitude and the activation energies, E , as calculated from the slope of the lines, have varied from 0.25 ev to 5.5 ev. The activation energies from low temperature results ($< 1000^\circ\text{C}$) are, as a rule, less than the activation energies reported from high temperature results ($> 1000^\circ\text{C}$).

This great dispersion of results may be due to the different *modi operandi* of the experimenters. Reported results have been obtained from ac measurements at various frequencies and dc measurements. Atmosphere control has ranged from air through vacuum to pure hydrogen. The material used for electrodes has varied. The purity of the specimens when at all reported was generally less than 2N5. Specimens have been single crystals or sintered polycrystalline material, the latter introducing the added complication of grain boundaries, and porosity. The porosity of sintered material has varied in large measure due to the differences in sintering time and firing temperature and atmosphere. These complex and confusing results emphasize the need for controlled experiments on high purity Al_2O_3 .

The strikingly common feature of pre-1960 results was usually interpreted in terms of a simple Wilson semi-conductor model as

Figure 1.1. A typical plot of the electrical conductivity of Al_2O_3 , pre-1960.

depicted in Figure 1.2. Consideration of the single-level impurity semi-conductor model as proposed by Wilson¹⁰ leads to an expression for the electrical conductivity as given by:

$$\sigma = \sigma_{01}\exp(-E_d/2kT) + \sigma_{02}\exp(-E_g/2kT) \quad (1.1)$$

where E_d = impurity level activation energy

E_g = characteristic band gap energy

and σ_{01}, σ_{02} = constants of relatively small temperature dependence.

In general $\sigma_{02} \gg \sigma_{01}$ and $E_g > E_d$.

At low temperatures the first exponential term in equation (1.1) dominates the expression.

In this, the extrinsic region, the conductivity is controlled by the type and amount of impurity. However, before 1960 a quantitative estimate of the type and amount of impurity was generally unknown. At higher temperatures, the second exponential factor dominates. In this, the intrinsic region, one measures the band gap energy, a property of the host lattice. In view of the large discrepancies in reported activation energies it is highly questionable whether the intrinsic region has ever been reached.

While the interpretation of electronic processes in Al_2O_3 in terms of the Wilson model is valid it is possible that the common features of pre-1960 results are due to ionic processes. In fact, comparing Al_2O_3 to an Alkali Halide and interpreting the results of electrical conductivity measurements as being due solely to ionic mechanisms, one finds that the common feature of the pre-1960 results are again explained. For, as Lidiard¹¹ shows, the experimental conductivity results obtained with ionic crystals follow, in general, a law of the form:

$$\sigma = \sigma_{01}\exp(-U_1/kT) + \sigma_{02}\exp(-U_2/kT) \quad (1.2)$$

with U_2 generally found to be twice U_1 and $\sigma_{02} \gg \sigma_{01}$.

Figure 1.2. Simple Wilson semiconductor model.

The first exponential term dominates this expression for low temperatures. The second exponential term dominates this expression for high temperatures. In the relatively low temperature region the electrical conductivity, σ , is sensitive to impurity concentrations, defect structure and to grain boundaries in polycrystalline materials, in short, the very same factors which led to the existence of impurity levels in the band model of Figure 1.2. Further, the values of the activation energies, U_1 , and U_2 , commonly measured, are close enough to the range of measured values of E_d and E_g to exclude any possible chance of determining the process of conduction, ionic or electronic, using as a basis the magnitude of the activation energy obtained from a plot of $\text{Log}\sigma$ vs $1/T$. Consequently, the results of electrical conductivity measurements of Al_2O_3 , when the total conductivity is measured, cannot be resolved into the distinct parts of ionic and electronic conduction.

Some experiments with Al_2O_3 have been reported where the ionic contribution to the total conductivity has been measured. The results of diffusion studies by Paladino and Kingery¹² and by Oishi and Kingery¹³ show that in the temperature range of 1670°C to 1905°C less than 5% of the total conductivity is ionic. The results of Laubitz and Matsumura,¹⁴ on the other hand, indicate that for the temperature region 700°C to 1300°C, the conduction process is almost totally ionic. On the basis of these results Al_2O_3 must be considered as a mixed electronic-ionic conductor, with the electronic mechanism predominating at high temperatures ($> 1300^\circ\text{C}$).

Investigations of the electrical conductivity of Al_2O_3 since 1960 have proceeded along two lines. The first and more generally pursued line has seen the use of impure Al_2O_3 still the subject of

measurement with renewed attempts to relate observed conductivity measurements to other transport phenomena, in particular, with thermoelectric power measurements. In these experiments the oxygen partial pressure of the atmosphere surrounding a test specimen has been varied in an attempt to correlate the electrical conductivity with the predicted formation of lattice defects due to a change in oxygen partial pressure. The second approach has seen the use of high purity Al_2O_3 as the subject of investigation. In this second method of approach to the measurement of the electrical conductivity the experimenter is faced with the problem of fabrication.

The one definite advantage in fabricating sintered Al_2O_3 specimens rather than purchasing single crystals is that the purity of the specimens is more easily controlled since a lower temperature ($\leq 1900^\circ\text{C}$) is used in sintering Al_2O_3 than in growing single crystal Al_2O_3 ($\approx 2040^\circ\text{C}$).

To date the results of both approaches have added the following information on the electrical conductivity of Al_2O_3 .

Pappis and Kingery¹⁵ (1961) have shown on the basis of electrical conductivity measurements as a function of oxygen partial pressure of the surrounding atmosphere that 3N Al_2O_3 in both the single crystal and polycrystal forms exhibits p-type semi-conduction at high oxygen partial pressures and n-type semi-conduction at low oxygen partial pressures when the specimen temperature exceeds 1300°C . They ascribe this behaviour to non-stoichiometric composition. In particular the dependence of the conductivity on oxygen partial pressure is consistent with the predicted formation of oxygen ion vacancies or interstitial aluminum ions. The electrical conductivity varied by less than 10% when measured by two and four terminal, ac, and dc, methods.

Laubitz and Matsumura¹⁴ have since confirmed that n-type semi-conduction predominates at high oxygen partial pressures. However, the sign of the thermoelectric power measurements of these latter experimenters while consistent with the type of conduction (n vs p) is the opposite of that obtained by Pappis and Kingery and Harrop and Creamer.¹⁶ This fact is mentioned to emphasize that discrepancies still exist.

Harrop and Creamer (1962) investigated the low voltage dc conductivity of 3N8 sapphire and obtained results similar to Pappis and Kingery. They claimed their results could be related to the iron content of the test specimens. However, Champion¹⁷ (1964) measured the dc electrical conductivity of ruby ($\text{Al}_2\text{O}_3 + \text{Cr}$) and showed that results were independent of the iron content of test specimens. The common feature to the pre-1960 results shows up in the results just quoted, that is in general, the conductivity is described by an expression of the type given in equations (1.1) or (1.2). On the other hand, the results of Atlas et al.¹⁸ do not show this behaviour and their work has followed the approach which utilizes pure Al_2O_3 .

Atlas et al. measured the ac electrical conductivity of sintered Al_2O_3 specimens by a 2-terminal technique over the temperature range 20 to 500°C. Specimens were fabricated by firing in air at about 1900°C. As well as fabricating specimens from 4N5 Al_2O_3 , they made specimens which were doped with various types of metallic impurities, in order to assess the effect of impurities on the electrical conductivity of Al_2O_3 ceramics. Further, some of the pure specimens were fired in different atmospheres to assess the role of intentionally introduced lattice defects on the total conductivity.

The results of this research program were: (1) metallic impurities as well as lattice defects enhance electrical conduction.

and (2) in the temperature interval investigated, the results of electrical conduction did not show straight line behaviour when $\log \sigma$ was plotted against $1/T$. The interpretation of these results, as pointed out by Atlas et al., was complicated by the unknown effects of grain boundaries, as well as by surface effects because sintered specimens were used and 2-terminal ac measurements were carried out. Since the total conductivity was measured one must conclude that either the added metallic impurities enhanced the pool of charged ionic carriers or that impurity levels (as in Figure 1.2) were introduced because of charge compensation effects which invariably introduce donor or acceptor levels into a normally forbidden energy gap (we note that the recent work of Matsumura¹³ gives support to the first of these alternatives - ionic conduction - since his measurements of the ionic contribution, σ_i , to the total conductivity, σ , have yielded transference numbers ($t_i = \sigma_i/\sigma$) of nearly unity for both highly impure Al_2O_3 specimens and very pure (6N) Al_2O_3 specimens).

As well as the surface effects which possibly influenced the results obtained by Atlas et al. there were further complicating factors such as the high porosity of the specimens and the fact that the Al_2O_3 used still contained 50 ppm of metallic impurity ions.

Porosity is usually considered as a separate phase of the material studied. Current theories¹⁹ which treat porosity as a separate phase show that the effect is negligible when the porosity is less than a few percent (the porosity of a specimen being defined as:

$$P = \frac{DT - DM}{DT} \times 100\%$$

where DT = true density of material

and DM = measured density of material).

The porosity of the specimens used by Atlas et al. ranged from 8% to 18%. It is also worthwhile noting that some metallic oxides do not dissolve in Al_2O_3 but, rather, combine with Al_2O_3 to form separate crystalline phases. In particular MgO has been used as a grain growth inhibitor during sintering because of its ability to react with alumina to form the separate spinel phase - $(MgO \cdot Al_2O_3)$. The ac conductivity of mixed crystal-phase ceramics is determined by the dielectric properties of both phases. A review of the work on mixed phase dielectrics has been given by Powers.¹⁹ In general, however, both the shape and distribution of particles of the minority phase are unknown so that even if the dielectric properties of both phases were known it still would not be possible to predict the effect of a second phase on the measured conductivity of a mixed system. Much more spectacular effects are attributed to electrode barriers and in the case of polycrystalline material to the barriers which are produced at grain boundaries. However, in order to understand the effect that boundaries produce it is necessary to discuss the quantities measured in electrical conductivity experiments in more detail.

Up to this point previous results have been considered; we will now discuss how some of these results have been obtained.

In some isolated cases both ac and dc conductivity results have been obtained using the same piece of experimental apparatus; this however, is the exception rather than the rule. The design of a cell for high temperature property measurements is usually restricted to the choice of either ac or dc measurements. Sometimes because of the problems specifically encountered, and sometimes because of the

choice of experimental parameters which will be varied. In particular, on the one hand, for medium frequency (10^{-1} to 10^7 cps) ac measurements the elimination of stray capacitances is a necessity whereas stray loss effects if very small can be tolerated while, on the other hand, even very small leakage current paths must be eliminated in dc measurements; the stray capacitance effect can be tolerated if it is small.

Regardless of whether the ac or dc method is employed, the conductivity can be obtained by three distinct techniques.

The simplest from the point of view of cell design is the two terminal method. Usually a specimen of known simple geometry is chosen, frequently a disk, of thickness t and diameter D . With a known potential difference, ΔV , across the faces of the disk specimen a measurable current, ΔI , will flow provided the resistance, R , of the specimen is not too high. The application of Ohm's law, if valid, yields the conductivity ($\sigma = \frac{\Delta I}{\Delta V} \cdot \frac{t}{\pi D^2}$).

Two terminal measurements are the hardest to interpret because surface effects and electrode-ceramic barrier effects are included in the conductivity results. Surface effects are due to the abrupt departure from lattice periodicity and are dependent on the method of handling and surface finishing utilized. While surface effects always exist in 2-terminal measurements, only surface finishing may be varied in order to assess the magnitude of the effects. This has not been done for Al_2O_3 . Surface effects can be eliminated from the conductivity results by using a 3-terminal technique. This consists essentially of selecting a central volume of the test disk for study. A measuring electrode connected to this central volume is termed the guarded electrode. Another electrode on the same face surrounding the central electrode, but separated from it by a small gap, is

termed the guard electrode or guard ring. By keeping the guard and guarded electrodes at the same potential the conductivity of the selected central volume may be measured. This method excludes gross surface effects, if some necessary precautions are taken (see section II) but the results are still influenced by the electrode-ceramic interface effects. Only Florrio²⁰ and Kelly⁹ have used 3-terminal ac conductivity techniques and the error in the reported measurements of the former was estimated at about 20%. Further, no attempt was made to compare two and three terminal results.

Four terminal measurements remove the effect of electrode-ceramic interfaces from conductivity results. The addition of two potential probes to the 2-terminal electrode system previously defined serves to illustrate the 4-terminal technique. The two probes are positioned in or onto the side of the disk specimen and the potential drop, $\Delta\phi$, across the measured distance, L , (distance between probes) noted. The conductivity ($\sigma = \frac{\Delta\phi}{\Delta I} \cdot \frac{L}{\pi D^2}$) measured in this manner is free from electrode effects. Since the applied potential (ΔV) is known, this method yields some knowledge about the magnitude of the resistance of the electrode barriers. Cohen²¹ showed that about 70% of the applied dc potential dropped across the anode area of single crystal Al_2O_3 at about 1000°C in vacuum, that is, a Platinum electrode-ceramic interface acted as a high resistance. Although 4-terminal measurements are free from these high resistance effects they contain, like 2-terminal measurements, surface effects.

When the conductivity of polycrystalline material is measured, the added complication of grain boundaries is introduced. Since it is expected that quite large departures from periodicity are encountered at grain boundaries, their effect may be likened to the effect of

free surfaces. Furthermore, effects may occur at grain boundaries such as the blocking of charge carriers which also may occur at metallic electrode-ceramic interfaces. These last considerations may well be the cause of the 10% discrepancy that Pappis and Kingery¹⁵ found between two and four terminal techniques. At still lower temperatures the effects may be even more pronounced, in which case, there would be little reason left for employing a 4-terminal measuring technique instead of a 2-terminal measuring technique.

As one progresses from 2-terminal to 3-terminal to 4-terminal techniques, the addition of each electrode, or probe, introduces further complications into the cell design, but removes some complicating factors from the results and therefore, in principle, allows for a simpler interpretation.

The applicability of Ohm's law has been tested infrequently. Cohen²¹ for example found that the conductivity depended on applied voltage for single crystal specimens tested in a vacuum environment. Harrop and Creamer¹⁶ found no such dependence when the environment was changed to air. While it is possible that other experimenters have satisfied themselves that the application of Ohm's law is valid, they have not reported it and yet in general they have made use of it.

In summary we state that the study of electrical conduction phenomenon in Al_2O_3 is complicated by (1) the very nature of Al_2O_3 and (2) the fact that high temperature property measurements must be made.

Recently renewed interest in Al_2O_3 has resulted from studies which employ ruby ($\text{Al}_2\text{O}_3:\text{Cr}$) lasers. Questions are being asked about the role of the Al_2O_3 lattice in laser phenomena. The result has been a generation of interest into the optical behaviour of Al_2O_3 . The response of Al_2O_3 to various modes of excitation (X-ray, γ -ray,

etc.) has resulted in reports of saturation effects²² and thermoluminescence.^{6,23}

Atlas and Firestone⁶ have reported the results of γ -ray induced thermoluminescence in Al_2O_3 . This phenomenon will be discussed in complete detail in section III of the present work, but for the moment we wish to note that Atlas and Firestone have found that the thermal activation energies obtained from electrical conductivity studies with various "doped" specimens corresponded with the thermal activation energies of trapping sites obtained from thermoluminescence studies.

This possibility of relating impurities and lattice defects to observed conductivity effects was a sufficient inducement to investigate thermoluminescence in 6N Al_2O_3 together with its electrical properties.

In summary we can now state the purpose of the present studies. This was:

- 1) to prepare dense sintered specimens of 6N Al_2O_3 and MgO doped 6N Al_2O_3
- 2) to evaluate the dielectric properties of pure and doped specimens, accurately, and consequently, the ac conductivity of these specimens
- 3) to investigate the phenomenon of thermoluminescence in the pure and doped specimens
- 4) to attempt to relate the results of thermoluminescence studies with observed conductivity results.

In section II we will discuss the precise measurement of electrical conductivity of pure and MgO doped Al_2O_3 .

In section III, the thermoluminescence will be discussed and in

section IV, the attempt to correlate the results of both studies will be presented.

SECTION II

ELECTRICAL CONDUCTIVITY MEASUREMENTS

2:1 Introduction:

In this section we will discuss the measurement of the electrical conductivity of specimens made of sintered pure Al_2O_3 and Al_2O_3 doped with MgO . The conductivity of specimens was measured by a 3-terminal technique in vacuum over the temperature range 20 to 1020°C and for frequencies of the applied field in the range 10^2 to 10^5 cps. The ac conductivity is actually derived from other measured parameters. In our case these parameters were the series capacitance and the dissipation factor of the specimen considered as a solid dielectric filling a precisely defined electrode arrangement.

The macroscopic response of a dielectric to an ac field of angular frequency, ω , may be characterized by the complex permittivity $\epsilon^*(\omega)$. The microscopic interpretation of the real part of the permittivity $\epsilon'(\omega)$ and of the imaginary part of the permittivity $\epsilon''(\omega)$ depends on the model chosen to represent the dielectric. The suitability of the model can be tested by comparison of the experimental observations and the predicted temperature and frequency dependencies of the dielectric constant ϵ'/ϵ_0 , and the dielectric loss factor, ϵ''/ϵ_0 (ϵ_0 representing the permittivity of free space).

Guarded measurements were made in order to avoid edge effects in the determination of sample capacitance and interelectrode conduction effects in the determination of the dissipation factor. Four criteria must be observed in making 3-terminal guarded measurements. Referring to Figure 2.1, the width of the guard ring, $(D_3 - D_2)/2$, must be at least four times greater than the thickness.²⁵ The gap $(D_2 - D_1)/2$ must be as small as possible.²⁵ Complete electrical shielding must be

Figure 2.1. Electrode geometry for a disk specimen

provided for both the high and guarded electrodes from the specimen to bridge and the potential of the guard and guarded electrodes must be the same, at least at bridge balance.²⁶ We will consider first the apparatus used and the procedure followed in measuring the dielectric properties of Al_2O_3 specimens. The results obtained will then be compared with previously reported values.

2:2 Apparatus and Specimens for Electrical Conductivity Measurements:

The Furnace: The furnace and associated pressure measuring apparatus have been described previously.⁹ The furnace, Degussa #HVOta4517 is basically a heater resistor sheet in a vacuum chamber as shown in Figure 2.2. Two Molybdenum heaters (A, B) are connected in parallel with water cooled copper current leads (C, D) from the power supply unit (Figure 2.10). The heater elements are completely surrounded by Molybdenum radiation screens. The arrangement of heaters and screens (minus the top set of 3 radiation screens) is shown in Figure 2.2.

During operation a bell-jar (Figure 2.3) encloses the heater assembly. The radiation screens surrounding the heaters make the hot zone approximately a black body cavity. A small hole in the top set of radiation screens was left for optical measurements. Temperature, for example, could be measured by means of an optical pyrometer mounted on the glass covered viewing hole in the top of the bell-jar.

The system was evacuated by an oil diffusion pump backed by a rotary gas ballast pump. Pressure in the range 10^{-3} to 10^{-5} mm Hg was measured by a calibrated Penning vacuum gauge. All these components have been manufactured by Leybold.²⁴ The lowest total pressure attained using Molybdenum heaters and screens was 1.1×10^{-5} mm Hg.

The furnace was used to fire specimens of aluminum oxide at high temperatures under controlled conditions. In order to control

Figure 2.2. Heater elements and radiation screens.

Figure 2.3 Experimental set-up for electrical conductivity measurements.

the experimental parameters, temperature and total pressure, as carefully as possible, the hand control of the current transformer was replaced by an automatic drive assembly. A typical automatic firing cycle (used for firing specimens for electrical conductivity measurements) is shown in Figure 2.4.

The firing cycle shown (within experimental error) was reproducible for all specimens used in electrical conductivity measurements. The relatively slow heating and cooling rates of about $4^{\circ}\text{C}/\text{min.}$ were used to prevent thermal shocks to both the furnace elements and the fired ceramics. The furnace was also used to heat, at low pressures, a specially designed 3-terminal cell over the temperature range of electrical conductivity measurements. The same heating and cooling rates, as above, were used.

Since the partial pressure of oxygen surrounding a test specimen determines at high temperature the equilibrium number of defects, measurements of oxygen partial pressure were carried out as a function of the temperature of a specimen positioned in the 3-terminal cell.

Three Terminal Cell Design: A 3-terminal cell was designed and constructed to measure the dielectric properties of sintered aluminum oxide specimens. Metal electrodes (e.g. fired on Platinum paste) were readily affixed to aluminum oxide specimens so that the cell, in essence, was to perform as an electrical connector between the sample at high temperatures in vacuum and the measuring apparatus at room temperature. The cell dimensions were dictated by the high temperature vacuum furnace available. The overall length was about 13" and the width of the cell about $1\frac{1}{2}$ ".

The basic 3-terminal cell, illustrated in Figure 2.5, is

Figure 2.4. A typical firing cycle used for sample preparation: The solid line represents temperatures measured with an optical pyrometer; the dashed lines are conjecture.

Figure 2.5. Schematic illustration of the 3-terminal cell used from measuring electrical conductivity.

similar to a doubly shielded coaxial connector. The guarded electrode connector (19) consists of a spring loaded Molybdenum rod which can slide freely over the polished surfaces of two fused quartz spacers (11, 18). A disk of Boron Nitride (6) prevents the steel spring from shorting to the brass flange (5). A stainless steel stop (15) restricts the travel of the guarded electrode to approximately $1/16''$ about the rest position shown in this figure.

The guard electrode completely surrounds the guarded electrode. The guard cylinder was constructed of two materials; Molybdenum (22) was used for the "hot zone" and stainless steel (14) for the cooler top region of the cell.

The outer jacket of the cell (23, 27, 15) was constructed similarly. This outer jacket was also spring loaded (9) to press the high electrode (25) firmly against a sample (26) which in turn was firmly pressed against the end faces of the guard and guarded electrodes.

A high purity Coors²⁷ aluminum oxide crucible (21) was used to insulate the high electrode (25) from the grounded base (27). It also served as an evaporation shield stopping most of the Molybdenum evaporated from the hot outer jacket from reaching exposed specimen surfaces.

The top of the cell was water cooled (10). Two platinum wires, the guarded (low) and unguarded (high) leads, were brought out through Kovar seals into General Radio type 874 connectors (1, 2, 3). Al_2O_3 tubing (20) insulated the high lead.

The cell as shown performed satisfactorily for prolonged periods of time at $1000^\circ C$. The cell was designed for the express purpose of performing 3-terminal capacitance measurements. However,

by shorting the guard and guarded electrodes, 2-terminal measurements can be made with this cell. To short out these two terminals a piece of Molybdenum was machined which could be press-fitted onto the end of the rod constituting the guarded electrode (see Figure II-1 in Appendix II-1). The outer diameter of this piece was the same as that of the guard and high electrodes. Spring pressure insured electrical contact between this piece and the guarded electrode, producing the desired effect.

The capacitance and loss produced by the Al_2O_3 crucible which is now between high and ground potentials (Figure II-1) are in parallel with the impedance resulting from a test specimen between these potentials. To a certain extent this and other stray capacitances can be taken into account (see results and analysis of 2-terminal measurements in Appendix II-1).

The values of electrical conductivity obtained by 2-terminal measurements, while not as accurate as 3-terminal measurements, are nevertheless of use in determining whether or not gross surface effects are an inherent feature of electrical conduction measurements of aluminum oxide.

The temperature of a specimen positioned in the cell was measured by means of a calibrated²⁸ thermocouple assembly (4), after (preliminary) temperature measurements with two thermocouples one directly above and one directly below the specimen, (4 and 20 respectively in Figure 2.5), showed that no thermal gradient existed along the cylindrical axis of the cell over the temperature range of electrical conductivity experiments, i.e. 20 to 1020°C. Only one thermocouple, at ground potential, was used in order to eliminate the enormous shielding problems that would be involved if a

thermocouple at any other potential was left in the cell.

The calibrated thermocouple assembly (4) consists of two wires (Tungsten 5% Rhenium vs Tungsten 26% Rhenium) immersed in refractory MgO and covered with a thin sheath of Molybdenum. The junction end of the assembly was press-fitted in the Molybdenum ring (24) which is approximately 1/16" from the sample surface. The other end of the assembly was silver soldered to the brass flange (5). The two thermocouple wires were connected to copper leads, the connection taking place in an ice bath reference junction. Temperature was measured as e.m.f. potentiometrically. A calibrated Tinsley Model 3184D potentiometer was used for this purpose.

The 3-terminal cell (Figure 2.5) finally constructed performed the following necessary functions:

- 1) it provided 3 electrical connections from a test specimen at elevated temperatures to a capacitance measuring assembly at room temperature
- 2) it provided complete electrical shielding of the high and low leads
- 3) it could be easily converted to a 2-terminal cell.

Oxygen Partial Pressure Measurements: Pappis and Kingery¹⁵ have shown that the electrical conductivity of aluminum oxide depends upon the oxygen content of the surrounding atmosphere. Measurements were carried out to determine the partial pressure of oxygen as a function of temperature in the furnace when the heater elements, radiation screens, and high temperature 3-terminal cell were in the position used for electrical tests. An MSIO²⁹ recording mass spectrometer was used for this purpose. This instrument, however, was designed for use with vacuum systems where the total pressure was less than 10^{-6} mm Hg.

Because of the high total pressure in the furnace chamber ($\geq 10^{-5}$ mm Hg) the individual peaks associated with nitrogen, water vapor, and some of the hydrocarbons from the diffusion pump oil exceeded the measuring capacity of the instrument when used under normal operating conditions. It was possible to measure the peak associated with ionized oxygen molecules (mass #32), but no quantitative estimate of the partial pressure of oxygen associated with this peak could be made, as with this instrument all peaks must be measurable in order to obtain a calibration.

The height of the oxygen peak was recorded as the furnace and its contents were heated up. The heating rate employed here was the same as that used previously for the firing of specimens (Figure 2.4). The height of the peak relative to the (instrument) background level was found to change by less than 10% for temperatures up to 1000°C, the highest temperature measured. This change in peak height was interpreted as a change of less than 10% of the oxygen partial pressure since at a given temperature and with a fixed volume, the peak height is proportional to the number of oxygen molecules in the furnace and hence is a measure of the partial pressure.

If it is assumed that the oxygen partial pressure, to start, is just what one would expect to find for normal air at 10^{-5} mm Hg, then the estimated partial pressure of oxygen is approximately 3×10^{-9} atmos, and it remains at this value within $\pm 10\%$ for specimen temperatures up to 1000°C.

The results of Pappis and Kingery indicated that the electrical conductivity of sintered Al_2O_3 would vary by less than 3% when the partial pressure of oxygen was varied between 2×10^{-9} atmos. and 4×10^{-9} atmos. at specimen temperatures greater than 1500°C. If one

extrapolates their results to account for the behaviour of the electrical conductivity of specimens at temperatures less than 1000°C it must be concluded that the variation of the electrical conductivity would be even less than 3%.

The above test measured variation of the partial pressure of the oxygen in the furnace as a function of temperature. It was concluded that the variation of electrical conductivity of a specimen of sintered alumina with this change in oxygen partial pressure would be less than a few percent for the range of temperatures, 20°C to 1020°C, covered during the present studies.

Sample Preparation and Analysis: In this section we shall discuss the preparation of dense, vacuum-sintered specimens with the emphasis being placed on the description of the specimens used in the present studies. These specimens were essentially oxide disks which had received their permanent shape and strength through sintering of a mass of loose grains.

Cominco³⁰ 6N Al_2O_3 powder was received in four, fifty gram lots. The spectroscopic analysis of each lot was supplied by the manufacturer. Cominco high purity aluminum oxide was supplied as a white powder composed of a mixture of phi and theta crystallographic forms. Microscopic analysis³⁰ showed that the Al_2O_3 particles were irregular in shape and varied in size. Most particles were less than 10μ in their greatest dimension, but sizes ranged up to 75μ ; the particles had some tendency to agglomerate. 4N MgO ³¹ was used as the doping agent. The steps taken to fabricate dense, pure and doped specimens are described hereafter; in brief, these steps consisted of:

- 1) the conversion of the crystal phases of the pure powder to the stable high temperature alpha form

- 2) the addition of the MgO powder to the 6N Al_2O_3 powder
- 3) the cold-pressing and sintering of specimens
- 4) the preparation of these fired specimens for electrical measurements.

Step 1: Phase conversion (ϕ , $\theta \rightarrow \alpha$)

Phase conversion of the ϕ , θ forms to the α form which is the stable high temperature crystal form was accomplished by firing in air for about 3 hours at about 1300°C . Twenty-five grams of each lot were enclosed in a Coors Al_2O_3 cup (with a top) and positioned in the interior of a SiC furnace.³²

The completeness of the conversion procedure was confirmed by X-ray diffraction studies.³² Table 2.1 is a list of the intensities of X-ray diffraction peaks obtained from the converted powder. Included, for the sake of comparison, are the reported values of these quantities for α Al_2O_3 . The discrepancies that exist between the intensities, listed for one and the same d-spacing, are actually less than the discrepancies that normally result between two X-ray diffraction patterns of the same material, and this is due to the variations which occur in the hand-packing of a powdered material into a standard powder holder.

Whereas every possible precaution was taken in the handling of the pure Al_2O_3 to prevent contamination there were certain stages in the fabrication process which by their very nature introduced an unknown element into purity control. For example, the effect, if any, when high purity Al_2O_3 is fired in an Al_2O_3 crucible of considerable less purity ($99.9^+\text{Al}_2\text{O}_3$) for 3 hours at 1300°C . We note, however, that after removing the cup from the furnace it was always found that a small layer of the pure powder had stuck to the inside of the cup. The material which was stuck was discarded and for each conversion

Table 2.1

Diffraction Pattern Data of Converted Cominco 6N Al_2O_3
Compared with Literature Values of Alpha Al_2O_3

Present Studies		Reported Values†		
d Å	I/I ₁	d Å	I/I ₁	hkl
3.48	67	3.479	75	012
2.55	92	2.552	90	104
2.38	38	2.379	40	110
2.17	1	2.165	<1	006
2.09	100	2.085	100	113
1.97	1	1.964	1	202
1.74	44	1.740	45	024
1.60	83	1.601	80	116
1.55	2	1.546	3	211
1.51	3	1.514	5	122
1.51	8	1.510	7	018
1.41	32	1.404	30	124
1.37	46	1.374	50	030
1.34	1	1.337	1	125
1.27	1	1.276	3	208
1.24	13	1.239	15	1.0.10
1.23	7	1.2343	7	119

† ASTM Standards Card # 10-173

(Ref. Nat. Bur. Standards (U.S.) Circ. 539 2 (1959))

run a new cup was used, thoroughly cleaned with detergent and rinsed with distilled water and finally pure alcohol.

Step 2: Addition of MgO

The pure alpha Al_2O_3 was now ready for cold-pressing. However, since the MgO doped specimens followed essentially the same procedure the addition of MgO to the pure alpha Al_2O_3 powder is now considered.

There was no knowledge of the particle size distribution. The only crystal phase of MgO is face centered cubic. Since one part in 10^4 parts of MgO consists of unknown impurities then 1% by weight is the maximum amount of the MgO that can be added to 6N Al_2O_3 without introducing more than 1 ppm of unknown impurity. Three different percentages by weight of MgO were added. The attempt was made to measure out 1%, 0.1% and .01% MgO by weight, however, as shown in Table 2.3, the final percentages actually added only approximate these conditions.

The MgO and alpha Al_2O_3 powders were weighed in a thoroughly cleaned polystyrene jar and polystyrene balls were added to it. The jar was filled with distilled water and capped. The jar was then clamped into a lathe and revolved at 35 rpm. Periodically, the jar was tapped to prevent powder from sticking to the walls. After milling for 100 hours the jar was set aside for a day to allow the powders to settle. The major portion of the added water was removed by filtering. The remainder was removed by heating the slurry in a Coors Al_2O_3 crucible (covered) in a muffle furnace at 1000°C for 1 hour.

Although the water helped to separate some grains that had been stuck together, thereby promoting a better milling action, nevertheless, in the process of settling the water was not beneficial since heavy particles (alpha Al_2O_3) settle faster than light particles (MgO) and

Table 2.3

Impurity content of test specimens (ppm)

Metallic Impurity		As	Al	Bi	B	Ca	Cu	Fe	Mg	Mn	Na	Pb	Si
Mass Name													
C1	-	-	-	0.1	0.1	0.1	0.1	0.1	0.3	0.1	-	0.1	0.1
C2	0.2	-	-	0.1	0.1	-	0.1	0.1	0.1	0.5	-	0.1	0.1
C5	-	-	<.01	0.1	0.1	<.01	0.1	0.1	75*	-	<.01	0.1	0.2
C3	0.2	-	<.01	0.1	0.1	<.01	0.1	0.1	770*	0.5	<.01	0.1	0.1
C4	0.1	-	<.01	0.1	0.1	0.1	0.1	0.12	7680*	-	.02	0.1	0.12

- Not Detected

* Intentionally Added

therefore a non-uniform mix was obtained. Consequently, the same milling procedure was followed again omitting all the water steps. This last stage, it is felt, led to a homogeneous mixture of the MgO and Al_2O_3 powders. No tests were performed at this point to ascertain the amount of MgO in the Al_2O_3 . These tests were performed, however, after the samples had been fired.

Step 3: Pressing and Sintering of Specimens

The method of sample fabrication available and therefore the one used consisted essentially of obtaining a cold-pressed sample which was then fired, in a vacuum furnace at a temperature and for a period of time which resulted in low porosity. The cold-press facilities of N.R.C. were used. Five masses were cold-pressed. These masses were labelled C1, through to C5, (C = COMINCO). The impurity contents of these masses are listed in Table 2.3. The listed impurity content is based on the spectrographic analysis supplied by the manufacturer of MgO and by the manufacturer of Al_2O_3 . With one exception the procedure followed in cold-pressing was as follows:

The pure powder or the doped powder was tamped in a rubber mold assembly. The rubber mold assembly design used is illustrated in Figure 2.6. The two pieces A and B are rubber brake cylinder parts and served as top and bottom, respectively, of the mold assembly. The outer rubber sheath was cut from bicycle tubing. The brass cylinder assembly served to give support to the thin rubber mold during the tamping operation. The bottom piece A was glued in position and after tamping, the top B was placed into the rubber mold assembly, firmly on top of the tamped powder. The excess length of rubber tubing allowed for the gluing of the top piece to the sides. The brass cylinder was then removed. To ensure that no oil would penetrate the assembly, the

Figure 2.6. Rubber mold assembly.

thin rubber envelope C was placed around it and the open end of C was tied in a knot. It should perhaps be emphasized that the rubber parts were carefully washed and dried before inserting the powder.

The rubber mold assembly was placed into an oil bath and the pressure in the bath slowly increased to 4×10^4 psi. This pressure was maintained for over one minute and then was slowly released. The rubber mold was carefully cut open and the pressed mass removed. With the exception of mass CI, all pressed masses fell apart (into a few pieces) at this stage and a second pressing operation was needed in order to obtain masses that could be handled without falling apart. A new mold was used each time.

Next, the pressed masses were fired in the vacuum furnace. A pressed mass was positioned on a pedestal of pure Al_2O_3 powder in a Coors Al_2O_3 cup which in turn was centered in the hot zone of the furnace.

The rate of heating and cooling and the length time held at a constant temperature were controlled automatically. The temperature of the fired piece was measured with an optical pyrometer. The temperatures quoted in Table 2.4, at which the various pieces were fired, are probably accurate within 50°C since no correction for the glass viewing cover in the bell-jar was applied. The times quoted are accurate to within a minute.

The pressed mass CI fired in this manner was cracked around the periphery upon removal from the furnace. The other masses were, to the eye, completely free of cracks. Sample C2 was fired first at 1800°C for one hour. The resulting dense mass was cut into two pieces (with a diamond saw) and one piece was refired at 1800°C for two hours. The refired piece was called C2B, the original piece, C2A.

In Table 2.4 the temperature at which a piece was fired, the time for which it was held at this temperature and the density of the finished specimen, are all recorded. Since separated phases usually have a density different from that of Al_2O_3 , a column of corrected densities is added which was obtained by considering that the MgO ($\rho = 3.570 \text{ gm/cm}^3$) reacted completely with Al_2O_3 ($\rho = 3.986 \text{ gm/cm}^3$) to form the separate phase of spinel ($\rho = 3.54 \text{ gm/cm}^3$). As seen, the corrected density of specimen C4A is closer to the densities measured for the other two doped specimens which perhaps lends some support to the supposition that complete reaction has taken place.

An attempt was made to measure the MgO and/or spinel content of the doped specimens by X-ray diffraction analysis. First the diffraction pattern of specimen C4A was obtained, since this specimen contained the most added MgO . The measured diffraction peak intensities were compared with the known peak intensities produced by MgO and spinel crystals. In Table 2.5 we illustrate the comparison between the intensities of observed peaks and major spinel peaks. None of the observed peaks corresponded to MgO peaks.

Approximate intensities were obtained because only a small portion of the total sample is spinel and, because the major $6\text{N Al}_2\text{O}_3$ portion produced a high background level of scattered X-rays. The conclusion, nevertheless, is that spinel has been formed. Further, since it was estimated¹⁴ that free MgO in concentrations $\geq 0.01\%$ should have yielded at least one measurable peak and since this peak was not observed then the concentration of free MgO is $\leq 0.01\%$.

Measurements of the most intense peak showed that the concentration of spinel varied in the approximate ratio of, 1.0: 0.11-0.18: ≈ 0.01 , for specimens with the MgO content in the respective

Table 2.4

Summary of Sintering Data

Sample Name	Firing Temperature (°C)	Total Pressure (mm Hg)	Firing Time (hrs)	Measured Density (gms/cm ³)	Measured Porosity (%)	Corrected Porosity (%)
C1	1800	2.0x10 ⁻⁵	1.0	3.72±.01	6.8	6.8
C2A	1800	4.8	1.0	3.82	4.3	4.3
C2B	1800	2.7	3.0	3.86	3.3	3.3
C5A	1820	2.0	3.0	3.92	1.7 ⁵	1.7 ⁵
C3A	1825	6.0	3.0	3.92	1.7 ⁵	1.7
C4A	1840	1.0	3.0	3.89	2.5	2.1

Table 2.5

X-ray diffraction peak data from a 1% MgO doped Al_2O_3 specimen compared with literature data for Al_2O_3 , MgO and Mg Al_2O_4

<u>Data from present studies</u>		<u>Data from ASTM cards</u>			
Area of (20) Scan = 25° - 66°					
d Å	(I/I ₁)†	Substance	d Å	I/I ₁	hkl
3.48	91	Al ₂ O ₃	3.479	75	012
2.85	3	Mg Al ₂ O ₄	2.85	50	220
2.55	100	Al ₂ O ₃	2.552	90	104
		MgO	2.431	10	111
2.43	6	Mg Al ₂ O ₄	2.43	90	311
2.38	52	Al ₂ O ₃	2.379	40	110
2.17	< 1	Al ₂ O ₃	2.165	< 1	006
		MgO	2.106	100	200
2.09	94	Al ₂ O ₃	2.085	100	113
2.02	3	Mg Al ₂ O ₄	2.01	70	400
1.97	1	Al ₂ O ₃	1.964	1	202
1.74	43	Al ₂ O ₃	1.740	45	024
1.64	1	Mg Al ₂ O ₄	1.674	20	422
1.60	78	Al ₂ O ₃	1.601	80	116
1.55	2	Mg Al ₂ O ₄	1.555	70	333
1.54	3	Al ₂ O ₃	1.546	3	211
1.51	3	Al ₂ O ₃	1.514	5	122
1.51	10	Al ₂ O ₃	1.510	7	018
		MgO	1.489	52	220
1.43	3	Mg Al ₂ O ₄	1.426	100	440

† The specimen analysed was a solid disk and was not rotated which produces random variation in peak intensities.

order of, 1.0%:0.1%:0.01%. These values, again quite approximate, are consistent with the assumption that spinel is formed and constitutes a separate phase.

Step 4: Preparation of Specimens Suitable for 3-terminal Conductivity Measurements (as well as for surface structure and thermoluminescence studies)

The dense sintered masses were cut into rough disk shaped pieces on a diamond saw. The rough surfaces of the cut disks were then finished to close tolerances by surface grinding with a diamond wheel (#150 grit). In general, the samples were cut to a thickness of about 0.1 cm with a diameter of about 2.0 - 3.0 cms. The major faces of the disk were checked for parallelism with a Sheffield depth gauge.³³ The parallelism was kept within ± 0.0001 ". The thickness of each specimen was obtained from micrometer readings at 30 points spaced more or less uniformly over the specimen surface. The cylindrical surface of a disk was ground with the same diamond wheel by clamping the piece in a lathe between two pieces of hardwood.

Electrodes were affixed to the specimens by firing on Hanovia #6082 pure Platinum paste. A thin even coating of Pt paste was applied to the surface of a specimen positioned at the center of slowly rotating turntable. The paste overlapped the edges. The turpentine and binder were removed by firing the coated specimens at about 900°C for nearly 1 hour in air. An open ended Al_2O_3 tubular furnace was used for this purpose.³² The resistance of the metallic electrode was measured and if it was less than 10 Ω the electrode was considered satisfactory; if not, another coating was fired on.

The variable time and temperature quoted here are due to differences between the thicknesses of the various coating attempts.

Thin layers evaporate quickly at about 1000°C. It is realized that these variables effect the thermal history of the specimens and can quite possibly influence the electrical behaviour of specimens so treated. Although this was the method chosen, an attempt was made later to try to bond pure Platinum foil to the surfaces to form electrodes since then, the time, pressure, and temperature could all be automatically controlled. However, as we will show in section 2.3 there were further difficulties encountered in preparing a conductivity specimen which made the fired on Pt past electrodes necessary.

Once Pt electrodes were affixed to the surfaces, the cylindrical surfaces were reground to remove any traces of Pt metal from the sides of the specimen. Then very carefully a small ring was cut in one of the electrodes using the point of a diamond as a lathe cutting edge. The ring area was free of Pt paste as judged by the fact that the resistance from the center to edge of this electrode was $> 10^8 \Omega$. Viewed microscopically the area contained some unconnected specks of Pt metal. This area formed the gap between the guard and guarded electrodes. The opposite face constituted the high electrode.

In cutting the gap two criteria of 3-terminal measurements were observed. First, the gap was made as small as physically possible with the available apparatus and secondly the width of the guard electrode was made at least four times greater than the thickness of the specimen. In this manner, then, five specimens complete with electrodes were obtained which were judged suitable for conductivity measurements. In Table 2.6, the dimensions of these samples are listed along with relevant measurement errors. The gap sizes listed in this table were obtained with a travelling microscope and represent the average gap computed from measurements at various diameters. The range of measured values for the gap sizes are included in the estimated error.

Table 2.6

Sample dimensions at room temperature

Sample Name	Thickness t (cms)	Guarded Electrode Diameter $(D_2 + D_1)/2$ (cms)	Major Diameter D_3 (cms)	Gap Size $(D_2 - D_1)/2$ (cms)
C2A	0.1000 ± 0.0003	1.5240 ± 0.0010	2.670 ± 0.001	0.020 ± 0.010
C2B	0.0987	1.5011	2.26 ₁	0.036
C3A	0.1000	1.5110	2.65 ₀	0.040
C4A	0.1005	1.5189	2.41 ₈	0.032
C5A	0.1013	1.5084	2.68 ₀	0.030

The Capacitance Bridge and Associated Equipment: The ac electrical conductivity of pure and MgO doped Al_2O_3 specimens was measured by means of the G.R. 1650 capacitance measuring assembly. This assembly consists essentially of the type 1615-A capacitance bridge, the type 1311-A Audio Oscillator and the type 1232-A Tuned Amplifier and Null Detector. A Wayne Kerr SL21 oscillator was used to extend the frequency range to 10^5 cps.

i) The oscillators: The maximum safe generator voltage was 30 volts per Kilocycle when the 1311-A was used. The voltage output of the Wayne Kerr oscillator was continuously adjustable from 0 to 30 volts. This latter oscillator was used for the three frequencies 10^5 , 5×10^4 and 2×10^4 cps.

ii) The detector: The type 1232-A detector provides continuous null detection (minimum of 1μ volt) for frequencies in the range 60 to 2×10^4 cps and two additional fixed detection positions for 5×10^4 cps and 10^5 cps.

iii) The capacitance bridge: The type 1615-A capacitance bridge is a standard laboratory instrument designed for precision measurements of capacitance and dielectric properties. The following ranges of measurement are available:

Capacitance (6 ranges): 10^{-17} to 10^{-6} farad: direct reading; six figure resolution, smallest division 10^{-17} farad.

Capacitance (6 ranges): 10^{-17} to 10^{-6} farad: direct reading; six figure resolution, smallest division 10^{-17} farad.

Dissipation factor (3 ranges): 0.000001 to 1.0 at 1 Kc, direct reading. Directly proportional to frequency at other frequencies. Four figure resolution; smallest division 0.000001.

Frequency: 50 cps to 10 Kc, useful with reduced accuracy to 100 Kc.

The accuracy of these ranges as quoted by the manufacturer and checked by a calibration procedure (appendix II-2) is as follows:

Capacitance - direct reading, internal standard.

At 1 Kc, $\pm (0.01\% + 0.00003 \text{ pf})$. Additional error

at higher frequencies and with high capacitance:

$$\pm 2 \times 10^{-5} f_{\text{kc}}^2\% + 2 \times 10^{-3} C_{\mu\text{f}} f_{\text{kc}}^2\%$$

At lower frequencies and with small capacitance, accuracy limited by bridge sensitivity.

Dissipation factor: Direct reading, (0.1% of measured value + 0.00001).

Basically the bridge is of the transformer-ratio arm type that uses a single decade of transformer voltage division and multiple, fixed, standard capacitors to provide the six decades of capacitance resolution. Both two and three terminal capacitance measurements are possible with this bridge.

3-Terminal Measurements: The specimens of Al_2O_3 situated in the specially designed high-temperature cell can be represented by a 3-terminal impedance network as shown in Figure 2.7. The basic circuit of the G.R. 1615-A bridge is shown in Figure 2.8, with the 3-terminal representation of a specimen inserted in position. The two transformer secondary windings on the Toroid are used as the ratio arms of the capacitance bridge with the standard capacitors, C_N , and standard resistors, R_N , forming the 3rd arm and the unknown capacitance and resistance, R_x and C_x , forming the last arm.

The specimen impedance between H and G is across the transformer windings. The transformer resistances and leakage inductances are, in practice, kept so small that quite low impedances or large capacitances can be connected from H to G before appreciable error results in bridge

Figure 2.7. A specimen and its equivalent 3-terminal representation: The central volume of the specimen is selected for study.

Figure 2.8. The basic bridge circuit: The impedance of an unknown is represented by the series arrangement of C_X and R_X .

readings. The only effect of the capacitance and the resistance added from G to L is to reduce the sensitivity of the detector. Consequently, only the capacitance and resistance of the unknown, selected for study, is seen by the effective bridge measuring circuit. In practice the bridge resistors, R_N , are adjusted (by adding capacitance) to read the dissipation factor of the unknown directly at 1 Kc. At balance the series capacitance C_x of the unknown is read directly. The dissipation factor of the unknown $D = R_x \omega C_x$ is read directly at 1 Kcp but for other frequencies, the bridge reading must be multiplied by the frequency in Kc. In order to maintain the stated accuracy of the bridge readings the frequency must be known to an accuracy of $\pm 0.1\%$. The bridge calibration can be checked by constructing and measuring a standard dissipation-factor.

Calibration procedure: The G.R. type 1404-A reference standard capacitor was used in conjunction with calibrated G.R. standard resistors to check the quoted bridge accuracy for both capacitance and dissipation factor readings. The procedure adopted was similar to that outlined in the bridge reference manual,³⁴ and is described completely in appendix II-2. This calibration check showed that, firstly, the capacitance values were accurate to $\pm 0.2\%$ and, secondly, the dissipation factor readings agreed within the quoted accuracy limits with the values of the constructed dissipation factor standards.

Standard capacitors have an associated, but unknown, amount of loss which amounts to about 10 ppm. Consequently, the accuracy of absolute dissipation factor measurement with this bridge and with other bridges commonly used (Wayne Kerr #221, or G.R. #716) is limited by this unknown amount of loss. This basic uncertainty in D results in a very high apparent error for small dissipation factor readings (see Figure 2.9).

Since the dissipation factor can be related to the ac conductivity when the dielectric constant is known then it follows that for Al_2O_3 with k' about 10 that the equivalent uncertainty in conductivity due to the uncertainty in D is

$$\Delta\sigma \approx \frac{f \times 10 \times \Delta D}{1.8 \times 10^{12}} \Omega^{-1} \text{ cm}^{-1}$$

For a frequency of 10^3 cps, then $\Delta\sigma$ is about $5 \times 10^{-14} \Omega^{-1} \text{ cm}^{-1}$.

In order to obtain the highest accuracy in readings with this bridge, the conductivity should be measured in the region where the dissipation factor of the specimen is ≥ 0.1 , as shown in Figure 2.9. The actual range of measurements included measured dissipation-factors as low as 10^{-5} where the basic inaccuracy is approximately 100%. However, these low readings are of use to compare low temperature conductivity results with previous reported values. It must be borne in mind that the G.R. 1650 bridge is probably the most accurate instrument for measuring D, or, for that matter, G, to date.

In general conductance readings are not as accurate as dissipation readings (the exception are bridges such as the Wayne Kerr #221, but it should be noted that proper 3-terminal measurements cannot be performed with this bridge as there is no provision for equalizing the potentials of the guarded and guard electrodes). For example, the conductance G of a specimen of thickness = 0.1 cm and cross sectional area = $\pi(1.5)^2 \text{ cm}^2$ is about $4 \times 10^{-6} \mu \text{ mho}$ for the case just quoted, with $\Delta\sigma$ about $5 \times 10^{-14} \Omega^{-1} \text{ cm}^{-1}$. Since the basic inaccuracy of G readings with the G.R. 1650 bridge is $10 \times 10^{-6} \mu \text{ mho}$ it follows then, that a more accurate conductivity value is obtained from the dissipation factor reading (that is, $\Delta D/D = 1.0$ and $\Delta G/G = 2.5$).

The calibration of the internal bridge capacitances can be performed easily by calibrating the largest internal standard (1000 pf).

Figure 2.9. The absolute accuracy of Tan δ readings with the G.R. 1650-A Capacitance measuring assembly.

Since any internal standard can be internally connected to the unknown terminals the next highest capacitance may then be calibrated by comparing it with the standard. Since the next highest standard is 100 pf capacitor it is necessary to apply $0.1 \times V$ across it where V is the voltage across the standard. This is readily accomplished by the accurate 10:1 transformer ratio arm taps.

Two terminal measurements may also be performed with this bridge. The basic bridge accuracy remains the same, however, some stringent requirements must be met to make full use of this accuracy. In the present studies these requirements could not be met fully, so the results of 2-terminal studies have been put into appendix II-1.

In summary the G.R. 1650 bridge fulfilled the following basic requirements of accurate 3-terminal dielectric measurements as a function of temperature:

- 1) at balance both the guard and guarded electrode of a specimen were at the same potential (within $1 \mu V$)
- 2) the bridge was balanced in a manner of minutes which eliminated problems normally encountered with drifting of the specimen temperature during balancing
- 3) the calibration mode of the bridge allowed for the continual check on the drift (with temperature and pressure) of internal standards.

2:3 Experimental Procedure:

Three terminal measurements: The experimental set-up is described in Figures 2.3 and 2.10. A specimen was usually heated to a temperature less than $500^{\circ}C$ and held at this constant temperature for about 12 hours. This initial heating was done to remove moisture from the cell parts and from the inner walls of the bell-jar. It was found that by

Figure 2.10. Schematic illustration of the experimental set-up for electrical conductivity studies.

doing this the total pressure in the furnace reached its minimum value in a relatively short time. When the temperature of the specimen was reasonably constant, bridge balancing was begun.

The two oscillators were left running continuously, so that the possibility of drifting frequency during equipment warm-up was eliminated. Since two oscillators were used, the procedure followed in selecting the first frequency was determined by the oscillator attached to the bridge. In order to select a frequency, the bridge was set to the "calibrate" mode. In this mode the specimen is disconnected from the bridge. The detector was set to peak at the given frequency. For all the frequencies between and including 10^5 cps to 5×10^2 cps, the inaccuracy was $\pm 0.1\%$. The inaccuracy of the 10^2 cps frequency readings was limited to $\pm 0.2\%$ but $\pm 0.1\%$ of this was due to the method of calibration.

Once the frequency of the field was chosen the magnitude of the voltage applied to the specimen was selected. In some cases it was found that the magnitude of the applied voltage affected both the value of the measured capacitance and value of the measured dissipation factor. In such a case, the voltage was varied over the complete range available at a given frequency. However, at temperatures above 200°C the variation of voltage had little effect on the measured parameters, less than 1% , so that just the upper and lower limit of the available voltage range was checked. The sensitivity of the detector was enhanced when high applied specimen voltages were used, thus, the readings of capacitance and dissipation were taken with the applied voltage as high as possible.

Once the applied voltage and the frequency had been selected the bridge was balanced. The capacitance and dissipation factor were recorded. The temperature was checked. This procedure was continued

for the frequencies 10^5 , 5×10^4 , 2×10^4 , 10^4 , 5×10^3 , 2×10^3 , 10^3 , 5×10^2 and 10^2 cps. Usually, but not always, the balance at one frequency, picked at random, was rechecked. The total pressure was noted both before and after the run through frequencies.

This procedure varied slightly for high temperatures after it was found that at about 1000°C the (paste) electrodes evaporated away in about one to two hours. The conductivity of specimen C2A, the more porous of the two prepared pure Al_2O_3 specimens, was measured first. After obtaining readings at 800°C , the sample was heated to about 1000°C and left overnight. Readings taken the next day indicated that the electrodes had evaporated. In subsequent runs the specimens with one exception were treated at a given temperature for about 12 hours before taking readings, if the temperature was less than about 800°C . A treating time of about 4 hours was used for temperatures above 800°C . The exception was specimen C3A, to investigate possible effects of a different heat treatment.

In testing specimen C3A, the frequency was fixed at 10^5 cps and the applied voltage at 30 volts. The specimen was treated for about 48 hours at 160°C . Then readings were taken every 4 hours at random temperatures. The minimum temperature was chosen because there was no voltage variation effects at this temperature and it was assumed, then, (and later shown to be right) that at higher temperatures there would also be no effects.

The first run with specimen C2A was classified as a test run since in a sense it was the guinea pig for conductivity measurements with the high temperature cell. The last run with specimen C3A was shortened because it was felt that all possible effects had shown up in previous results. The three intervening runs (C2B, C4A, and C5A)

were conducted in such a manner as to insure that reproducible results were obtained.

It is known that the conductivity of Al_2O_3 measured as a function of temperature often exhibits thermal hysteresis, that is thermal cycling is usually required in order to obtain reproducible results. Consequently, room temperature measurements were reproduced, but always after the sample had been heated to as high as 500°C . With the exception of sample C4A there were no signs of thermal hysteresis. The variations of conductivity of sample C4A with thermal cycling are discussed in the next section dealing with results.

Two terminal measurements: Sample C2A, with two new fired on platinum paste electrodes and no gap in them was placed in the high temperature cell. A Molybdenum adaptor was used to insure complete shorting of the guard and guarded electrodes of the cell, Figure II-1 in appendix II-1. The specimen was soaked for about 12 hours at each temperature before balancing the bridge. Two terminal readings were taken for the frequencies 10^4 and 10^5 cps with the applied voltage of 30 volts. The specimen was then removed and replaced by 3 small spacers. The spacers were cut from a ground ruby rod. The diameter of the ruby rod was close to the thickness of specimen C2A (0.100 cm vs 0.973 cm). The lengths of the spacers were kept below 0.1 cm. The spacers were thoroughly cleaned in boiling HCl and then boiling distilled H_2O before inserting them in the position previously occupied by specimen C2A. The position of the spacers in the cell is illustrated in Figure II-2, appendix II-1. It was possible that the Molybdenum spacer (25), Figure 2.5, might shift while the cell was assembled so three runs, at room temperature, were carried out while the spacers were placed at different positions. The capacitance and dissipation factor results

obtained differed so insignificantly that it was assumed, during the third set of measurements, that the cell was aligned. The attempt was then made to measure the 2-terminal capacitance and dissipation factor of the assembly as close as possible to the previously used temperatures and pressures.

Additional 3-terminal measurements: An attempt was made to obtain electrical conductivity measurements at temperatures in excess of 1000°C. Although the attempt was unsuccessful due to a breakdown in the existing furnace, the method chosen shows considerable promise for future high temperature measurements and will therefore be discussed briefly.

Platinum foil (.001" thick) was bonded to the surfaces of specimen C4A (1.0% MgO). The bonding was accomplished by heating the specimen in vacuum for $1\frac{1}{2}$ hours at 1400°C, with the Pt foil firmly pressed (about 20 psi) against each face. The gap was cut in one piece of foil in the same manner as used for the paste electrodes. Pt wires were spot welded directly to the Pt foil, to form the guard, guarded and high electrodes. This new method had the following advantages over the previously described one:

- 1) it is easier with this process of bonding to reproduce the pressure applied, the temperature, and even the bonding atmosphere (pO_2). This removes the uncertainty from the thermal history encountered in the previous method
- 2) there are fewer moving parts in the cell and therefore less likelihood of a breakdown
- 3) 3-terminal electrical conductivity measurements can now be carried out at temperatures close to the melting point of Platinum. A check on gross surface conduction effects can now be made, in particular cell leakage currents which occur in the atmosphere close to the sample surface.

Besides these advantages the new method produced some difficulties which were not fully overcome:

- 1) the thin pure Platinum foil was found to be very brittle when bonded to Al_2O_3 . This may have been due to the vacuum heat treatment. A small piece of Platinum wire had been welded to the center of one of the Platinum foil pieces so that after bonding a longer piece could be easily welded to it to form the central guarded electrode connection. After bonding this piece of wire was so brittle that it broke with but little handling. Several attempts were then made to arc weld a Platinum wire to the sample using the wire and Platinum foil as electrodes. After several attempts which simply pulled patches of the foil away from the ceramic, a successful connection was made. A thicker piece of foil may overcome this difficulty.
- 2) the brittleness of the Platinum foil made it extremely difficult to obtain a smooth-edged guard ring gap. The foil had the tendency to rip under the cutting action of a sharp diamond.

The dimensions of the gap finally cut are listed in Table 2.7.

Table 2.7

Dimensions of Platinum Foil Electrodes

D_1 (cms)	D_2 (cms)	Gap (cms)
$1.3993 \pm .0030$	$1.5589 \pm .0015$	$0.080 \pm .005$

The gap width is twice that encountered in the case of paste electrodes. The final assembly of electrodes and specimen is illustrated in Figure 2.11.

Figure 2.11. A modified version of the 3-terminal cell; the added thermocouple TC1 was kept at ground (guard) potential.

The gradient across the specimen was now measurable at all times by the arrangement of the thermocouples TC₁ and TC₂ as shown.

The same procedure as described previously was used with this modified version of the cell to obtain electrical conductivity measurements of specimen C4A.

2:4 Results:

The results of 3-terminal dielectric measurements are presented in tabulated form in appendix II-3. The accuracy of these final results depends on the magnitude of the measured dissipation factor. In Figure 2.9 the absolute accuracy of the $\tan \delta$ readings is illustrated for the range of values encountered in the present studies. Typical error analysis is presented in appendix II-4 for the case of $\tan \delta \geq 0.1$. The value of the dielectric constant (k') is accurate to within $\pm 3\%$. The values of the dielectric loss factor (k'') and the ac conductivity are as accurate, if $\tan \delta \geq 0.1$. For smaller $\tan \delta$ readings the absolute error associated with these quantities is given by the sum of the error in Figure 2.9 and 3.4%. For example, the error in a conductivity value, quoted for $f = 10^5$ cps and $\tan \delta = 10^{-4}$, is equal to 14%.

The reproducibility of results listed in the appendix was determined on the basis that measurements taken at random temperatures would lie on a smooth curve unless thermal hysteresis was involved. These effects only showed up in the results of C4A (see Figure 2.12). The room temperature electrical conductivity of this specimen differed from its original value after the specimen had been heated to 500°C. Subsequent runs of this type showed that the 500°C heat treatment had removed the thermal hysteresis.

The room temperature results are voltage dependent. A decrease in the voltage from 100 v to 10 v produced a decrease in the measured

dissipation factor of 4 to 5%, and a negligible decrease in measured capacitance of $< .01\%$. The initial room temperature $\tan \delta$ measurements of C4A varied with this change of applied voltage by about 8 to 10%. The final measurements varied by only 4 to 5%. For temperatures greater than 200°C the maximum variation was less than 1%.

This is a rather insignificant percentage variation relative to the inherent measurement inaccuracy, nevertheless, the effect is real and for this reason the voltage applied to the test specimens in these studies has been listed at the beginning of the tabulated results.

Every attempt was made to insure that measurements at various temperatures were performed with the same total pressure of the surrounding atmosphere. In general the total pressure was about 1.2×10^{-5} mm Hg. However, during the run with specimen C5A, a leak in the vacuum system caused the total pressure to rise to about 4.0×10^{-5} mm Hg.

The 3-terminal electrical conductivity measurements are illustrated in Figure 2.12, where, conventionally, the logarithm of the ac conductivity is plotted as a function of the reciprocal absolute temperature. It is apparent that straight line behaviour of the resulting curves is not obtained. The slope of most of the high temperature results tends to an asymptotic value which yields an activation energy of 1.4 to 1.5 ev. The slopes of lines drawn through the results in the temperature region 200°C to 500°C yield an activation energy of about 0.5 ev.

A cross over region connects these two possible straight line regions. There is, however, no trend in this region which may be related to either the porosity or the MgO content of the specimens in a consistent manner.

Figure 2.12. Summary of electrical conductivity results; frequency as a parameter (0, 1, 2—9 stands for 10^5 , 5×10^4 , 2×10^4 — 10^2 cps, respectively). The effect of heat treatment on specimen C4A is indicated by the additional numbered dots.

In Figure 2.14, the high frequency measurements with the doped specimens are compared with the results of Atlas et al. In spite of the many differences between the specimens and methods of measurements, both the shape of the $\log \sigma$ vs $1/T$ plot and the magnitude of the conductivity are similar.

In the temperature region 200° to 500°C in which the results are compared, the present studies indicate that the higher the added MgO content the higher the electrical conductivity and, as well, the more porous the specimen the higher the electrical conductivity.

In the higher temperature region 750°C to 1000°C where no previous comparable work exists, the present studies illustrate the reverse impurity effect, that is, the higher the added MgO content, the lower the electrical conductivity.

The effect of thermally cycling specimen C4A is illustrated in Figure 2.12 where the initial measurements (1st run) are compared with the final, reproducible measurements (3rd run).

The Dielectric Constant: The dielectric constants (k') of the pure and doped specimens as a function of temperature are illustrated in Figures 2.15 and 2.16 respectively. The dispersion of the dielectric constant at low frequencies and high temperatures increases with both increasing density and increasing added MgO content. The dielectric constant as a function of temperature at fixed frequencies illustrates an anomaly in the region of temperature close to 500°C . This anomaly is related to density and impurity content; at low frequencies and high temperatures the dielectric constant increases with both increasing density and increasing added MgO content. This is readily seen by comparing the results for the more porous and more heavily doped C4A with those for C5A.

Figure 2.14. A comparison of the electrical conductivity results of MgO doped Al_2O_3 specimens.

Figure 2.15. The dielectric constant of pure Al_2O_3 and MgO doped Al_2O_3 specimens as a function of frequency at selected temperatures.

Figure 2.16. The dielectric constant of pure Al_2O_3 and MgO doped Al_2O_3 specimens as a function of temperature at selected frequencies.

A discrepancy between the present studies and previous work shows up in the comparison of our results with those of Atlas et al. They found that a 470 ppm MgO doped Al_2O_3 sample yielded the value of about 19.0 for k' at 500°C when the measuring frequency was 10^2 cps. For a 4N5 Al_2O_3 specimen under the same conditions, these workers quote a value between 10 and 11 for the dielectric constant whether the pure specimen was annealed in pure O_2 at 1225°C or annealed in H_2 at 1225°C . We found that the dielectric constant for all the MgO doped specimens was less than 19.0 for temperatures as high as 800°C and with any measuring frequency in the range 10^2 to 10^5 cps. For our pure material, the dielectric constant was about 15 for specimen C2B and slightly higher for the more porous C2A at temperatures close to 500°C and with the measuring frequency at 10^2 cps.

In the present studies we note that within the temperature range 20 to 500°C there is a correlation between the porosity of the specimen and the dielectric constant although it cannot be separated from the effect of added MgO content in the case of doped specimens. In the work of Atlas et al. there appears no porosity effect and this is perhaps why the effect of added impurities stands out.

The Dielectric Loss Factor (k''): The typical behaviour of the dielectric loss factor as a function of frequency is illustrated in Figure 2.17, and, equivalently, as a function of temperature in Figure 2.18. In general the dielectric loss increases as the temperature is increased or as the frequency is decreased. The slope of the loss curve at 270°C in Figure 2.17 is -0.5, and therefore the loss can be expressed by the function $A/f^{\frac{1}{2}}$ where A is a constant, at least at this temperature, and then to a good approximation this law holds for other temperatures. The dielectric loss is therefore, in general, not due to free charge

Figure 2.17. The typical behaviour of the dielectric loss factor as a function of frequency at various temperatures.

Figure 2.18. The typical behaviour of the dielectric loss factor as a function of temperature; as the frequency is decreased the anomaly shifts to lower temperatures.

conduction losses, since these latter losses have a frequency dependence of $1/f$.

The fact that parts or all of the $\log k''$ vs $\log f$ curves yield a slope of close to $-.5$ is not inconsistent with previous work. For instance, while Atlas et al. obtained from their doped specimens slopes of -1.0 , Florrio's 3-terminal measurements yield values from -1.0 to -0.5 and the work of Von Hippel³⁵ and of Matsumura¹⁴ values closer to -0.5 . Tallan and Detwiller³⁶ obtained slopes of -1.0 to 1.0 when the $\log$ of the dissipation factor was plotted as a function of $\log f$ and if one ignores the relatively small dispersion in their dielectric constant measurements then slopes of -1.0 to 1.0 are obtained for the corresponding $\log k''$ vs $\log f$ plots.

Two Terminal Measurements: One of the aims of performing accurate conductivity measurements was to assess the effect of gross surface contributions to the total conductivity. In Figure 2.19 the results of the 2-terminal measurements are compared with the results of 3-terminal measurements for the pure specimen C2A. Although there are many assumptions made in obtaining these measurements, and these are discussed fully in appendix II-1, nevertheless the observation that the 2-terminal conductivity results are higher than the 3-terminal conductivity results is consistent with the notion of high ~~conductivity~~ surface ~~effects~~ *conductivity*.

Additional Three Terminal Measurements: Some additional 3-terminal measurements were carried out on specimen C4A to which pure Pt electrodes had been bonded. The accuracy of the measurements were reduced due to the difficulty in cutting the guard ring and as well due to the missing spots of Pt on the surface area covered by the guarded electrode. The inaccuracy was estimated at about 10% for $\tan \delta$ readings greater than 0.1.

Figure 2.19. Comparison of 2-terminal and 3-terminal ac electrical conductivity results obtained from one and the same specimen of 6N Al_2O_3 (C2A).

The highest temperature reached with the specimen in position was 990°C when due to a breakdown in the existing furnace, measurements could no longer be carried out. It must be noted that with the new cell design it was necessary to monitor the water cooling supply in order to attain a minimal temperature gradient across the specimen. The results are compared in Figure 2.20. The results are tabulated in appendix II-5 where the temperature gradient as well as the total pressure are included since these factors may have influenced the results.

Although there is good agreement between the different methods of measuring the electrical conductivity of specimen C4A, the fact that there are now more readings in the temperature range 800°C to 1000°C and therefore more detail in the shape of the curve illustrates how careful one must be in interpreting the slope from the high temperature conductivity results.

If specimen C4A was inhomogeneous, one would then expect that the conductivity would depend on the volume of the specimen selected for testing. The good agreement between the results is perhaps indicative of the homogeneity of the specimens since 6% less of the central volume of the specimen was used with platinum foil electrodes than with platinum paste electrodes.

Dissipation Factor Behaviour: A typical plot of the dissipation factor (k'/k'') as a function of temperature is illustrated in Figure 2.21. The observed data can be considered to result from two loss mechanisms; the one a high temperature loss, and the other a low temperature loss. We will now consider the attempt to analyse the data on this basis.

2:5 Discussion of Results:

The effect of porosity as a separate phase cannot be separated from the effect of spinel as a separate phase in the results of the MgO

Figure 2.20. Comparison of electrical conductivity measurements on a 1% MgO doped Al_2O_3 specimen using different types of electrodes; the rectangle represents the estimated increase of inaccuracy.

Figure 2.21. The typical behaviour of dissipation factor results as a function of temperature. The data are resolved visually into two processes.

doped specimens and further, since both the pore shape and its distribution are unknown there is little possibility of accounting for the effect of porosity on the behaviour of the dielectric parameters of the pure Al_2O_3 specimens. The fact remains nevertheless that all the results in the present studies are determined in part by the effects of separate phases.

We have illustrated the typical temperature dependence of the loss mechanism (Figure 2.18) and indicated (Figure 2.21) the possibility of resolving the problem of analysis into two parts: the one a high temperature behaviour and the other a low temperature behaviour typical of the loss predicted by a Debye type function. The functional form of this low temperature loss will depend on the model chosen to represent the loss mechanism. Without any loss of generality we will consider first a simple Debye mechanism to obtain a specific functional form. We will show that the Debye function can be easily converted into the more realistic forms predicted by interfacial polarization mechanisms and by impurity-vacancy complex polarization mechanisms.

A typical plot of the dissipation factor as a function of temperature is illustrated in Figure 2.22, using the results of specimen C5A (0.01% MgO) at 10^5 cps. By considering the dielectric loss as being composed of two independent processes; the one a high temperature loss which leads to the observed conductivity result ($\sigma_0 \exp(-E_1/kT)$) and the other a debye type loss due to the relaxation of permanent dipoles, then, the illustrated dissipation factor behaviour can be expressed in the following manner:

$$\text{Tan } \delta = \frac{(1 - x)\omega\tau}{1 + x\omega^2\tau^2} + D_0 \exp(-E_1/kT) \quad (2.1)$$

where ω = angular measuring frequency

τ = a characteristic relaxation time

Figure 2.22. The dissipation factor as a function of temperature at 10^5 cps resolved into two processes:

$$\tan \delta = \frac{A\omega\tau_0 \exp(E_2/kT)}{1 + \omega^2\tau_0^2 \exp(2E_2/kT)} + D_0 \exp(-E_1/kT)$$

The R.N.S. fit between theory and experiment is illustrated in (A) for a 0.01% MgO doped Al_2O_3 specimen and in (B) for a 0.1% MgO doped Al_2O_3 specimen.

$$x = k'_{\infty} / k's$$

k'_{∞} = high frequency dielectric constant

$k's$ = static dielectric constant

D_0 = constant

The mechanism of dielectric loss most commonly considered is the relaxation of permanent or induced dipoles characterized by a relaxation time, τ , and an activation energy, E , associated with the rotation of the dipole. The simplest model based on rotation of a dipole between equilibrium positions separated by a single energy barrier predicts a relaxation time of the form $\tau_0 \exp(E_2/kT)$ and a dissipation factor of the form used in equation (2.1). Bottcher⁶³ defines k'_{∞} as the dielectric constant at a frequency sufficiently high that the relaxation process under consideration no longer occurs in which case k'_{∞} is nearly equal to $k's$, that is, x is about unity.

Restricting attention to the Debye loss only, the condition for a dissipation factor maximum is $x\omega^2\tau_m^2 = 1$, in which case the maximum is given by $\tan \delta_m = \frac{1-x}{2x^{\frac{1}{2}}}$. From Figure 2.22, this maximum should occur for $\tan \delta_m$ about $10^{-1.5}$ so that the parameter x is seen to have a value close to unity. In order to obtain the precise value of x it is necessary to locate the maximum of the Debye loss precisely. Since, in fact, this could not be done we only illustrate in Figure 2.22 the effect of resolving the observed data into the two processes summed in equation (2.1).

The theoretical curves shown in this figure were obtained by a least squares fit subject to the following conditions:

$$1) \quad \tan \delta (T_1) = D_0 \exp(-E_1/kT_1)$$

where T_1 is the highest temperature of measurements and

$$1.4 \text{ ev} \leq E_1 \leq 1.5 \text{ ev}$$

2) $0.5 \text{ ev} \leq E_2 \leq 0.6 \text{ ev}.$

The first condition was obtained from the high temperature conductivity results and the second condition was obtained from the conductivity results in the temperature region 200 to 500°C.

The discrepancies between theory and experiment may be due in part to the stringent conditions on the choice of activation energies but no other reasonable assumptions for these energies are available. They may also be due to the wrong choice of the loss function. However, in favor of the choice of this function is the reasonable fit it gives to the experimental data and as well the reasonable explanation for the displacement of $\tan \delta$ (max) to lower temperatures as the frequency is decreased. This last mentioned behaviour of $\tan \delta$ is illustrated in Figure 2.23. The displacement of $\tan \delta$ (max) to lower temperatures as the frequency is decreased is predicted from the maximum condition:

$$T (\text{max}) = -E_1 / (k \log (\omega \tau_0)) \quad (2.2)$$

The function $(1 - x) \omega \tau / (1 + x \omega^2 \tau^2)$ can now be replaced by the function $A \omega \tau / (1 + \omega^2 \tau^2)$ since the value of x has been shown to near unity. The condition for maximum remains the same, namely, $\omega^2 \tau_m^2 = 1$. For low temperatures, that is below 500°C, the high temperature part of equation (2.1) is negligible. At low temperatures, $\tan \delta$ is well represented by $A \omega^{-1} \tau^{-1}$, at least, as far as its temperature dependence is concerned. A plot of $\log \tan \delta$ vs $\log \omega$ is then a straight line of slope -1, if A is frequency independent. However, this is not observed, instead a slope of about -.5 is observed. It is known that Debye type capacitors have a loss factor k'' which is dependent on frequency in a manner that a plot of $\log k''$ vs $\log \omega$ yields a slope of -1.0. We therefore exclude all models that lead to Debye type loss mechanisms.

Figure 2.23. The dissipation factor of a pure Al_2O_3 specimen: As illustrated in (A) the loss represented by a Debye type function has a maximum in the temperature direction which shifts to lower temperatures as the frequency is decreased. As illustrated in (B) the slopes at various temperatures yield the empirical relation $\tan \delta \approx f^{-2}$.

For example, the dissipation factor for impurity-vacancy complexes as derived by Lidiard for ionic conductors is of the form used here for the low temperature $\tan \delta$ observations, and even though the possibility of $\text{Mg}^{2+}(\text{Al}^{3+})_v$ type complexes are imaginable for vacuum sintered MgO doped Al_2O_3 specimens, there is no frequency dependence in the parameters that make up A to explain away the observed frequency behaviour.

— — In many of the investigations of the dielectric properties of Al_2O_3 , an interfacial polarization mechanism has been proposed to explain the high apparent dielectric constant and losses that were measured.^{9,15,20,21,36} If two distinct phases exist in a dielectric, differing from each other in dielectric constant and conductivity the effect of an applied field is to produce an accumulation of charge at the phase interfaces and thereby to produce a net polarization. A generalized treatment of the case of conducting particles uniformly distributed throughout a dielectric has been treated by Sillars.³⁷ For this case the dissipation factor is given by:

$$\begin{aligned} \tan \delta &= \frac{B\omega\tau}{B + (1 + \omega^2\tau^2)\epsilon_\infty/\epsilon_1} & (2.3) \\ \epsilon_\infty &= \epsilon_1 \left[1 + \frac{cn(\epsilon_2 - \epsilon_1)}{\epsilon_1(n-1) + \epsilon_2} \right] \\ B &\equiv cn^2\epsilon_1/[\epsilon_1(n-1) + \epsilon_2] \\ \tau &\equiv [\epsilon_1(n-1) + \epsilon_2]/4\pi\sigma_2 \end{aligned}$$

where ϵ_1 , ϵ_2 , are the real parts of the complex permittivities of the insulating and conducting portions of a crystal, c is the fractional volume of conducting phase, σ_2 is the conductivity of the more conducting phase, and n is a measure of the eccentricity of the conducting particle (one for a flat plate, three for a sphere and approximately the square of the axial ratio for extremely prolate

spheroids). The necessary condition for a dissipation maximum is

$$\omega^2 \tau_m^2 = (B\epsilon_1/\epsilon_\infty + 1) \quad (2.4)$$

and the magnitude of the dissipation factor maximum is given by

$$\tan \delta_m = B\epsilon_1/2\epsilon_2[1 + B\epsilon_1/\epsilon_\infty] \quad (2.5)$$

We note the similarity of equations (2.1) and (2.2) to (2.3) and (2.5).

The existence of the spinel phase in the MgO doped Al_2O_3 specimens has already been noted, it is not known whether or not this is a more conductive phase or for that matter what are its dielectric properties as a function of frequency and temperature. In the case of pure Al_2O_3 there is the obvious second phase of porosity but again the shape and distribution of the pores is unknown. The specimens used in the present studies were sintered. Grain boundaries are common to all the specimens. The role of grain boundaries is quantitatively uncertain although qualitatively it is expected they serve in an otherwise periodic lattice as sources of defects exceeding the normal distribution predicted by Shottky or Frenkel. They may thereby produce electrical double layers.³⁶ The common possibility that an electrical double layer, consisting of a net surface charge and a compensating space charge under the surface, exists at the external boundary of a specimen because of an equilibrium concentration gradient of defects. In the simple case of stoichiometric Al_2O_3 if the energy to form a cation vacancy is less than that required to form an anion vacancy an excess of cation vacancies will be emitted into the crystal and the surface will contain cation and anion vacancies in excess of their bulk equilibrium values. The surface would therefore behave like a ~~an n-type~~ ^{negatively charged} (metal-excess) material. Mass balance and

electroneutrality are maintained by the existence of a ~~p-type~~ ^{positively charged} metal-deficient region below the surface. If the loss behaviour observed is due to interfacial polarization associated with the higher conductivity of the surface double layer then the appropriate model is simply a dielectric containing layers of conducting material, in which case $n = 1.0$ so that equations (2.3) to (2.5) are simplified. If we now assume that the permittivities are essentially the same then $\tan \delta_{\max} \approx t_s/t_{\text{total}}$ where, t_s , is the effective thickness of the space charge double layer.

Using the most reliable value for the low temperature dissipation factor maximum of 0.024 on a 1 mm thick specimen, (G5A), the effective thickness of the conducting layer is about 24μ . Thus the observed conductivity is not truly a surface phenomenon, but instead occurs in a volume element extending under the surface to a depth comparable to the observed grain size of about 30μ .

With these assumptions, then

$$\tan \delta = \frac{2(t_s/t)\omega\tau}{1 + \omega^2\tau^2} \quad \text{for small } T$$

$$\text{and } \tau = \frac{\epsilon}{4\pi\sigma} = \frac{\epsilon}{4\pi\sigma_0} \exp(E_2/kT) \quad \text{for small } T$$

Where ϵ is the assumed common representation of the real parts of the respective permittivities of both phases.

On the basis of this model the observed variations of dissipation factor for low temperature can be interpreted as variations in the activation energy and pre-exponential factor for conduction in the double-charge layer. The slope of the $\log \tan \delta$ vs $\log \omega$ plot is now seen to be different from -1.0 if any of the factors t_s , ϵ , and σ_0 are frequency dependent.

For small T , $\tan \delta \rightarrow \omega^2 \frac{t_s}{t} \frac{4\pi\sigma_0}{\epsilon} \exp(-E_2/kT)$

In order to obtain the slope $-.5$ the quantity $(t_s \sigma_0/\epsilon)$ must vary as $\omega^{-3/2}$.

However, there is no theoretical foundation at present for this expression; furthermore, the high temperature portion of $\tan \delta$ still leads to a slope of -0.5 on the $\log \tan \delta$ vs. $\log \omega$ plot which we cannot account for.

If we now consider the possibility of double charge layers occurring at grain boundaries we must then make some assumptions as to the distribution and shape of these barriers. In dielectric theory³⁸ the need for a distribution of relaxation times is often encountered in order to obtain an empirical fit. However, even if the low temperature behaviour of the results could be represented in this fashion we are forced to explain the frequency dependence of the high temperature behaviour. In view of the lack of high temperature results and consequently the uncertainty introduced in the assumption that the loss is due to two mechanisms, we have instead attempted by additional experiments to gain some insight into the nature of the defects that could possibly produce the observed dielectric loss.

In summary, the temperature dependence of the dielectric loss can be interpreted by any of the mechanisms mentioned which lead to equation (2.1). Preference is given to the double layer interfacial polarization mechanism because grain boundaries and electrode-ceramic interface barriers are common to the specimens. The frequency dependence of the results cannot be satisfactorily interpreted on the basis of any of the proposed loss mechanisms. We note that the predictions of the blocking theories of Friauf³⁹ and MacDonald⁴⁰ have been compared to the results reported herein and do not provide a

satisfactory frequency dependence.

Since the pure Al_2O_3 used in these studies represented a decrease in impurity by 50 ppm over the material used by Atlas et al., and since, furthermore, the specimens were considerably more dense, it was felt that the free electron conduction losses reported by these workers at 500°C would dominate the conduction mechanism. We have apparently complicated the interpretation of results by reducing both porosity and impurity. The free electron conduction loss measured by these workers is either masked by a polarization mechanism or the electrons are so effectively trapped at defects that their mobility has been reduced to but a fraction of what one could expect. In the next section we consider in detail thermoluminescence studies which were initiated in an attempt to gain insight into the defect structure of the specimens.

SECTION III

THERMOLUMINESCENCE IN ALUMINUM OXIDE

3:1 Introduction:

The phenomenon of light emission from a substance as it is heated at temperatures well below those required for normal black-body radiation is termed thermoluminescence. To observe thermoluminescence energy must first be stored in the substance. This is usually accomplished by excitation with high energy radiation or particles. Aluminum oxide excited by γ -radiation,^{6,41,42} U.V. light,³ neutrons,^{22,44} mechanical strain,⁴² or heat,⁴⁵ exhibits thermoluminescence.

In aluminum oxide, thermoluminescence is believed to occur when, due to thermal excitation, either electrons or holes leave sites at which they were metastably trapped and subsequently recombine with other trapped holes or electrons. A qualitative explanation of thermoluminescence in aluminum oxide can be given in terms of an energy band model.

3:2 A Model for Thermoluminescence in Aluminum Oxide:

One of the many possible energy band models of Al_2O_3 is shown in Figure 3.1.

The valence electrons of the host constituents, Aluminum and Oxygen atoms, fill the highest occupied band, the valence band. Impurities and other defects in the lattice usually give rise to discrete, localized levels in the forbidden energy gap, called luminous centers. The ground state of each luminous center is occupied. Impurities and defects also give rise to the unoccupied levels which are called traps. These traps may also be unoccupied metastable

3.1. The model proposed for thermoluminescence in Al_2O_3 .

excited states of the luminous centers.

Excitation may take place, for example, by photon absorption in the lattice resulting in the transition $a \rightarrow b$, Figure 3.1. Electrons from the valence band are then raised into the lowest unoccupied energy band, the conduction band, where they can migrate freely. The states in the valence band vacated by the electrons, positively charged holes, are also mobile. These migrate to the luminous centers and capture the ground state electrons, thus emptying the centers which then become capable of recapturing the conduction electrons. However, during this excitation process some electrons will be captured by the traps and will only be able to return to their normal states via the conduction band. Such a return journey can be initiated by heating, then trapped electrons are thermally excited into the conduction band and return to the ground state of the luminous centers by either a radiative or a non-radiative transition, the light emitted during the radiative transitions being characteristic of the luminous centers.

If the specimen is rapidly raised to a fixed temperature sufficient for the release of trapped electrons then the light output will decay with time. If however, the temperature of the specimen is raised continuously from a low to a high value relative to the temperature at which trapped electrons are thermally released, the light output will be seen to start at zero, rise to a maximum and fall to zero again. A display of the light intensity as a function of the temperature as the specimen is heated at a constant rate is termed a glow curve.⁴⁶ The glow curve characteristic of the model just discussed consists of a single peak; the temperature at which maximum glow occurs being a measure of the energy, E_T , required to release a

trapped electron and the area under the peak being a measure of the number and location of traps. Furthermore, the light released during thermoluminescence can under certain circumstances be analysed spectrographically. Such emission studies will yield a measure of the number and location of luminous centers, since a measurement of the frequency of the emitted light is a measure of the activation energy, E_L , of the luminous centers, and the intensity of the emitted light is a measure of the number of luminous centers.

3:3 The Analysis of Glow Curves:

In general a considerable amount of theoretical work has been done to predict the shape of glow curves.⁴⁷ However, in previous work with Al_2O_3 only the simplest of theories has been used to explain thermoluminescence phenomena. First or second order theory when applied to the model of Al_2O_3 , Figure 3.1, yields a glow curve which has a single peak. Since glow curves, however, seldom consist of a single peak but rather a complex series of overlapping peaks it has generally been assumed that each peak in a complex glow curve can be related to an independent process. For example, Figure 3.12 illustrates a complex glow curve which was obtained from a γ -irradiated single crystal of Al_2O_3 . It consists of four overlapping peaks and therefore, using the above assumption, there are four independent processes involved. In terms of the model, Figure 3.1, this glow curve may be interpreted as being due to the successive emptying of traps of energy depths $E_1 \leq E_2 \leq E_3 \leq E_4$ as the crystal is heated up.

The problem of a quantitative interpretation of glow curves has consisted of attempts to resolve the curves into separated peaks each of which may then be analysed by itself on the basic assumption that the individual processes involved are independent and their effects

additive.

One extensively used approach to this problem of resolving a complex curve into separated peaks is an experimental procedure called "saw-tooth annealing".⁴⁸ This method consists of heating a specimen and recording the light output until just after the first maximum (pt. A Figure 3.12) is over and then allowing the specimen to cool until the light output falls to the background zero level. The peak obtained in this manner is termed a "resolved peak". This process of heating and cooling is then repeated for peak after peak until all the "resolved peaks" are obtained. The series of "resolved peaks" so obtained are analysed in terms of a theory based on a physical model of the specimen. The application of first or second order theory leads to a quantitative measure of the trap depth energies.

The most extensive work so far reported, that of Atlas and Firestone,⁶ for γ -irradiated 4N5 Al_2O_3 , consisted of just such a resolution into "peaks" with the subsequent application of Grossweiner's first order theory.⁴⁹ Most of the resolved peaks were related to impurities intentionally introduced into pure Al_2O_3 and to defects introduced by varying the atmosphere in which the high purity Al_2O_3 was fired.

There are, however, three objections to the reported work of Atlas and Firestone:

- 1) Grossweiner's analysis contains a mathematical error
- 2) the method of "saw-tooth annealing" leads to a series of "resolved peaks" which still includes overlapping effects.

It, further, leads to a derived value of one of the theoretical parameters, the attempt frequency factor, which, so far, is inconsistent with a physically interpretable

value of this quantity

and 3) no attempt was made to justify the use of first order theory in describing the observed "resolved peaks".

We consider first the basis of Grossweiner's work which is a relation developed by Randall and Wilkins.⁴⁶ The energy of an electron trap, E , is considered to be single-valued. An electron once released from a trap must recombine with a luminous center, that is the possibility of retrapping is not considered. The recombination process may be either a radiative transition in which case light will be emitted or a non-radiative transition in which case energy is re-distributed in the lattice by phonon-electron collision processes. Denoting the probability of radiative transitions by P_r , and the probability of non-radiative transitions by $P_{n.r.}$, the luminous efficiency, η , becomes:

$$\eta = \frac{P_r}{P_r + P_{n.r.}}$$

η is assumed to be constant; that is, there is the constant probability of light emission. The electrons in traps have a Maxwellian distribution of thermal energies so that the probability per second of an electron escaping at a temperature T is:

$$P = s \exp(-E/kT) \quad (3.1)$$

where k = Boltzmann Constant

and s = Attempt Frequency Factor

If the trap is regarded as a potential box then the factor, s , expresses the product of the frequency with which the electron hits the sides of the box and the reflection coefficient.⁵⁰ Mott and Gurney⁵⁰ have shown by an order of magnitude calculation that the value of, s , should be less than the frequency of a lattice vibration

which is of the order of 10^{13} sec^{-1} . The temperature variation of the attempt frequency factor is considered negligible relative to the exponential factor in equation (3.1)

Under these conditions, the intensity of emitted light, I , is proportional to the rate, dn/dt , at which electrons escape from the traps which in turn depends in part on the number, n , of electrons in the traps and in part on the probability of escape, so that the following first order kinetic equation results:

$$I = -C \frac{dn}{dt} = CPn \quad (3.2)$$

where C is a constant which depends on the luminous efficiency and on the geometry of the measuring system. Of immediate consequence is the exponential decay of the intensity of emitted light with time when the temperature is constant:

$$I = I_0 \exp(-t/\tau) \quad (3.3)$$

$$\text{where } \tau = \exp(E/kT)/s \quad (3.4)$$

Heating at a constant rate (β°/sec), the predicted form of the light output, the Randall and Wilkins relation, becomes:

$$I = C n_0 s \exp\left(-u - \frac{sE}{\beta k} \int_u^\infty \frac{\exp(-x)dx}{x^2}\right) \quad (3.5)$$

where n_0 = number of traps initially filled and $u = E/kT$.

Grossweiner stated that if a glow curve described by equation (3.5) was sufficiently resolved to obtain a measure of the temperature, T^* , at which the intensity is a maximum and the temperature, T' , at which the intensity first reaches one half the maximum value, then the thermal activation energy, E , of a trap would be given by:

$$E = 1.51 k \frac{T^* T'}{T^* - T'} \quad (3.6)$$

with an uncertainty of $\pm 5\%$ if $u > 20$, and $s/\beta > 10^7$.

This, however, is incorrect. The result should be:

$$E = 1.46 k \frac{T^* T'}{T^* - T'} \quad (3.7)$$

with an uncertainty of $\pm 5\%$ if $u \geq 17$, and with no restriction on s/β .

The mathematical steps taken in arriving at equation (3.7) starting with equation (3.5) are presented as a separate topic since they provide the basis for a new method of analysis of glow curves. The use of equation (3.7) is restricted to glow curves where an unambiguous determination of T^* and T' can be made. If, however, the experimental method of saw-tooth annealing is used to obtain the "resolved peaks" from which T^* and T' are to be determined, then the values of T^* and T' contain overlap effects and the uncertainty increases. For instance consider a first order glow curve obtained by heating a hypothetical substance at the constant rate, $\beta^\circ/\text{sec.}$, as shown in Figure 3.2A. The method of saw-tooth annealing yields the "resolved peak", section A to B, as shown. The shaded area under the section B to C represents the luminous energy that would be stored had this 'specimen' been instantly cooled on reaching the temperature T_B during the first heating up cycle. However, in an experiment there is a finite amount of time involved at T_B and temperatures close to T_B as the sample is cooled, so that a portion of the intensity at T_B decays continuously. It would be difficult to calculate the exact intensity of the peak obtained as the sample is re-heated to T_C . In Figure 3.2 this effect is illustrated by the small shaded area which peaks at T . The application of saw-tooth annealing to a hypothetical specimen, in principle, leads to two "peaks" as shown, whereas the continuous heating of this hypothetical specimen from T_A to T_C yields but one first order glow curve.

Consider now a particular case in which a hypothetical specimen

Figure 3.2. The application of saw-tooth annealing to theoretical first order glow curves: (A) The first order glow curve obtained by heating a hypothetical substance from T_A to T_C . The possibility of two "peaks" is illustrated when two runs of heating from T_A to T_B are carried out; (B) Two overlapping first order processes described by E_1 , E_2 , and T_1^* and T_2^* have been added to illustrate that the saw-tooth annealed section A to B will yield a trap depth energy, E , which is inaccurate due to overlap effects.

produces the glow curve illustrated in Figure 3.2B which is the sum of two overlapping first order curves. In this particular case the second major peak is already sufficiently resolved to yield T_2^* and T_2' so that a theoretical curve could be fitted to this section. Subtracting this theoretical curve from the complete glow curve results in the isolation of the first major 'peak' which in turn can be analysed by measuring T_1^* and T_1' . Saw-tooth annealing will give two (at least) "resolved peaks" on heating to T_C . The first "resolved peak" section A to B contains overlap effects due to the neighboring peak as shown. The trap depth energy, E , obtained from this annealed peak by measuring T^* and T' is seen to differ from the value, E_1 , used to draw the curve. It is readily shown that:

$$E \approx E_1 \frac{(T_1^* - T^*)}{(T^* - T_1')}$$

(The second "resolved peak" obtained on heating again to T_C contains a contribution from the process responsible for the first major peak, that is it contains the luminous output illustrated by the small shaded peak in Figure 3.2A).

Additional criteria are necessary to account for overlap effects when saw-tooth annealing is the procedure followed. A nebulous factor of 10 to 20% was used by Atlas and Firestone to account for overlap effects in saw-tooth annealed peaks obtained from Al_2O_3 specimens. Values of T^* and T' obtained from these "resolved peaks" were used to calculate a value of the trap depth energy as given by Grossweiner's formula. However, due to the uncertainty in the values of T^* and T' due to the overlap effects, the value of E obtained in this manner is questionable.

The uncertainty in E that results from overlap effects is

considered in appendix III-1, where it is shown that with even the most conservative assumptions, the experimental error may be as high as 40%. If overlap effects cannot be properly accounted for then the experimental procedure of saw-tooth annealing is of little value.

The condition for maximum glow predicted by the Randall and Wilkins relation is:

$$\frac{s}{\beta} \frac{E}{k} = u^* \exp(u^*)$$

so that once a value E is obtained, the value of the attempt frequency factor can be calculated. It is interesting to note that values of the attempt frequency factor derived in this manner, using some of the data of Atlas and Firestone, are as high as 10^{22} sec.⁻¹; a factor of 10^9 higher than the upper limit as set by Mott and Gurney. We will elaborate this point in section 3:8.

3:4 Purpose of the Study of Thermoluminescence in Al₂O₃:

In previous work impurities and lattice defects were related to annealed "peaks" of Al₂O₃ glow curves. Since the trap depth energies were in doubt for the three reasons given above, the thermoluminescence properties of Al₂O₃ were investigated.

The ultimate aim of the luminescence studies reported here was to measure the activation energies of electrons and/or holes which characterize traps and centers, because the activation energies obtained in these studies are related to the thermal activation energies measured in electrical conductivity experiments when the phenomenon of electrical conduction is due to the motion of electronic charge carriers; that is, luminescence studies yield information about the electronic contribution to the total conductivity.^{50,51}

In view of the problems encountered in the analysis of the

results of previous work, this section, section III, is devoted to the discussion of luminescence studies and the analysis of results obtained from γ -irradiated, 6N Al_2O_3 and MgO doped 6N Al_2O_3 , specimens. The attempt to relate these studies with the results of previously discussed electrical conductivity work will be considered as a separate topic in section IV.

3:5 The Apparatus and Specimens Used for Luminescence Studies:

Specimens: A description of the samples used for luminescence studies is presented in Table 3.1. Experiments on Linde and N.R.C. Al_2O_3 specimens were included because a considerable amount of the previously reported investigations of luminescence (and conductivity) in Al_2O_3 have dealt with specimens fabricated by the Linde Company into single crystals or fabricated by the individual researcher into sintered specimens starting with Linde Al_2O_3 powders.

The surfaces of each specimen were finished by employing the technique described in conductivity measurements. The thickness of each specimen was 0.1 cm, and the diameter varied from 2.0 to 2.7 cms.

Excitation of Samples: The test specimens were irradiated by Co^{60} γ -rays by placing them in the center of an AEC #220 GAMMACELL for exactly one hour. Thus all specimens received the same nominal dose of 5×10^5 Roentgens, this dosage being selected to reproduce the experimental conditions of Atlas and Firestone.⁶ The exact value of the dosage is not important, as first Hunt and Schuler⁵¹ and then Levy and Dienes⁴⁴ have shown that the effects of the radiation already reach saturation at a value of about $2 \times 10^3\text{R}$.

Apparatus for Glow Curve Experiments: The apparatus used for the thermoluminescence studies is shown in Figure 3.4. It consists of a light-tight vessel containing a heating assembly at one end and a

Table 3.1

Specimens used for thermoluminescence studies

Sample Name	Major Constituents	Remarks
C1B C1D C1E	6N Al_2O_3	Three specimens cut from the sintered mass (C1) described in section II.
C5A C3A C4A	6N Al_2O_3 + 0.01% MgO 6N Al_2O_3 + 0.1% MgO 6N Al_2O_3 + 1.0% MgO	One specimen of each of the respective masses (C5), (C3), (C4), described in section II.
N.R.C.	$\approx$ 4N Al_2O_3	Three vacuum sintered specimens† 1.3% porous.
Linde	$\approx$ 4N Al_2O_3	A single crystal from Linde.

† Obtained from Dr. M. Laubitz, N.R.C.

Figure 3.4. Schematic illustration of the apparatus used for thermoluminescence studies.

water cooled photomultiplier detector at the other. Irradiated specimens are clamped against the stainless steel insert (C) by tightening four screws in the stainless steel ring (E). When mounted, the specimens are positioned directly above the window of the detector.

The stainless steel insert (C) is press fitted into a copper disk (D) to which a flat spiral heating element is silver soldered (B). A Boron Nitride ring (H) acts as a heat flow barrier between the heater assembly and the photomultiplier tube.

Temperature was measured by a thermocouple corrected for the effect of a temperature gradient across the specimen; this correction factor was obtained in a dummy run. Subsequently, all temperature measurements were made with the Chromel-Alumel⁵² thermocouple (A) imbedded in the stainless steel insert. The heater assembly was powered by a G.R. variac transformer coupled to the synchronous motor drive described in section II. A typical heating rate is shown in Figure 3.3. It was found that approximately 50°C sections of the heating rate could be visually approximated by straight lines.

The detector (M) was part of an Eldorado (PH-200) Universal Photomultiplier Photometer containing an R.C.A. 931A photomultiplier tube. The current sensitivity of the Photometer covered 5 ranges: 10^{-3} to $10\mu\text{A}$ in decade steps. Output of the Photometer was displayed on a Philips 10 mv. strip chart recorder.

Preliminary measurements indicated that the mean dark current level rose as a specimen was heated from 375°C to higher temperatures. The effect was not completely reproducible and so the upper useful limit of approximately 375°C was established for experiments with this apparatus.

Apparatus for Emission Studies: Emission studies were carried out at

Figure 3.3. (A) Typical heating rate used in thermoluminescence and emission studies. (B) Correction factors for emission apparatus (supplied by Dr. F. Lipsett).

Dr. F. Lipsett's N.R.C. laboratory, using his equipment. A description of the apparatus has been published.⁵³ The apparatus consisted essentially of a reflection grating monochromator equipped with an automatic scanning device over wavelengths from 3000 Å to 6000 Å. The basic optical system is shown in Figure 3.6. The specimen shown in this figure was replaced by an Al_2O_3 specimen mounted in the heater assembly of the thermoluminescence apparatus just described. The grating apparatus was used as a single monochromator to obtain emission data because of the low level of light intensity emitted by the specimens. The wavelength bandpass of the instrument used in this manner was estimated to be approximately 100 Å.⁵⁴ The short time available to use the equipment resulted in very few completed emission studies.

3:6 Experimental Procedure:

Three types of experiments were carried out; glow curve experiments, decay studies and emission studies. The procedure used for each type is now discussed.

The procedure followed in obtaining a glow curve consisted of heating a specimen at a constant rate and recording the light output as a function of time on the most sensitive range of the equipment possible at any particular time, right up to the maximum temperature which corresponds to about 375°C. The temperature of the specimen was continuously recorded as a function of time on another recorder, with the time axes of both the light output and temperature recorders synchronized by small dc pulses. Glow curves were then plotted from the recorder charts.

The reproducibility of thermoluminescence experiments carried out with this apparatus depended to a large extent on obtaining

Figure 3.6. Basic optical system.†

† Copied with permission from photograph supplied by Dr. F. Lipsett of N.R.C. Canada.

reproducible heating rates. Reproducible results were obtained in the temperature interval 50 to 300°C.

Decay studies consisted of holding constant the power input to the thermoluminescence heater assembly, at some particular temperature during a heating cycle, and recording the light output as a function of time. Since, however, the heater had a large thermal inertia, 5 to 15 minutes were required for it to reach a constant temperature after the power input was stabilized. The degree of constancy of temperature required in decay studies is discussed in detail in appendix III-2. It appears that an error of $\pm 3^\circ$ in temperature measurements leads to an uncertainty of $\pm 20\%$ in a measured decay time constant. Decay studies with the present apparatus were restricted to intense peaks because with an intense peak the decay can be followed for a time comparable to the drift time involved in achieving a constant temperature.

To obtain emission data the specimens were attached to Dr. Lipsett's apparatus. The light output of irradiated specimens heated at a constant rate was scanned continually from 2000 Å to 6000 Å, to find emission bands. Once emission bands were found, the length of scan was restricted to cover just the wavelengths of the bands. The recorded emission bands were corrected for photomultiplier tube response effects using the supplied⁵⁴ correction factors (see Figure 3.3).

3:7 Results:

Effects of γ -irradiation: The data presented in this section are a direct result of γ -irradiation since unirradiated specimens did not exhibit luminescence. The effects of γ -irradiation are annealed out when a specimen is heated to 400°C. The sintered specimens used in these experiments were white to the eye before irradiation. Upon irradiation, some visible colour changes occurred. The N.R.C. material

turned slightly brownish. The 1.0% and 0.1% MgO doped specimens turned slightly yellowish and the 0.01% MgO doped specimen turned slightly yellow. The 6N Al_2O_3 specimens showed no visible colour changes.

It has been shown⁴³ that γ -irradiation produces new absorption bands in Al_2O_3 ; the visible colour changes noted above probably result from new absorption bands in the specimens. However, absorption studies with sintered specimens are complicated by grain boundary scattering and particle size effects so that experimental verification of the nature and wavelength location of new absorption bands could not be obtained. It is generally found in optical studies with single crystals that the emission band maximum is displaced to higher wavelengths relative to the absorption band maximum.⁵⁵ Consequently the existence of emission bands can be used to infer the existence of absorption bands at lower wavelengths. The fact that the 6N Al_2O_3 specimens did not change colour upon irradiation whereas all other irradiated specimens did seems to suggest that impurities lead to new absorption bands and hence emission bands.

Emission Studies: The complete results of emission experiments are presented in Appendix III-8. The two most intense emission bands recorded at 3300 Å and 5150 Å are illustrated in Figure 3.5. Although there is not a considerable amount of data, the inference that γ -irradiation produces new absorption bands in Al_2O_3 is borne out in fact by the existence of the emission bands which only appear when the Al_2O_3 specimens are irradiated.

The 5150 Å emission band found in the MgO doped Al_2O_3 specimen and the 5500 Å emission band found in the N.R.C. Al_2O_3 specimen are probably due to impurities since these bands do not appear in pure Al_2O_3 .

(A)

(B)

Figure 3.5. Typical results from emission studies: The experimental data (solid lines) and the same data corrected for photomultiplier tube response and grating anomalies (dashed lines) are illustrated; in (A), for a γ -irradiated 6N Al_2O_3 specimen and in (B), for a γ -irradiated 1.0% MgO doped Al_2O_3 specimen: Light emitted from the specimens, heated at a constant rate, was analysed with a grating monochromator; scan speed of about 10^3 Å/min.

The 3300 Å emission band was the only one detected in the wavelength range 3000 to 6000 Å in 6N Al₂O₃. Since the absorption band peak wavelength would be less than 3300 Å, one would not expect any colour change in irradiated 6N Al₂O₃, as indeed was the case.

Thermoluminescence Studies: Typical glow curves obtained from the Al₂O₃ specimens are presented in Figures 3.7 to 3.12. The most intense peak of a glow curve of each specimen was arbitrarily set at 100 and all other peaks were scaled accordingly. In Table 3.3 are listed the ratios of the maximum intensity of each observed peak to the maximum intensity of the most intense peak observed. For successive runs with one and the same specimen, the peak position could be reproduced within 2°C in the temperature range of 50 to 300°C and the peak intensity within 5%. The three N.R.C. specimens gave reproducible results within this accuracy so that one typical glow curve only has been shown. This was not the case for the 3 specimens cut from the starting sintered mass of 6N Al₂O₃ and consequently all glow curves have been included which are typical of each specimen.

Decay Results: The results of decay studies attempted with the previously described thermoluminescence are presented in appendix III-3. Only those results are included for which the decaying light intensity was measurable for a period of time greater than the drift time of the apparatus, and for which the temperature remained constant within ±1°. The decay data that was obtained was fitted to the decay laws of first and second order which as will be shown in the next section are:

$$I = I_0 \exp(-t/\tau)$$

$$\text{and } I = I_0/(1 + t/\tau)^2 \dots, \text{ respectively.}$$

As shown in appendix III-3, the decay data for specimen C3A is

Figure 3.7. A typical glow curve obtained from a γ -irradiated 6N Al_2O_3 specimen (solid line): In (A), the experimental curve is resolved into three first order processes (dashed lines); in (B), the experimental curve is resolved into two second order processes (dashed lines). The result of subtracting the sum of the fitted theoretical curves is indicated by the open circled points.

Figure 3.8. Typical glow curves obtained from γ -irradiated 6N Al_2O_3 specimens (solid lines): The experimental curves are shown resolved into first order processes (dashed lines); the result of subtracting the theoretical curves from the experimental curves is indicated by the open circled points.

Figure 3.9. Typical glow curve from a 0.01% MgO doped Al_2O_3 specimen (solid line): In (A), the result of subtracting a theoretical first order curve from the most intense peak suggests the possibility of a new "peak" at about 150°C; in (B), the dots represent the result of subtracting two separated second order processes; a third second order theoretical curve was fitted to the dots.

Figure 3.10. Typical glow curve from a 0.1% MgO doped Al_2O_3 specimen (solid line): In (A), the result of subtracting two theoretical first order processes (dashed lines) is indicated by the open circled points; in (B), the dots represent the result of subtracting two second order processes (dashed lines); a third theoretical curve was fitted to the dots.

Figure 3.11. Typical glow curve from a 1.0% MgO doped Al_2O_3 specimen (solid line): In (A), the most intense peak is fitted by a first order process; in (B), the dots represent the result of subtracting two second order processes (dashed lines); a third theoretical curve was fitted to the dots.

Figure 3.12. Typical glow curves obtained from a Linde sapphire (A) and from specimens of Linde micropolishing Al_2O_3 sintered by N.R.C. (B). The glow curve in (B) was resolved into three first order processes; the high temperature peak was saw-tooth annealed.

well represented by a first order decay; however, in this particular case the drift time of the apparatus was nearly 16 minutes. Several attempts were made in subsequent decay studies to reduce the drift time. Since the temperature always rose during this period of time, these attempts consisted of reducing the power input to the heater slightly when a decay experiment was initiated. Results of these decay studies obtained in this manner for sample C5A are presented in the appendix III-3; however, attempts to reproduce this data failed. The results obtained from sample C5A seem to indicate that second order theory provides a better fit in comparison to the fit obtained from first order.

In view of the difficulties encountered in the decay studies reported here, the results of these measurements do not unequivocally determine the choice of the theory, first or second order, which should be used. However, these are the simplest of the current theories⁴⁷ of thermoluminescence and we will use them in the analysis of glow curves.

3:8 Discussion of Results:

A New Method of Glow Curve Analysis: In the preceeding section we have presented the experimental glow curves of 6N Al_2O_3 and MgO doped 6N Al_2O_3 . In this section we will consider the analysis of these curves, the primary aim being the determination of trap depth energies.

In previous work aluminum oxide glow curves were analysed in terms of first order theory with the exception of one peak in one glow curve which was analysed in terms of second order theory²³, but since no attempt was made to compare theory and experiment, it is not known whether or not first or second order theory actually describes the observed phenomenon of thermoluminescence. We will show that any of

the experimental glow curves obtained in the present studies can be fitted better by a series of overlapping second order processes than by a series of overlapping first order processes. Since first order theory was used more commonly as the basis of analysis than second order theory, we consider the former theory first in presenting our new method of analysis.

The Randall and Wilkins' relation developed in section 3.3 is taken as the starting point for the analysis of first order glow curves. The intensity as a function of temperature is given by this relation as:

$$I = C n_0 s \exp(-u - \int_u^{\infty} \frac{s E}{\beta k} \frac{\exp(-x)}{x^2} dx) \quad (3.5)$$

This description of the light output, however, contains the parameters C , n_0 , s , and E . Although these parameters are considered independent of temperature, their magnitudes are unknown. The procedure of deriving an expression for the energy, E , in terms of quantities which are obtained directly from an experimental glow curve is now considered.

The integral in equation (3.5) can be approximated by the expression:

$$\frac{\exp(-u)}{u^2} S(u)$$

$$\text{where } S(u) = \sum_{n=0}^N (n+1)! (-1)^n / u^n$$

N being chosen such that $|(-1)^N (N+1)! / u^N| / S(u) \leq 10^{-5}$, *for a given value of u .*

This approximation is derived by Δ integrations by parts and is ~~valid~~ *attainable when* ~~to 10 ppm where~~ $u \geq 17$.

By denoting the temperature of maximum glow (I^*) by T^* a normalized expression for a first order glow curve is obtained which is independent of C , and n_0 , thus:

$$I_n = I/I^* = \exp(u^* - u + \frac{s}{\beta} \frac{E}{k} [\frac{\exp(-u^*)}{u^{*2}} S(u^*) - \frac{\exp(-u)}{u^2} S(u)]) \quad (3.8)$$

Differentiation of equation (3.5) with respect to, T , and setting the result equal to zero, yields the following relation:

$$\frac{s}{\beta} \frac{E}{k} = u^{*2} \exp(u^*)$$

Substitution of this last relation into equation (3.8) reduces the latter to a form wherein, s , and, β , do not appear explicitly, thus:

$$I_n(T, E, T^*) = \exp(u^* - u + S(u^*) - \exp(u^* - u) S(u) \frac{(u^*)^2}{(u)^2}) \quad (3.9)$$

With the intensity in this form, we see that if values of E and T^* are available then the intensity can be calculated at any temperature. At the particular temperature $T' < T^*$, the normalized intensity will have the value 0.5. It follows that:

$$0.5 = \exp(u^* - u' + S(u^*) - \exp(u^* - u') S(u') \frac{(u^*)^2}{(u')^2}) \quad (3.10)$$

Firstly, the value of E will be derived in terms of T^* and T' with the use of Grossweiner's approximations in order to compare results; then a more rigid analysis will be considered.

Grossweiner assumed that $u > 20$ and $u^*/u' \approx 1.0$. These assumptions reduce $S(u)$ to ≈ 1.0 and, hence, equation (3.10) becomes:

$$0.5 = \exp(u^* - u' + 1.0 - \exp[u^* - u'])$$

which with

$$N' \equiv u' - u^* = \frac{E}{k} \left(\frac{1}{T'} - \frac{1}{T^*} \right)$$

yields

$$1.693 = N' + \exp(-N')$$

Solving this relation for N' yields the value 1.461, differing from the value 1.51 quoted by Grossweiner.

With Grossweiner's approximations therefore applied to the expression for the normalized intensity the value of E is given by:

$$E = \alpha k \frac{T^* T'}{T^* - T'} \quad (3.11)$$

where $\alpha = 1.461$.

It should be emphasized that equation (3.11) was derived with the help of Grossweiner's approximations and that whereas Grossweiner had previously derived this relation, his derivation proceeded along different lines. The assumption that u^*/u' be > 1.0 was considered by him to be valid only for those values of $s/\beta > 10^7$. No such restriction appears in the present derivation of equation (3.11). For a value of $u \approx 17$ and a value of $T^* \approx 600^\circ$, the value of s/β was calculated to be $\approx 10^3$, very much smaller than the minimum value of 10^7 imposed by Grossweiner.

We can also compute the values of alpha with the only restrictions placed on equation (3.1) being:

$$u \geq 17$$

$$\text{and } \frac{\Delta S(u)}{S(u)} \leq 10 \text{ ppm}$$

Starting with arbitrary values of E and T^* , a value of T' was obtained from equation (3.10), using an I.B.M. 1620 computer to perform the rather lengthy calculations to eight significant figures. Once a value of T' was obtained, the corresponding value of alpha could be calculated from the expression:

$$\alpha \equiv E/k \frac{T^* T'}{T^* - T'}$$

Table (3.3) illustrates the variation in the values of alpha computed in this manner. On the basis of these results it is seen that $\alpha = 1.46$ when used in equation (3.11) will yield a value of the trap depth energy accurate to within 5% as long as $E/kT \geq 17$.

In conclusion then, if a first order glow curve is sufficiently resolved to obtain a measure of T' and T^* then a value for the trap energy depth is given by:

$$E = 1.46 k \frac{T^* T'}{T^* - T'}$$

to $\pm 5\%$ for $u \geq 17$.

Table 3.3

Computed results of the exact solutions of equations
3.10 and 3.16 expressed in terms of the parameter

$$\alpha = E(T^* - T') / kT^*T'$$

(A) 1st Order Theory

<u>E Chosen (ev)</u>	<u>T* Chosen (°K)</u>	<u>T' Calculated (°K)</u>	<u>α Calculated</u>
0.20	128.8	119.4	1.42
0.40	122.2	117.7	1.46
0.40	171.2	162.5	1.47
0.40	249.4	230.2	1.42
0.50	300	278.9	1.46
0.50	325	301.2	1.41
0.60	300	282.7	1.42
0.60	325	303.9	1.49
0.60	350	326.8	1.41
0.60	375	348.5	1.41
0.60	400	370.1	1.41
0.70	450	417.4	1.41
0.70	475	438.9	1.41
0.80	300	286.7	1.43
0.80	325	309.5	1.43
0.80	350	332.1	1.43
0.80	375	353.9	1.47
0.80	400	376.9	1.42
0.80	425	399.1	1.42
0.80	450	421.1	1.41
0.80	475	443.0	1.41
0.80	500	464.7	1.41
0.80	525	486.3	1.41
0.90	575	533.6	1.41
0.90	600	555.1	1.41
1.00	300	288.9	1.48
1.00	325	312.4	1.44
1.00	350	335.5	1.43
1.00	375	358.4	1.43
1.00	400	381.2	1.43
1.00	425	403.9	1.43
1.00	450	426.4	1.43
1.00	475	448.9	1.42
1.00	500	471.2	1.42
1.00	525	493.3	1.42
1.00	550	515.4	1.42
1.00	575	537.4	1.41
1.00	600	558.9	1.42
1.00	650	602.5	1.41
1.00	675	623.9	1.41

Table 3.3

(A) 1st Order Theory: Continued

E Chosen (ev)	T* Chosen (°K)	T' Calculated (°K)	α Calculated
1.10	750	692.8	1.40
1.20	300	290.9	1.45
1.20	325	313.9	1.51
1.20	350	337.8	1.44
1.20	375	361.0	1.44
1.20	400	384.1	1.44
1.20	425	407.2	1.43
1.20	450	430.1	1.43
1.20	475	452.9	1.43
1.20	500	475.6	1.43
1.20	525	498.2	1.43
1.20	550	520.7	1.42
1.20	575	543.1	1.42
1.20	600	565.4	1.42
1.20	800	740.2	1.41
1.30	850	787.6	1.40
1.40	300	292.2	1.44
1.40	325	315.8	1.46
1.40	350	338.9	1.52
1.40	375	362.9	1.44
1.40	400	386.3	1.44
1.40	425	409.6	1.44
1.40	450	432.8	1.43
1.40	475	455.9	1.43
1.40	500	478.9	1.43
1.40	525	501.8	1.43
1.40	550	524.6	1.43
1.40	575	547.3	1.43
1.40	600	570.0	1.42

Central value ($\pm$ range) $\alpha = 1.46 \pm .06$

Table 3.3

(B) 2nd Order Theory

E Chosen (ev)	T* Chosen (°K)	T' Calculated (°K)	α Calculated
0.50	300	276.3	1.65
0.50	325	297.6	1.64
0.60	300	278.9	1.75
0.60	350	323.1	1.65
0.60	400	365.5	1.64
0.80	300	284.4	1.70
0.80	350	328.9	1.70
0.80	400	373.1	1.67
0.80	450	416.5	1.66
0.80	500	458.9	1.66
0.80	525	480.3	1.64
1.00	300	287.3	1.71
1.00	325	310.2	1.70
1.00	350	332.9	1.70
1.00	375	355.5	1.70
1.00	400	378.0	1.69
1.00	425	400.3	1.68
1.00	450	422.5	1.68
1.00	475	443.9	1.71
1.00	500	466.4	1.67
1.00	525	488.2	1.66
1.00	550	508.9	1.70
1.00	575	531.4	1.65
1.00	600	552.7	1.65
1.20	300	288.9	1.78
1.20	325	312.5	1.71
1.20	350	335.6	1.71
1.20	375	358.5	1.71
1.20	400	381.4	1.70
1.20	425	403.9	1.71
1.20	450	426.6	1.70
1.20	475	449.1	1.69
1.20	500	471.5	1.68
1.20	525	493.7	1.68
1.20	550	515.8	1.68
1.20	575	537.8	1.67
1.20	600	558.9	1.71
1.40	300	290.7	1.73
1.40	325	313.9	1.77
1.40	350	337.5	1.72
1.40	375	360.7	1.72
1.40	400	383.8	1.71
1.40	425	406.8	1.71

Central value ($\pm$ range) $\alpha = 1.71 \pm .07$

The value of the attempt frequency factor is given by:

$$s = \frac{k_B}{E} u^{*2} \exp(u^*)$$

and the computed values of the normalized intensities can be compared with experimental values since

$$I(\text{experimental}) = I^*(\text{experimental}) I_n(T, E, T^*)$$

Further the value of the predicted decay time constant as given by:

$$\tau_0 = \exp(E/kT)/s$$

can be compared with the value of the time constant obtained from decay studies where a plot of the logarithm of the decaying light intensity as a function of time for a first order process is a straight line, the slope of which is a measure of the decay time constant.

Up to this point we have assumed that retrapping processes are negligible but the possibility should exist that an electron, once freed, may be captured by another trap or may even return to the trap from which it is removed. When all the traps are filled then we can expect that the return to empty luminous centers is appreciable, however, a state in which only a few of the traps are filled is bound to occur sooner or later and then we can expect the decay kinetics to be modified by the possibility of retrapping. We will represent this state by a simple generalization of equation (3.5). Let us assume that there are N traps, n of them occupied. Thermal vibrations may lift an electron into the conduction band where it will stay for only a very short time because it is immediately captured either by empty luminous centers, of which there are approximately n , or by empty traps, of which there are $N-n$. If the capture cross section of empty centers is A , and the capture cross section of empty traps is B , then the probability of an electron escaping from one of the occupied traps

is:

$$\frac{A n}{A n + B (N - n)} \quad \text{where } n \leq N$$

and the basic kinetic decay equation becomes:

$$I = -C \frac{dn}{dt} = C s n \exp(-E/kT) \frac{A n}{A n + B (N - n)} \quad (3.12)$$

When the probability of retrapping is negligible, that is as $B \rightarrow 0$, then it is readily seen that this equation reduces to the Randall and Wilkins relation. In the particular case where $A = B$, that is when the probability of capture by a luminous center is the same as the probability of capture by a trap, then the differential equation of decay becomes second order in n , thus:

$$I = -C \frac{dn}{dt} = \frac{C s}{N} \exp(-E/kT) n^2$$

It is readily seen from equation (3.12) that when the decay is initiated with the traps completely filled, that is $N = n$, then at least to start the decay is exponential. However, as the traps are emptied during decay then, in general, a bimolecular decay law is followed. Because of the drift time involved in decay measurements it is not known whether or not an exponential portion was masked during the drift time.

Mathematical expressions are available which are based on even more general treatments of the possibility of retrapping than that developed here.⁴⁷ However, because of the exploratory nature of the present luminescence studies we will restrict the discussion of the effects of retrapping on the decay kinetics to two cases only, with a consequent great simplification of the analysis. Thus we will consider the case where retrapping is a dominant process, and also the case where the retrapping and recombination processes are comparable. These two special cases lead to the following second order rate equation:

$$I = -C \frac{dn}{dt} = C \gamma n^2 \exp(-E/kT) \quad (3.13)$$

where γ has the following interpretations:

$$\gamma = s/N$$

when the probabilities of retrapping and recombination are equal⁵⁶
and when the probability of recombination is negligible⁵⁷

$$\gamma = n_0 A v$$

where v = average velocity of a conduction electron.

With the assumption that γ was temperature independent we have applied the previously discussed method of normalization to equation (3.13) and have obtained the following interesting results:

The maximum number of trapped electrons, n^* , was found to be given by:

$$n^* = n_0 / (1 + n_0 \frac{\gamma}{\beta} \frac{E}{k} \frac{\exp(-u^*)}{u^{*2}} S[u^*]) \quad (3.14)$$

The condition for maximum glow yielded the relation:

$$\frac{\gamma}{\beta} \frac{E}{k} = \frac{u^{*2} \exp(u^*)}{2n^*} \quad (3.15)$$

From these two equations the following expression for n_0 was obtained:

$$1/n_0 = (2 \frac{\gamma}{\beta} \frac{E}{k} \frac{\exp(-u^*)}{u^{*2}} - \frac{\gamma}{\beta} \frac{E}{k} \frac{\exp(-u^*)}{u^{*2}} S[u^*])$$

An expression for the normalized intensity was obtained which, when equation (3.14) and (3.15) were inserted, reduced to:

$$I_n(T, E, T^*) = \frac{4.0 \exp(u^*-u)}{(2.0 - S(u^*) + \exp(u^*-u) S(u) (u^*/u)^2)^2} \quad (3.16)$$

Once again the method of normalization has resulted in a theoretical description of the intensity which depends on just two parameters, T^* , and, E ; the parameter T^* being measurable, and the parameter E being the desired value of the trap depth energy.

As in the previously treated case of first order theory, we

considered the approximations: $u^*/u' \approx 1.0$ and $S(u) \approx 1.0$ which, when inserted into equation (3.16) when the intensity has a value of 0.5 yielded the following relation:

$$0.5 = \frac{4.0 \exp(u^*-u')}{(1.0+\exp(u^*-u'))^2}$$

from which an approximate value of E in terms of T^* and T' was obtained, thus:

$$E = 1.76 k \frac{T^* T'}{T^* - T'}$$

However, as shown in Table 3.3 more precise calculations yield:

$$E = 1.70 k \frac{T^* T'}{T^* - T'} \quad (3.17)$$

which is accurate to $\pm 5\%$ when $u \geq 17$ and $T' < T^*$.

Comparison of this value of E with the value of E predicted by first order theory for the same values of T^* and T' leads to the interesting result that E (2nd order) is about $1.2 \times E$ (1st order).

The decay law for second order theory which follows from equation (3.13) when the temperature is constant is:

$$I = I_0 / (1 + \gamma n_0 \exp(-u)t)^2 \quad (3.18)$$

The decay time constant, τ , for second order theory is seen to be:

$$\tau = \exp(u) / \gamma n_0 \quad (3.19)$$

If experimental decay data can be fitted to an expression of the form given by equation (3.18) then the magnitude of the decay time constant can be found and the value of, (γn_0) , calculated from equation (3.19). Now the interpretation of the predicted first order time constant was simplified because it contained just two parameters, E and s , both of which were obtained directly from the analysis of the

glow curve. The interpretation of the predicted second order time constant is, on the other hand, complicated by the inclusion of the parameters γ , and n_0 ; γ , itself, being a further combination of parameters. However, with some reasonable assumptions as to the allowed values of the parameters which made up the product γn_0 we will show, in the next section, that the second order decay data obtained in the present studies are consistent with the magnitude of γn_0 although we will not be able to state definitely which of the two special cases of retrapping is the more likely.

The previous discussion of glow curve analysis yields two distinguishing factors between 1st and 2nd order theory. The first and perhaps the most important factor is the difference between the first order decay law and the second order decay law. The second distinguishing factor is the difference in shape between a first and second order glow curve. The initial rise in intensity of the leading edge of both a first and second order glow curve is given approximately by the same expression, $I \propto \exp(-u)$, but on the lagging edge of a peak the intensity of a first order glow curve decreases significantly faster than that of a second order glow curve.

In the next section we will analyse the experimental glow curves in an attempt to ascertain whether or not simple first or second order theory describes the observed thermoluminescence phenomena.

The Analysis of Experimental Glow Curves: In Figures 3.7 to 3.12 we have included theoretical first and second order glow curves along with the experimentally obtained glow curves to illustrate the effect of glow curve analysis. The parameters (E, T^*) necessary for the generation of these theoretical curves and the parameters derived from these curves (s, T') are presented in Tables 3.4 and 3.5; the former

- 3.4

TABLE 3.4
Fitted Values of the Parameters

Sample	Intensity Relative to Peak Max of 3.4	Peak Label	T_0 °C	T_1 °C	$\frac{E}{(T_1 - T_0)}$ eV	E (eV)	Asymptotic Frequency Factor, s, sec ⁻¹	Heating Rate, °C/min
CLB	4	3	56.5	44.5	1.35	1.08	1.0×10^{14}	1.7
6N Al ₂ O ₃ Fig. 3.7a	48	3	103.1	84.6	0.92	0.88	1.7×10^9	2.5
	8	3	212.2	189.0	1.23	1.20	1.2×10^{10}	2.9
CLD	48	3	103.5	86.7	0.95	0.94	1.2×10^{10}	2.7
6N Al ₂ O ₃ Fig. 3.8a	8	3	238.3	184.5	1.11	1.15	2.9×10^9	3.1
	<2	3	(~265)	-	(?)	-	-	(3.2)
CLF	46	3	107.2	86.2	0.82	0.85	2.7×10^8	2.5
6N Al ₂ O ₃ Fig. 3.8E	9	3	231.1	178.5	1.22	1.21	2.0×10^{10}	2.9
	<2	3	(~260)	-	(?)	-	-	(2.9)
35H + 0.01% MgO Fig. 3.9a	<1.5	3	(~850)	-	(?)	-	-	(2.7)
	16	3	127.4	109.4	1.07	1.02	2.6×10^{10}	2.8
	3	3	(~175)	-	(?)	-	-	(2.8)
	3	3	269	~173	-	0.87	3.5×10^5	2.6
	3	3	(~310)	-	(?)	-	-	(2.6)
CLG + 0.1% MgO Fig. 3.10a	1	3	(~370)	-	(?)	-	-	(2.9)
	14	3	131.5	111.5	1.11	1.10	1.7×10^{11}	2.7
	6	3	(~135)	-	(?)	-	-	(2.7)
	7	3	262.5	223.4	0.86	0.87	2.0×10^5	2.8
	2	3	(~320)	-	(?)	-	-	(2.8)
CLH + 1.0% MgO Fig. 3.11a	3	3	(~380)	-	(?)	-	-	(2.4)
	100	3	134.4	110.1	0.81	0.80	1.9×10^7	2.7
	6	3	(~165)	-	(?)	-	-	(2.9)
	14	3	255	162	-	0.97	3.0×10^5	2.8
	13	3	(~305)	-	(?)	-	-	(2.5)
CLJ + 0.01% MgO Fig. 3.12a	1	3	30.5	21.5	0.90	0.82	1.2×10^9	2.3
	14	3	145.5	10.0	1.45	1.24	6.3×10^9	2.3
	14	3	(~235)	-	(?)	-	-	(3.0)
	14	3	(~235)	-	(?)	-	-	(3.0)
	75	3	372.5	157.5	3.20	3.24	5.1×10^{12}	1.5

Table 3.5

Second Order Glow Curve Parameters

Sample	Peak Label	T* (°C)	E(used) (ev)	Intensity Relative to Peak "F" of C4A	Heating Rate (°/min)
C1B					
6N Al ₂ O ₃	B	103.1	1.10	48	2.5
Fig. 3.7B	C	212.1	1.42	8	2.9
C5A	F	127.4	1.05	16	2.8
+0.01% MgO	G	185	1.29	8	2.8
Fig. 3.9B	H	260	1.29	3	2.6
C3A	F	131.3	1.29	14	2.8
+0.1% MgO	G	185	1.29	23	3.0
Fig. 3.10B	H	255	1.29	7	2.9
C4A	F	134.4	.94	100	2.7
+1.0% MgO	G	185	1.29	33	2.9
Fig. 3.11B	H	255	1.29	24	2.9

summarizing the results of first order analysis and the latter summarizing the results of second order analysis.

In the preceding section we showed that if a glow curve was sufficiently resolved to obtain a measure of T^* and T' then a value of the trap depth energy, E , could be calculated and, further, that this value of E together with the value of T^* were all that was necessary to generate a theoretical (first or second order) normalized curve. Now, in order to compare the shape of the normalized curve with the shape of an experimental peak, the value of the experimental intensity when a maximum, I^* , must be measured and then the experimental peak intensities normalized since $I(\text{exp}) = I_N I^*$. Consequently to compare theory and experiment, the three parameters I^* , T^* and E , are necessary. The rather lengthy calculations involved in obtaining the values of I_N from equations (3.9) or (3.16) which are necessary for the comparison of theory and experiment were performed with the aid of an I.B.M. 1620 computer. Further, with this computational aid, the values of I^* , T^* and, T' and I' , were interpolated from experimental intensities and temperatures rather than read directly from a glow curve peak. The interpolation program is described fully in appendix III-4.

In the process of fitting a theoretical curve to an observed peak the three parameters T^* , $I^*(\text{exp})$, and E are considered variable, at least within the limits of the experimental errors associated with their choice; ΔT^* , ΔI^* and ΔE , respectively. Consequently, the best fit between theory and experiment would be obtained when the R.M.S. deviation between predicted and observed intensities is a minimum for those values T_1^* , I_1^* , and E_1 , such that:

$$E - \Delta E \leq E_1 \leq E + \Delta E$$

$$T^* - \Delta T^* \leq T_1^* \leq T^* + \Delta T^*$$

$$I^* - \Delta I^* \leq I_1^* \leq I^* + \Delta I^*$$

The following is meant by the "fitting" of a theoretical curve to an experimental peak:

Only those values of the experimental intensities were fitted which were judged to be free from overlap effects. Experimental intensities read at equal ($\approx 2^\circ\text{C}$) intervals of temperature were fed into the computer. I^* , I' , T^* and T' were obtained by interpolation (appendix III-4). The value of E predicted by equation (3.11) for a first order process was calculated. A theoretical curve was computed; theoretical intensities being calculated for temperatures corresponding to input experimental temperatures. Then, the R.M.S. deviation between the theoretical and the normalized experimental intensities was calculated. The value of E was incremented by ± 0.01 ev until the R.M.S. deviation was a minimum. In this manner a value of E , termed E (used) was obtained such that:

$$E(3.11) - \Delta E \leq E(\text{used}) \leq E(3.11) + \Delta E$$

where ΔE is the error in E due to inaccurate temperature measurements.

In the analysis that we now present only E was treated as adjustable parameter. The values of I^* and T^* once found, were held fixed in further computations. As we will show, this stringent requirement does not seriously effect the analysis or the conclusions based on the results of such analysis. A calculation of the error in trap depth energy due to approximations in analysis and due to experimental errors is presented in appendix III-6. In discussing the analysis of the experimental glow curves emphasis is placed on the pure and doped Al_2O_3 glow curves. Because of the apparent

differences of glow curves obtained from pure Al_2O_3 and glow curves obtained from MgO doped specimens and consequently the need for variations in analysis we will discuss the curves obtained from these materials separately.

Analysis of 6N Al_2O_3 Glow Curves: Consider the glow curve of specimen ClB, Figure 3.7, which is typical of the pure Al_2O_3 specimens. In terms of independent first order processes this glow curve can be thought of as the sum of three first order processes; one peaking at about 57°C , one at 103°C and the last at 212°C . In order to assess the amount of overlap, between three such processes, tentative values of T^* and T' were assigned to each peak as if no overlap existed and then values of E for each peak were calculated from equation (3.11). With these values of E , and with the values of T^* and I^* read from the glow curve, theoretical first order curves were obtained using equation (3.9). These theoretical curves were sketched onto the experimental curve. In this manner it was found that the 103°C peak and the 212°C peak did not overlap. Obviously the 103°C peak overlaps the peak at 57°C as seen in Figure 3.7, but the values of T^* and T' of the 103°C as read from the experimental curve are not effected by a first order process characterized by $T^* = 57^\circ\text{C}$ and $E = 1.0 \text{ ev}$ (these last values being first guesses to the quantities).

Theoretical first order curves were fitted to the non-overlapping peaks at 103°C and 212°C . The theoretical curve fitted to the 103°C peak was subsequently subtracted from the experimental curve and a peak was obtained in the region of 57°C which, in turn, was fitted by a first order curve since we had supposedly removed overlap effects. It is seen that over 90% of the total light output from specimen ClB (as it was warmed slowly after γ -irradiation) is accounted for by the

sum of the three first order processes, as illustrated in Figure 3.7.

The theoretical curves shown in Figure 3.7 were obtained using the values of E (used) and T^* listed in Table 3.4. These parameters also yielded the listed values of the attempt frequency factor, s , associated with each process.

In Figure 3.7 we have illustrated the effect of fitting second order theoretical curves to the 103° peak and the 212° peak. The values of E , T^* and I^* necessary for these curves are listed in Table 3.5. No attempt was made to fit the 57°C peak. The value of E predicted by second order theory is given in equation (3.17). Three values of E were tried in order to assess the effect of fitting second order curves. Since E (2nd order) is about $1.2 E$ (1st order) and E (1st order) had already been computed, then, in fact, it was only necessary to try the three values:

$$1.2xE \text{ (1st)}, 1.2xE \text{ (1st)} + 5\%, 1.2xE \text{ (1st)} - 5\%$$

The value of E used to fit the 103°C peak was $1.2xE \text{ (1st)} + 5\%$, whereas the value of E used to fit the 212°C peak was $1.2xE \text{ (1st)}$. That is, of the six theoretical curves generated, the two characterized by these parameters provided the best fit.

Comparing Figures 3.7A and 3.7B it is readily seen that a slight modification of first order theory provides a better fit between theory and experiment for the high temperature peak, whereas the low temperature peak lies somewhere between the two fitted peaks. However, the complete verification of the choice of theory must wait for precise decay measurements and as well, the experimental verification that the luminous efficiency is a constant (a basic assumption) must be obtained.

The fit between 1st order theory and experiment for those peaks where analysis was possible in the glow curves of CLD and CLE, is

illustrated in Figures 3.8A and 3.8B, respectively. No attempt was made to try second order theory because of the satisfactory fit obtained, although on the basis of the results obtained when fitting with second order curves in the previous case (ClB) it is expected that the high temperature peak would be better represented by a second order process.

Referring to Table 3.4, it is seen that, in general, the trap energies are about 1.0 eV and that the attempt frequency factors are $\leq 10^{13} \text{ sec}^{-1}$ with the exception of the 57°C peak of ClB where $s = 1.0 \times 10^{14} \text{ sec}^{-1}$. However, not too much importance should be attached to the results obtained from the analysis of this peak because firstly, it only shows up with sample ClB where the initial heating was slower than elsewhere and consequently the values of E and s found could not be compared with the results obtained from the other pure specimens; secondly, the value of E (used) calculated for this peak was obtained on the basis that the 130°C peak was fitted by a first order process and consequently overlap effects should have been perfectly accounted for by simply subtracting the 130° theoretical peak from the experimental glow curve but since the 130°C is not perfectly represented by a first order process overlap effects have probably distorted this peak.

In comparing the differences that are obtained when fitting the experimental peaks with first order curves on the one hand, and second order curves on the other hand, it should be noted that subtraction of the theoretical first order curves from the experimental ones left "peaked" remainders at about 125°C as illustrated in Figures 3.7 and 3.8 by the areas enclosed by open-circled points whereas second order theory removes this effect of a new and probably spurious "peak". In further discussion we will refer to this effect, which appears in the

analysis of other glow curves as well, simply as the fast fall-off of first order theory.

The Analysis of MgO doped Al_2O_3 Glow Curves: The attempt was made to fit first order and then second order theory to the observed glow curves. Figures 3.9 to 3.11, illustrate the effect of fitting both theories. In general, the characteristic glow curves are readily resolved into separated second order processes, while, the fast fall off of first order theory resulted in too many discrepancies. As illustrated in Figures 3.9 to 3.11, one needs but three second order processes to describe the observed phenomenon whereas one would need four first order processes - the extra peak occurring at 150°C because of the fast fall off of the first theoretical curve. The better fit of second order theory is consistent with the decay data obtained from these specimens.

The glow curves were analysed in the following manner. Firstly, it was assumed that the major peak of each curve was free of overlap effects. Second order theoretical curves were fitted to these peaks. Since first order curves had already been fitted this amounted to trying values of E which were:

$$1.2 \times (E \text{ 1st}), 1.2 \times (E \text{ 1st}) + 5\%, 1.2 \times (E \text{ 1st}) - 5\%$$

where $E(1st)$ is the energy used for the best fitting first order process.

Secondly, it was assumed that the 255°C maximum of C3A was also sufficiently resolved to obtain a measure of T^* and T' free of overlap effects where T' was now the temperature for which the glow had reached half the maximum value on the high temperature side of the peak. Both first and second order theoretical curves were fitted to this peak. Now, the intensity of this characteristic peak varies from specimen to specimen in a manner which suggests that it depends on the MgO content.

As the MgO content is decreased from 1% through 0.1% to 0.01% the intensity drops from 24 to 7 to 3, respectively, as shown in Table 3.4. A tenfold decrease in added MgO results in a threefold decrease in intensity. It was assumed that the parameters describing the 260°C maximum of C3A could then be used for the same peak of the other doped specimens. In Figures 3.9 to 3.11 we illustrate the effect of fitting second order curves to the 260°C characteristic maximum of the other doped specimens with the energy for these curves being exactly the same as that used for specimen C3A.

The two theoretical second order curves obtained in this manner for the characteristic glow curve of each specimen were subtracted from the experimental curves. In Figures 3.9, 3.10 and 3.11 the result of this subtraction is indicated by the full circled points peaking in the temperature region 160°C to 180°C. Second order theoretical curves, characterized by the same trap depth energy value, are shown fitted to these points. In fitting these latter peaks some arbitrary selection of maximum intensity was exercised so that the resulting fit would exhibit the minimum amount of overlap.

The parameters used for the second order curves are presented in Table 3.5. It should be realized that a better fit between theory and experiment could have been obtained by allowing all the parameters (T^* , E , I^*) for each theoretical curve to vary; however, even without this, the present studies definitely show that the glow curves can be resolved into independent second order processes, in the sense that over 95% of the total light output observed during the thermoluminescence experiments is accounted for by the sum of three second order processes.

Correlation of Decay Data: The measured decay time constants can now be compared with theoretical predictions. The decay time constant, τ ,

for second order theory was shown to be:

$$\tau = \exp(E/kT)/\gamma n_0$$

where $\gamma = s/N$ for equal probability of retrapping and recombination and $\gamma = n_0 A v$ for maximum retrapping effects.

The predicted decay time constant for first order theory was shown to be:

$$\tau = \exp(E/kT)/s$$

The measured decay for C3A at $150 \pm 3^\circ\text{C}$ was shown to fit the predicted exponential 1st order decay with a time constant of 562 seconds.

Referring to Figure 3.10, it is seen that this decay is predominately the decay of a peak with unknown theoretical parameters. Note, the decay of the major peak at 130°C has a predicted time constant of less than 100 seconds and does not interfere with the measured decay data. If we equate then the first order predicted time constant to the observed time constant and use an attempt frequency factor, s , which is $\leq 10^{13} \text{ sec}^{-1}$ then the following relation results:

$$562 \geq \exp(E/k(150 + 273))/10^{13}$$

It follows that $E \leq 1.3 \text{ eV}$; a value which is consistent with all other obtained values for E . However, since it has been shown that theoretical first order processes cannot be used in this temperature interval it now becomes necessary to find the reason why a second order process should exhibit first order decay after a considerable amount of the traps have been emptied (the drift time was ≈ 16 minutes for this decay experiment). It was found that such phenomenon is indeed possible if one assumes that there are present in the specimen luminous centers not normally occupied by an electron. As pointed out by Mott and Gurney this state of affairs is more likely to happen when a certain number, N_2 , of frozen-

in interstitial ions with an equal number, N_2 , of vacant lattice points occur in the lattice, besides the N_1 interstitial atoms that are normally found at a given temperature. In which case there are $N_1 + N_2$ possible traps but only N_1 electrons available. If we denote by v the number of normally unoccupied impurity centers the probability of an electron escaping from one of the occupied traps becomes:

$$\frac{A(n+v)}{A(n+v) + B(N-n+v)}$$

again if $A = B$, the basic rate equation becomes:

$$-\frac{dn}{dt} = s \exp(-E/kT) (n+v)n/N$$

When, at some stage in the decay process, $n \ll v$, the decay is seen to be exponential.

There is the possibility that this occurs for specimen C3A for which first order decay is observed since there is a high probability that vacuum sintering introduced a frozen-in defect structure in the specimen. However, confirmation of this hypothesis should be tested by more exacting decay studies. One may note that if in general, $v \ll n_0$ (the original number of trapped electrons), then the glow intensity will be essentially second order but as the electrons are released from traps the shape of the glow curve will change from the slow fall off of second order to the relatively quicker fall off of first order theory. Referring back to the discrepancy observed in fitting the most intense maximum of C1B with a second order curve (Figure 3.7) it is possible that the effect just discussed would remove this discrepancy; detailed decay studies would be necessary, however, to confirm this conjecture.

The remaining decay data (obtained from specimen C5A) was

satisfactorily fitted to the second order decay law. Comparing the time constants obtained by fitting the decay data with the theoretical predictions results in the following three equations:

$$\gamma_1 n_{01} = 1.6 \times 10^{10} \text{ sec}^{-1} \text{ (at } 123.5^\circ\text{C)}$$

$$\gamma_2 n_{02} = 2.2 \times 10^{11} \text{ sec}^{-1} \text{ (at } 181.1^\circ\text{C)}$$

$$\gamma_3 n_{03} = 1.7 \times 10^9 \text{ sec}^{-1} \text{ (at } 247.5^\circ\text{C)}$$

A rather rough order of magnitude calculation of the number of trapped electrons responsible for each of the three peaks is presented in appendix III-5, where the estimates of the original number of trapped electrons, n_{01} to n_{03} are all shown to be greater than 10^{15} per cm^3 and hence:

$$\gamma_1 \lesssim 10^{-5}, \gamma_2 \lesssim 10^{-4} \text{ and } \gamma_3 \lesssim 10^{-6} \text{ sec}^{-1} \text{ cm}^{-3}$$

We can now consider the two proposed cases of retrapping separately to see if the parameters involved in γ are consistent with known order of magnitude calculations.

Case I, equal probability of retrapping and recombination where $\gamma_i = s_i/N_i \approx s_i/n_{0i}$ ($i = 1, 2, \text{ or } 3$). From the decay data alone it follows that the attempt frequency factors are less than 10^{13} sec^{-1} .

Consequently, the possibility exists that the probability of retrapping is equal to the probability of recombination.

Case II, the probability of recombination is small relative to the probability of retrapping. In this case $\gamma_1 = n_{01}Av$, but since the average velocity of a conduction electron, v , is of the order of 10^7 cm/sec , then it follows from the previously derived values for γ_1 and n_{01} that the capture cross section of a luminous center, A , is of the order of 10^{-27} cm^2 . A typical high value for A is of the order of 10^{-16} cm^2 . Consequently, the possibility exists that the

probability of recombination is small relative to the probability of retrapping.

We note that on the basis of these order of magnitude calculations it is not possible to choose between Case I or Case II.

Comparison with Previous Work: Atlas and Firestone reported a first order annealed "peak" at 269°C characterized by a trap depth energy of 2.9 ev for a MgO doped Al_2O_3 specimen. Except for the temperature location being close to the temperature location of the 260°C peak found in the present studies there is no comparison between their work and the work reported herein.

Lehmann and Gunthard reported a peak at about 90°C with a second order trap depth of 1.31 ev, a value close to the characteristic 1.29 ev found by us. They investigated the u.v. excitation of sapphire. Since the sample contained about 10 ppm of Mg, it is possible that this metallic impurity or its associated defect structure leads to the observed effect. Since they have not reported the heating rate or for that matter whether or not it was linear, no attempt was made by us to fit a theoretical curve to the published experimental curve.

The basic defect structure of the MgO doped Al_2O_3 specimens depends to a large extent on the solubility of MgO in Al_2O_3 . We have given evidence for the predominant formation of the spinel phase. There still exists the possibility that $\leq 0.01\%$ MgO has either not reacted with Al_2O_3 and constitutes a separate phase or that all or part of the Mg in this MgO has replaced some Al ions, either substitutionally or interstitially.

Yamaka⁶⁴ has obtained glow curves for various MgO specimens with and without additional coloration. He associates the various peaks with oxygen or magnesium excess, but his data are not adequate

enough to yield thermal activation energies. Eisenstein⁶⁵ has shown by cathodoluminescence studies that 2.4 ev and 2.7 ev emission are enhanced by excess Mg. 3.6 ev emission shows a long decay.

The variation of glow peak intensities with MgO doping may be indicative of the excess MgO in the lattice in which case the emission observed at 2.4 ev could be compared with Eisenstein's results.

A number of U.V. irradiation induced paramagnetic defects have been found in MgO.⁶⁶ These defects were interpreted either as F-centers or as trapped holes on oxygen ions adjacent to positive ion vacancies. An attempt by Lehmann and Gunthard to find such defects in Al_2O_3 single crystals irradiated with U.V. light was unsuccessful. Since it is possible to increase the number of defects by γ -irradiation, EPR measurements may possibly yield some insight into the nature of the centers in γ -irradiated Al_2O_3 .

In summary the analysis of the MgO doped Al_2O_3 glow curves has shown that:

- 1) the experimental glow curves are consistently described by second order theory
- 2) there are three major peaks due to the release of electrons from three traps
- 3) the relation of decay data and glow curve data is as consistent with equal probabilities of trapping and recombination as with the probability of recombination being small
- 4) the total number of emission centers, of the order of 10^{15} ,

excludes the possibility of thermoluminescence effects originating from the unknown impurities if the effects are reasonably interpreted as originating in surface grains

- 5) the only correlation between the doped Al_2O_3 glow curves and the pure Al_2O_3 curves is the fact that both yield a peak at about 260°C . This cannot be due to the free Mg concentration of both the pure and doped specimens. It may be due to the associated lattice vacancies introduced when Mg replaces Al in the Al_2O_3 lattice, since, for direct substitution $2\text{Al}^{3+} = 2\text{Mg}^{2+} + (\text{O}^{2-})_{\text{v}}$. As well, it may be due to the presence of interstitial aluminum ions and oxygen ion vacancies introduced into the lattice by the high temperature firing in vacuum.

The Analysis of the N.R.C. Glow Curves: A typical glow curve from the N.R.C. specimens is illustrated in Figure 3.12. Theoretical first order glow curves have been included for comparison where analysis was possible. The parameters for these theoretical curves are listed in Table 3.4. In the table the peaks of this material are correlated to the peaks of the pure and doped specimens on the basis of temperature location. The rather low intensity of the 260°C peak either excludes Mg as the source of this peak or there happens to be very little free Mg in the N.R.C. material; a possibility not easily checked. Again, since this specimen was vacuum sintered, the 260° peak may possibly be related to defect structure.

A satisfactory fit between first order theory and experiment is obtained for this glow curve. The high temperature peak is cut off at the maximum usable limit of the apparatus. The section of this peak

shown in Figure 3.12 is equivalent to the saw-tooth annealed "peaks" described in Section 3.3. The analysis of this section of the high temperature peak yielded a value of 3.2 eV for the trap depth energy and a value of about 10^{22} sec^{-1} for the attempt frequency factor. Both these values are inconsistent with all other values for these quantities derived in the present studies. Since it is possible that there are severe overlap effects due to a still higher temperature neighboring process these values are not given any weight. However, it should be noted that relatively high values of E and s were obtained by Atlas and Firestone particularly for high temperature annealed peaks analysed in terms of first order theory. The value of $E = 2.9 \text{ eV}$ for the 269°C "peak" of their MgO doped specimen leads to a value of $s = 10^{23} \text{ sec}^{-1}$, (using the condition for maximum glow and with $\beta = 1.4^\circ\text{C/min}$). These high values of the attempt frequency factor are inconsistent with the Mott and Gurney interpretation of the attempt frequency factor and possibly indicate the need for a change in the basic kinetic equation.

The glow curve for sapphire is illustrated in Figure 3.12. No attempt was made to analyse it. There is little correlation between this glow curve and the N.R.C. curve. The 260°C peak shows up again. The peaks at about 130°C and 165°C may be linked to Mg concentration but again this is pure conjecture.

3:9 Proposed Model for Thermoluminescence in Aluminum Oxide:

Thermoluminescence has been observed in γ -irradiated vacuum sintered pure Al_2O_3 and in MgO doped Al_2O_3 . For the first time, a comparison has been made between the predictions of glow curve theories and the experimental results. The majority of the characteristic peaks in the 6N Al_2O_3 and MgO doped Al_2O_3 glow curves are interpretable in

terms of second order theory. The low temperature peaks of the $6N$ Al_2O_3 glow curves lie somewhere in between both representations. In terms of the model proposed in section 3.2, the observed peaks are related to the thermal emptying of electron traps. The trap depth energies were found for the majority of observed peaks by a normalization technique which allows for the comparison of theory and experiment when only 3 parameters are known; E , T^* and I^* , respectively. All the parameters are directly obtained from the observed glow curve if no overlap exists. Since in the present studies the problem of overlap was severe, at least in the curves from the doped specimens, the results finally obtained for the thermal activation energies are considered to be only indicative of these quantities rather than a final quantitative measure which would then characterize the respective peaks.

The need for accurate decay measurements has been fully stressed. The need for the accurate measurement of luminous efficiency has not. Since the assumption that the efficiency is constant has been used throughout the present work it should be checked. Grossweiner,⁵⁸ has indicated an experimental technique for determining the efficiency. However, within the scope of the present studies as outlined in section 3.4, the use of this basic assumption is justified by the extremely good fit between the proposed theory and experiment.

The model with electron traps proposed in section 3.2 leads to photoconductivity. Up to the present time there have been no reports of photoconductivity in Al_2O_3 . One confirmation of the existence of electron traps in Al_2O_3 is given by the reported existence of Kramer's effect.² Bohun⁵⁹ showed a close correlation between the rate of emission of electrons and the intensity of thermoluminescence for an Al_2O_3 specimen. The explanation given for the observed Kramer effect

is that a "trapped electron has a probability $P = s \exp(-E/kT)$ of escape per unit time into the conduction band from where it may either recombine with a luminescence center or if it is near the crystal surface it may escape from the crystal by thermal activation (as in thermionic emission)". Another confirmation of the existence of electron traps in Al_2O_3 comes from the work of Atlas and Firestone.

They showed a direct variation of glow peak temperature with cation ionization potential and we note that the glow peak temperature is a measure of the trap depth energy whether first or second order theory is used. Since the trapping energy for holes increases with the height of the trapping levels above the valence band, the trap depth energy would be an inverse function of the appropriate cation ionization potentials in direct contrast to the case of trapped electrons where the trapping energy increases with the ionization potential for the appropriate transition (modified by the Madelung potentials and dielectric constants of Al_2O_3 ¹⁸).

If all the present results are interpreted as being due to trapped electrons then the following energy models, Figures 3.14A and 3.14B, can be ascribed to the 6N Al_2O_3 and MgO doped Al_2O_3 specimens, respectively. Irradiation of 6N Al_2O_3 with 10^5R of Co^{60} γ -rays fills the electron traps. As the material is slowly heated electrons are first released from traps with very little retrapping; the average trap depth energy for this process is about 1 ev. At still higher temperatures, deeper trap levels at about 1.4 ev are emptied but now some amount of retrapping is involved. From emission studies it appears that electrons once freed from any of these traps are captured from the conduction band by centers which are about 3.7 ev (optically) below the conduction band edge.

Figure 3.17. Energy level scheme for (1) 6% Al_2O_3 and (3) 0.1% MgO doped Al_2O_3 : Electron traps filled by γ -irradiation are emptied thermally into the conduction band and electrons return to the labelled luminous centres predominantly by radiative capture.

The average trap depth of the traps filled by γ -irradiation of the MgO doped specimens is about 1.3 ev. Two types of luminous centers are operative; for temperatures below 100°C, the electrons freed from the traps return to centers at about 3.4 ev below the conduction band and for temperatures above 100°C, the electrons freed from traps return to centers 2.4 ev below the conduction band.

We cannot, on the basis of the present work, state definitely the nature of the traps and centers operative in the thermoluminescence phenomena. We will discuss some possibilities.

A model proposed for the 6N Al_2O_3 depends on anion and cation vacancies only, that is, lattice defects are considered as the dominant perturbation which give rise to energy levels in a normally forbidden band and hence to the observed thermoluminescence effects. This is consistent with the work of Atlas and Firestone where additions of 200 to 900 ppm of impurities to 4N5 Al_2O_3 were needed to observe a difference in glow curve structure whereas the same or even more pronounced difference in structure was observed when the 4N5 Al_2O_3 , without added impurities, was annealed in O_2 or H_2 .

There are two simple possibilities for lattice defects in vacuum sintered Al_2O_3 : Interstitial aluminum ions or oxygen ion vacancies. Either one would indicate an increase in the lattice constant. The actual physical density would increase for interstitials and decrease for vacancies.⁶¹ No such density changes have been reported for Al_2O_3 .

High temperature diffusion studies indicate that Al^{3+} ion diffusion is much greater than O^{2-} diffusion. However, as reported by Pali⁶⁷ and Coble, O^{2-} diffusion is enhanced by grain boundaries in polycrystalline Al_2O_3 as is the Chloride ion diffusion in the alkali Halides. The apparent diffusion coefficient for O^{2-} was estimated to

exceed that for Al^{3+} at grain sizes less than in $20\ \mu$. Since the measured grain size of the specimens used in thermoluminescence studies was about $30\ \mu$, it is not possible on the basis of diffusion data to estimate the number of vacancies in the specimens. Further, in the case of KCl where again the positive ion transport number is much larger than that of the negative ion, Sietz⁶² has assumed that the negative ion vacancies move about under thermal agitation in the company of positive ion vacancies since pairs of vacancies are more mobile than the negative ion vacancies themselves.

A pair of vacancies is considered to eject a positive ion vacancy on the capture of an electron to form an F-center. A measurable dielectric loss peak should be observed for the orientation of the dipoles formed by such vacancy complexes. Since at present we cannot discard either the $(\text{O}^{2-})_v$ or $(\text{Al}^{3+})_i$ or vacancy complex it is necessary to consider all three as possible defects in any model for thermoluminescence. Further, in the case of the Mg doped specimens, the luminescence need not originate in the compensating oxygen ion vacancies, it may be caused by the thermal ionization of Mg^{2+} to the trivalent state Mg^{3+} .

It must be noted that the present studies have been carried out in a rather restricted range of wavelengths of light; $3000\ \text{\AA}$ to $6000\ \text{\AA}$. The present studies have indicated that the glow curves of γ -irradiated Al_2O_3 specimens can be analysed successfully in this region, however, these studies can and should be extended to cover a wider wavelength region. In particular, more attention should be given to the measurement of the frequency of the emitted light, and to the precise determination of decay data. Since the present studies have essentially reduplicated the experimental conditions of Atlas and Firestone then

these studies should, as these workers have pointed out, be extended to cover a wider range of temperature. The extended studies should be correlated with photoconductivity measurements as well as thermoelectric power and Hall Effect measurements.

It may be argued that these experiments are best interpreted when pure single crystals are used as test specimens, but since these are presently unavailable, then pure, dense, polycrystalline specimens can and should serve as the basis of perfecting experimental techniques and building up an experimental and theoretical foundation which could be immediately utilized the day pure single crystals are available.

SECTION IV

Conclusions:

The trap depth energies measured by thermoluminescence experiments would be directly related to the thermal activation energies of electrical conductivity experiments if these latter experiments had been a measure of the electronic contribution to conduction in Al_2O_3 .^{50,60} The frequency dependence of the dielectric loss data excludes any such interpretation of the conductivity data and therefore it may be concluded that the present studies show no clear correlation between the total conductivity of Al_2O_3 and its luminescence properties.

Either there is no correlation or a mechanism of loss has masked the electronic mechanism so effectively that the correlation is not obvious. This can be experimentally checked by additional experiments. In the present studies MgO was added to Al_2O_3 but we now know that a separate phase was formed, and consequently, the impurity addition should be chosen for its solubility in Al_2O_3 . The experiments reported herein should be repeated by varying the surrounding atmosphere of the test specimen both during fabrication and during measurements. The loss mechanism may be a direct function of this atmosphere as suggested by Tallan and Detwiller.³⁶

The homogeneity of the specimens can be checked by varying the size of the guarded electrode on one and the same specimen, each time measuring the electrical conductivity.

The necessity for high temperature results has been stressed. The method of Platinum bonding appears promising. The effect of the electrode-ceramic interface barrier may be ascertained to a certain extent by changing the electrode material. It may turn out that the

wide use of Platinum as electrode material should be discontinued.

The object of the present studies has been fulfilled. It is felt that the accuracy afforded by 3-terminal, guarded, measurements and the simplicity of the proposed method of glow curve analysis can be and should be considered in future investigations of the physical properties of oxide ceramics.

REFERENCES

1. Ryshkewitch, E., "Oxide Ceramics", Academic Press, New York (1960).
2. Gilles, A., J. Phys. Rad. 13, 247 (1952).
3. Dunkleman, L., Fowler, W. B., and Hennes, J. P., Appl. Opt. 1, 695 (1962).
4. Linde Bulletin F-8727.
5. Kramer, J., Z. Physik 129, 34 (1951); 133, 629 (1952).
6. Atlas, L. M. and Firestone, R. F., J. Amer. Ceram. Soc. 43, 476 (1960).
7. Kingery, W. D., "Introduction to Ceramics", John Wiley and Sons, New York (1960).
8. Cohen, J., Bull. Amer. Ceram. Soc. 38, 441 (1959).
9. Kelly, P. J., M.Sc. Thesis, Carleton University, Ottawa, Canada.
10. Wilson, A. H., "The theory of Metals", Cambridge University Press (1958).
11. Lidiard, A. B., Handbuch Der Physik Vol. ; Editor Flugge, S., Springer-Verlag, Berlin (1957).
12. Paladino, A. E., and Kingery, W. D., J. Chem. Phys. 37, 957 (1962).
13. Oishi, Y., and Kingery, W. D., J. Chem. Phys. 33, 480 (1960).
14. Matsumura, T., and Laubitz, M. J., (Heat and Solid State Div. of Appl. Phy. N.R.C.) Private Conversation.
15. Pappis, J., and Kingery, W. D., J. Amer. Ceram. Soc. 44, 459 (1961).
16. Harrop, P. J., and Creamer, R. H., Brit. J. Appl. Phys. 14, 335 (1963).
17. Champion, J. A., Brit. J. Appl. Phys. 15, 633 (1964).
18. Atlas, L. M., Hikaru Nagao, and Nakamura, H. H., J. Amer. Ceram. Soc. 45, 464 (1962).
19. Powers, A. E., "Proceedings of the Second Conference of Thermal Conductivity" (Appl. Phys. Div. N.R.C. Canada) Page 280 (1962).
20. Florrio, J. V., J. Amer. Ceram. Soc. 38, 187 (1959).
21. Cohen, J., J. Phys. Chem. Solids, Pergamon Press 16, 285 (1960).
22. Levy, P. W., Disc. Faraday Soc. 31, 118 (1961).

23. Lehmann, H. W., and Gunthard, Hs. H., J. Phys. Chem. Solids, Pergamon Press 25, 941 (1964).
24. Leybold (Through Degussa Frankfurt Germany).
25. A.S.T.M. Standards 6, (1949).
26. General Radio, Form 681-H, June 1957.
27. Coors Porcelain Company, Golden, Colorado.
28. Pyrometer Company of America, Inc., Penndel, Pa., U. S. A.
29. Publication 2032-69, Associated Electrical Industrials Limited, (Instrumentation Division), Manchester, England.
30. The Consolidated Mining and Smelting Company of Canada Limited (Montreal 2, Canada).
31. L. Light and Co. Ltd., Polye Colnbrook, Buckinghamshire, England.
32. Facilities of the Heat and Solid State Div. of N.R.C., Montreal Rd., Ottawa, Canada.
33. Sheffield (Gauge Model #1000) Dayton, Ohio.
34. General Radio, Form No. 1615-0100-A, October 1963.
35. Von Hippel, A., M.I.T. Tech. Report 126 (1958).
36. Tallan, N. M., and Detwiler, D. J., J. Appl. Phys. 34, 1650 (1963).
37. Sillars, R. W., J. Inst. Elec. Engrs. (London) 80, 378 (1937).
38. Brown, F., Jr., Handbuch Der Physik Vol. XVII; Editor Flugge, S., Springer-Verlag, Berlin (1956).
39. Friauf, R. J., J. Chem. Phys. 22, 1329 (1954).
40. MacDonald, J. R., Phys. Rev. 92, 4 (1953).
41. Rieke, J. K. and Daniels, F., J. Phys. Chem. 61, 629 (1957).
42. Gabrysh, A. F., Eyring, H., LeFebvre, V., and Evans, M. D., J. Appl. Phys. 33, 3389 (1962).
43. Mitchell, E. W. J., Rigden, J. D., and Townsend, P. D., Phil. Mag. 5, 1013 (1960).
44. Levy, P. W., and Dienes, G. J., Phys. Rev. 94, 1409 (1945).
45. Cutler, I. B., Bates, S. L., and Gibbs, P., Bull. Amer. Phys. Soc. 2, 300 (1957).
46. Randall, J. T., and Wilkins, M. H. F., Proc. Royal Soc. (London) 184A, 366 (1945).

47. Garlich, G. F., Handbuch Der Physik Vol. XXVI; Editor Flugge S., Springer-Verlag Berlin (1958).
48. Chormley, J. A., and Levy, H. A., J. Phys. Chem. 56, 548 (1952).
49. Grossweiner, L. I., J. Appl. Phys. 24, 1306 (1953).
50. Mott, N. F., and Gurney, R. W., "Electronic Processes in Ionic Crystals" 2nd Edition, Oxford Press (1948).
51. Hunt, R. A. and Schuler, R. H., Phy. Rev.; 89, 664 (1953), 94, 1409 (1954).
52. Hoskins Mfg. Co., Detroit 8, Michigan.
53. Lipsett, F., (Accepted for Publication) British J. Photoelectric Photometry (1965).
54. Lipsett, F., (N.R.C. Canada) Private Conversation.
55. Leverenz, H. W., Introduction to Luminescence of Solids, John Wiley and Sons, Inc., New York (1950).
56. "Preparation and Characteristics of Solid Luminescent Materials", John Wiley and Sons, New York (1948).
57. Weyl, P. K., J. Chem. Phys. 26, 547 (1957).
58. Grossweiner, L. I., and Matheson, M. S., J. Chem. Phys. 22, 1514 (1954).
59. Bohun, A., Czech. J. Phys. 3, 394, 430 (1953); 4, 88, 99, 91, 139 (1954); 5, 65, 100, 224 (1955).
60. Harrison, S. E., Phys. Rev. 93, 52 (1954).
61. Mott, N. F., and Littleton, M. J., Trans. Faraday Soc. 34, 485 (1938).
62. Sietz, F., Revs. Modern Phys. 18, 384 (1946).
63. Bottcher, C. J. F., "Theory of Electric Polarization", Elsevier Publishing Co., London (1952).
64. Yamaka, E., Phys. Rev. 96, 293 (1954).
65. Eisenstein, A., Phys. Rev. 93, 1017 (1954).
66. Wertz, J. E., Orton, J. W., and Auzins, P., Disc. Faraday Soc. 31, 140 (1961); J. Appl. Phys. 33, Suppl. 1, 322 (1962).
67. Paladino, A. E., and Coble, R. L., J. Amer. Ceram. Soc. 46, 133 (1963).

Two terminal ac conductivity measurements were obtained by modifying the existing 3-terminal cell, described in section II. The experimental arrangement is illustrated in Figure II-1. As shown, the sample resistance and capacitance are in parallel with a cell resistance and capacitance. However, at a given temperature and total pressure, only the two values, C_{T_1} and D_{T_1} , are obtained at bridge balance. It is necessary then to eliminate from these measured quantities the effects of the cell capacitance and resistance.

In principle one can eliminate the effect of the cell capacitance and resistance by measuring it. This can be accomplished by replacing with vacuum the volume of space occupied by the test specimen. The balance conditions of the bridge with the specimen first in and then out yields the dielectric properties of the specimen.

In practice it was necessary to use spacers to hold the electrodes a sample thickness apart. The experimental arrangement of cell and spacers is illustrated in Figure II-2. The external circuit (bridge, leads, etc.) has not been shown in either Figure II-1 or Figure II-2 since it remained the same for both sets of measurements. The three spacers with diameters approximately equal to the thickness of the specimen (C2A) were cut from a precision ground ruby rod.

It is readily seen, from the equivalent network in Figure II-2, that bridge balance yields the two additional values C_{T_2} and D_{T_2} . The four numbers obtained from measurements first with the sample in and then with the sample out and spacers in are sufficient, as we will now show, to obtain a rough measure of the dielectric properties of a solid specimen.

Figure II-1. (A) Experimental arrangement for 2-terminal measurements.
 (B) The series and parallel representations of sample and cell.

Figure II-2. (A) Experimental arrangement for 2-terminal measurements of cell capacitance. (B) The series and parallel representations of spacers and cell.

The following relations hold at bridge balance when the specimen is in the cell (see Figure II-1):

$$C_x + C_c = \frac{C_{T_1}}{1 + D_{T_1}^2}$$

and

$$\frac{1}{R_x} + \frac{1}{R_c} = \omega D_{T_1} C_{T_1}$$

or equivalently

$$C_x = C_{T_1} - C_c \quad \text{--- } \alpha$$

and

$$G_x = \omega D_{T_1} C_{T_1} - G_c \quad \text{--- } \beta$$

The following relations hold at bridge balance when the specimen has been replaced by the spacers (see Figure II-2):

$$C_s + C_c = \frac{C_{T_2}}{1 + D_{T_2}^2}$$

$$\frac{1}{R_s} + \frac{1}{R_c} = \omega D_{T_2} C_{T_2}$$

or equivalently

$$C_s = C_{T_2} - C_c \quad \text{--- } \gamma$$

$$G_s = \omega D_{T_2} C_{T_2} - G_c \quad \text{--- } \delta$$

where, C_s , is the capacitance of the volume of space occupied previously by the sample and now by vacuum and spacers, and, G_s , is the conductance of this capacitance. We denote by C_{vac} the capacitance value that C_s would have if there had been no spacers and we denote by $C_{spacers}$, the capacitance of the three ruby spacers. It follows that

$$C_s \approx C_{vac} + C_{spacers}$$

but since

$$C_{spacers} \lesssim 2 \times 10^{-2} C_{vac}$$

then

$$C_s \approx C_{vac}$$

and consequently $C_s = C_{T_2} - C_c \approx C_{vac} \text{ --- } \gamma'$

We denote by G_{vac} the conductance value that C_s would have had if there had been no spacers and we denote by $G_{spacers}$ the conductance of the three spacers. It follows that

$$G_{vac} + G_{spacers} + G_{cell} \approx \omega D_{T_2} C_{T_2}$$

Now $G_{vac} = 0$, so that if we assume that $G_{spacers} \ll G_{cell}$,

then $G_{cell} \approx \omega D_{T_2} C_{T_2} \text{ --- } \delta'$

We will justify the assumption used but first we consider the derivation of the dielectric properties of a specimen on the basis that the assumption is valid.

The following two relations for the parallel capacitance and the conductance of a specimen are derived from equations α , β , γ' , δ' :

$$(C_x)_p \approx C_{T_1} - C_{T_2} + C_{vac}$$

$$(G_x)_p \approx \omega D_1 T_1 - \omega D_2 T_2$$

The dissipation factor of the specimen $\text{Tan } \delta = \frac{(G_x)_p}{\omega (C_x)_p}$

By definition, the dielectric constant $k' = (C_s)_p / C_{vac}$

the loss factor $k'' = k \text{ Tan } \delta$

and the ac conductivity $\sigma = \frac{f k''}{1.8 \times 10^{12}} \Omega^{-1} \text{ cm}^{-1}$

when f is in cps.

The dielectric parameters just derived still contain edge effect errors but these we will ignore relative to the larger inaccuracy ($\approx 2\%$) in putting $C_{vac} \approx C_s$. We consider now the assumption that $G_{spacers} \ll G_{cell}$.

The volume of space occupied by the spacers is about 0.2% of the volume occupied by the specimen. There is, as well, about 100 times more Al_2O_3 in the "cup" (#21, Figure 2.5) than in the specimen. The "cup" and spacers have about the same resistivity ρ and thickness, t , but the cross-sectional area, A , of the cup is at least 10^6 larger than that of a spacer.

Since

$$\frac{G_{\text{cell}}}{G_{\text{spacers}}} \propto \frac{A_{\text{cell}}}{A_{\text{spacers}}}$$

it follows that the assumption $G_{\text{cell}} \gg G_{\text{spacers}}$ is valid.

Experimental procedure:

The attempt was made to measure the capacitance of the assemblies (Figures II-1 and II-2) at the same temperature and with same total pressure of the surrounding atmosphere in order to apply the previous considerations of 2-terminal theory to specimen C2A.

Results:

Using the outlined theory, the dielectric parameters of sample C2A have been calculated. It is seen that the attempt to match conditions was reasonably successful. The results are tabulated in Table II-1.

Discussion of results:

The accuracy of the 2-terminal measurements reported herein is in doubt because of the lack of a reproducibility test. For example, a greater number of measurements would be required to ascertain whether or not the Al_2O_3 cup exhibits thermal hysteresis. It was assumed in the theoretical discussion that the cell capacitance and resistance would not change between successive runs and consequently any hysteresis

Table II-1

Results of 2-terminal measurements of the ac conductivity of a
specimen of 6N Al₂O₃ (C2A)

A) With the sample in the cell

Frequency Cps	Capacitance C _{T₁} (pf)	Dissipation Factor D _{T₁}	Temperature (°C)	Pressure (mm Hg)
10 ⁵	151.6	.0030	27	4 x 10 ⁻⁵
10 ⁴	151.6	.0040		
10 ⁵	155.65	.0273	421	1.7x10 ⁻⁵
10 ⁴	167.96	.237		
10 ⁵	163.17	.0624	575	1.7x10 ⁻⁵
10 ⁴	227.91	.491		
10 ⁵	170.03	.0813	735	1.7x10 ⁻⁵
10 ⁴	259.50	.620		

B) With the sample out; with 3 ruby spacers in

Frequency Cps	Capacitance C_{T_1} (pf)	Dissipation Factor D_{T_1}	Temperature (°C)	Pressure (mm Hg)
10^5	121.01	.0028	17	3.8×10^{-5}
10^4	121.95	.0127		
10^5	122.01	.0172	423	1.9×10^{-5}
10^4	128.43	.201		
10^5	127.53	.072	731	1.7×10^{-5}
10^4	182.80	.599		
10^5	125.17	.051	573	1.5×10^{-5}
10^4	150.6	.410		
10^5	120.09	.0025	26	1.5×10^{-5}
10^4	121.45	.0125		(rerun)

C) Derived parameters

Temperature (°C)	Frequency (cps)	Cp (pf)	k'	Tan δ	k''	$\sigma \times 10^{10}$ ($\Omega^{-1}\text{cm}^{-1}$)
R.T.	10^5	34.0	9.9	.0034	.034	19
	10^4	33.0	9.6	.0084	.078	4
422	10^5	37.0	10.8	.058	.625	347
	10^4	40.0	11.6	.328	3.82	212
574	10^5	41.0	12.0	.092	1.10	610
	10^4	50.0	14.5	.48	6.94	385
733	10^5	44.8	13.1	.102	1.33	740
	10^4	56.5	16.4	.630	10.4	575

effects could have produced large inaccuracies in the quoted results. We note though that the measurements were only carried out to $\approx 750^\circ\text{C}$ in order to avoid Mo contamination on the Al_2O_3 cup.

The result of the 2-terminal measurements when compared with the results of 3-terminal measurements are indicative of a high conductivity surface effect at low temperatures. The results of both methods tend to coincide as the temperature is increased from 500°C on up. Since we know of no comparable measurements we propose that a study of the possibility of the existence of high conductivity surface be examined in a more sophisticated manner.

Appendix II-2

Calibration of the G.R. 1650 capacitance bridge.

The capacitance standards of the bridge were calibrated initially on the assumption that the internal 100 pf standard was absolutely correct. This assumption was checked by measuring a standard 3-terminal capacitor, G.R. type 1404-A, with the standard certificate value of 1000.005 pf $\pm$ 5 ppm. At all frequencies in the range 10^2 to 10^5 cps the value of this capacitance as read from the bridge agreed within 0.01% with the calibrated value.

The calibration of dissipation factor readings proceeded in the following manner:

The standard of dissipation factor was the 1404-A calibrated capacitor with its known loss of less than 10 ppm at 1000 cps. Loss was added in the form of a calibrated resistor in series with the capacitor to obtain a calibrated value of dissipation factor, $D = \omega RC + D_d$.

The circuit of the 3-terminal capacitor with added series resistance, R , is shown in Figure II-3. The direct capacitance between standard capacitor terminals H and L is C_d , and the loss in the standard is represented by the dissipation factor, D_d .

Figure II-3. Equivalent circuit of the dissipation-factor standard.

The stray capacitance from the junction, H, of R and C_d to ground, G , is represented by C_g and any loss by D_g . The stray capacitance across R is represented by C_R . The errors produced by the residuals, C_R , D_g ,

and D_d may be determined from the more exact relations:³⁴

$$C_{BL} = C_d (1 + D_g^2) (1 + \omega^2 R^2 C_R^2) x$$

$$\left[1 - D'_{BL}^2 \frac{C_R}{C_d + C_g} + D' (D_d - D_g) \frac{C_g}{C_d + C_g} + \dots \right]$$

$$\text{where } D'_{BL} = \omega R (C_d + C_g)$$

$$\text{and } D_{BL} = (D'_{BL} + D_d) \left[1 - D'_{BL}^2 \frac{C_R}{C_d + C_g} + D'_{BL} (D_d - D_g) \frac{C_g}{C_d + C_g} + \dots \right]$$

Now, the dissipation factor of the 1404-A standard capacitor is less than 10^{-5} , but the exact value is not known. Consequently, we ignore the residual D_d in the calibration that follows. It is realized fully that the error introduced by ignoring D_d reflects in the absolute measuring accuracy of the present studies (see Figure 2.9).

The standard 1404-A 1000 pf capacitor was connected to the bridge as shown in Figure II-4A. The value of capacitance, $(C_d + C_g)$, measured in this manner included not only the usual direct capacitance, C_d , but also all internal stray capacitance, C_g , from the H-terminal center conductor and wiring to the case. Then, a type 1432-J decade resistor was connected to the standard capacitor as shown in Figure II-4B.

From the calibrated values of $(C_d + C_g)$, R , and $\omega = 2\pi f$, the dissipation factor $D' = \omega R (C_d + C_g)$ was calculated. The stray capacitance, C_R , across the resistor was obtained by measuring with the bridge the effective capacitance C_{BL} when the resistor was connected as shown in Figure II-4B. With the resistor in this circuit replaced by a direct connection from bridge H terminal to capacitance H terminal the capacitance, C_d , was measured.

Figure II-4. (A) Arrangement for the measurement of $C_d + C_g$. (B) Arrangement for the measurement of a constructed dissipation-factor standard.

The error from the measured C_{BL} and C_d is given by

$$\text{error} = [D'_{BL}{}^2 \frac{C_R}{(C_d + C_g)}] = \frac{C_d - C_{BL}}{C_d}$$

When this error cannot be neglected the correct dissipation factor, D_{BL} , is obtained from the value of D'_{BL} and is

$$D_{BL} = D'_{BL} [1 - \text{error}]$$

In Table 4A, we have listed the measured dissipation factor values, the calculated dissipation factors and the corrected dissipation factors obtained with the operating frequency at $1000.0 \pm .2$ cps and with the generator output voltage set at 100 volts.

Table 4A
Dissipation factor readings

R Added	C_{BL} Measured	D' Constructed	D Measured	$\frac{D' - D}{D} \times 100\%$	D_{BL} Corrected
11,000	999.444 pf	.071221	.071200	< .1%	.071182
10,000	999.538	.064746	.064740	< .1%	.064717
1,000	999.983	.006475	.006473	< .1%	.006475
100	999.986	.000648	.000642	.53%	.000648
10	999.982	.000065	.000064	1.54%	.000065
1	999.982	.000007	.000006	17%	.000007

Note: $C_d = 999.987$ pf
 $C_d + C_g = 1030.470$ pf

In order to assess the effect of applied voltage (as discussed in Section II) the generator output voltage was reduced to 10 volts. The readings taken agreed exactly with those in Table 4A. The applied voltage was reduced to 1 volt but then the sensitivity of the detector was reduced by such a large factor that precise balance points could not be obtained.

The values of the corrected dissipation factor readings, (D_{BL}), agreed with the values of the constructed dissipation factors, D' , within the quoted accuracy (see Figure 2.9).

Appendix II-3 Tabulated results of 3-terminal electrical
conductivity measurements.

The voltage applied to the test specimen depended on the frequency of the applied field and was as shown in the following tables.

<u>Frequency (cps)</u>	<u>Voltage Applied (volts)</u>
100745.0	030.
050322.0	030.
020319.0	030.
010032.0	100.
004984.0	100.
001992.0	030.
000933.6	030.
000497.7	010.
000192.2	003.
000099.5	003.

THESIS TABLES

C2A DATA

6N-AL2O3

TEMP= 26. C, 1000/TEMP= 3.342 PRESS= 3.0E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	14.824		9.176		
50322.0	14.834	.00015	9.184	.00138	3.876E-11
20319.0	14.839	.00024	9.187	.00224	2.528E-11
10032.0	14.841	.00027	9.189	.00248	1.387E-11
4984.0	14.843	.00027	9.190	.00256	7.102E-12
1992.0	14.846	.00028	9.192	.00265	2.938E-12
993.6	14.848	.00027	9.193	.00255	1.411E-12
497.7	14.850	.00027	9.194	.00256	7.085E-13
192.2	14.855		9.197		

TEMP= 160. C, 1000/TEMP= 2.308 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.097		9.347		
50322.0	15.107	.00020	9.353	.00188	5.263E-11
20319.0	15.114	.00036	9.357	.00342	3.863E-11
10032.0	15.117	.00048	9.360	.00450	2.512E-11
4984.0	15.120	.00061	9.362	.00578	1.602E-11
1992.0	15.126	.00084	9.365	.00792	8.774E-12
993.6	15.132	.00110	9.369	.01033	5.703E-12
497.7	15.138	.00144	9.373	.01352	3.740E-12
192.2	15.161	.00249	9.387	.02345	2.504E-12

TEMP= 164. C, 1000/TEMP= 2.287 PRESS= 2.4E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.106		9.353		
50322.0	15.114	.00020	9.358	.00188	5.266E-11
20319.0	15.121	.00040	9.362	.00380	4.294E-11
10032.0	15.124	.00050	9.364	.00469	2.617E-11
4984.0	15.128	.00064	9.366	.00606	1.680E-11
1992.0	15.134	.00090	9.370	.00849	9.398E-12
993.6	15.140	.00178	9.374	.01070	9.254E-12
497.7	15.146	.00149	9.378	.01400	5.871E-12
192.2	15.159	.00192	9.386	.01804	1.926E-12

TEMP= 270. C, 1000/TEMP= 1.841 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.316	.00130	9.483	.01241	8.551E-10
50322.0	15.338	.00211	9.497	.02007	5.611E-10
20319.0	15.364	.00341	9.512	.03247	3.688E-10
10032.0	15.386	.00457	9.526	.04355	2.420E-10
4984.0	15.415	.00633	9.544	.06051	1.375E-10
1992.0	15.470	.00996	9.578	.09540	1.055E-10
993.6	15.530	.01428	9.615	.13739	7.284E-11
497.7	15.618	.02075	9.670	.20069	5.549E-11
192.2	15.825	.03075	9.798	.30130	3.217E-11

THESIS TABLES

C2A DATA

GR-AL203

COI

TEMP= 578. C, 1000/TEMP= 1.555 PRESS= 1.2E-05 mm Hg

FREQ	CP	DS	KPR	KZPR	SIG
100745.0	15.622	.00836	9.672	.08088	4.520E-09
50322.0	15.591	.01232	9.715	.11578	3.340E-09
20319.0	15.805	.02021	9.768	.19785	2.233E-09
10032.0	15.937	.02930	9.867	.28915	1.611E-09
4984.0	16.141	.04245	9.993	.42427	1.174E-09
1992.0	16.601	.06470	10.278	.66504	7.359E-10
993.6	17.149	.08186	10.618	.86922	4.753E-10
497.7	17.850	.09555	11.051	1.05609	2.920E-10
192.2	18.987	.10571	11.756	1.24275	1.323E-10
99.5	19.840	.12338	12.283	1.51559	6.277E-11

TEMP= 587. C, 1000/TEMP= 1.162 PRESS= 1.3E-05 mm Hg

FREQ	CP	DS	KPR	KZPR	SIG
100745.0	16.784	.06034	10.392	.62713	3.510E-08
50322.0	17.323	.07996	10.726	.85767	2.397E-08
20319.0	18.278	.10291	11.316	1.16468	1.314E-08
10032.0	19.137	.11516	11.848	1.36461	7.605E-09
4984.0	20.105	.13132	12.448	1.63482	4.526E-09
1992.0	21.601	.16181	13.574	2.16413	2.554E-09
993.6	22.991	.19673	14.234	2.80048	1.543E-09
497.7	24.700	.24685	15.295	3.77332	1.053E-09
192.2	27.689	.32625	17.143	5.13327	5.572E-10
99.5	30.710	.46486	19.014	6.83895	4.000E-10

TEMP= 639. C, 1000/TEMP= .899 PRESS= 1.3E-05 mm Hg

FREQ	CP	DS	KPR	KZPR	SIG
100745.0	20.066	.14408	12.423	1.78988	1.001E-07
50322.0	21.335	.17210	13.210	2.27347	6.313E-08
20319.0	23.371	.22716	14.470	3.26718	3.712E-08
10032.0	25.394	.28019	15.722	4.40545	2.413E-08
4984.0	27.948	.36173	17.304	6.25889	1.351E-08
1992.0	32.448	.52728	20.090	10.33333	1.172E-08
993.6	36.948	.72890	22.876	16.67509	5.254E-09
99.5	59.930	2.87127	37.105	106.54030	5.661E-09

TEMP= 987. C, 1000/TEMP= .793 PRESS= 1.3E-05 mm Hg

FREQ	CP	DS	KPR	KZPR	SIG
100745.0	22.583	.20179	13.982	2.82155	1.575E-07
50322.0	24.390	.25100	15.101	3.79047	1.058E-07
20319.0	27.493	.35009	17.022	5.95948	6.727E-08
10032.0	30.642	.44913	18.972	8.52113	4.745E-08
4984.0	34.832	.60256	21.566	12.99505	3.591E-08
1992.0	41.987	.93086	25.996	24.19923	2.673E-08

THESIS TABLES

CZA DATA

6R-AL2O3

COR

TEMP= 478. C, 1000/TEMP= 1.331 PRESS= 1.1E-05 MM HG

FREQ	CP	DS	KPK	KZPK	SIG
100745.0	15.229	.02220	9.429	.25993	1.174E-00
50322.0	15.383	.03492	9.524	.33202	5.290E-09
20319.0	15.744	.05943	9.747	.57933	6.333E-09
10032.0	16.204	.07885	10.032	.79110	4.433E-09
4984.0	16.634	.09818	10.423	1.02339	2.431E-09
1992.0	17.875	.12330	11.067	1.36470	1.371E-09
993.6	18.840	.14635	11.669	1.70797	9.428E-10
497.7	20.022	.17419	12.390	2.13947	5.970E-10
192.2	22.000	.21910	13.821	2.98453	3.166E-10
99.5	23.950	.28059	14.828	4.16076	2.259E-10

TEMP= 587. C, 1000/TEMP= 1.162 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPK	KZPK	SIG
100745.0	16.784	.06034	10.592	.62713	3.210E-01
50322.0	17.323	.07996	10.726	.80767	2.357E-00
20319.0	18.278	.10291	11.316	1.16468	1.314E-00
10032.0	19.137	.11516	11.840	1.36461	7.600E-09
4984.0	20.105	.13132	12.448	1.63482	4.520E-09
1992.0	21.601	.16181	13.574	2.16413	2.354E-09
993.6	22.991	.19673	14.234	2.60048	1.543E-09
497.7	24.700	.24685	15.293	3.71332	1.043E-09
192.2	27.889	.33442	17.143	5.73330	6.121E-10
99.5	30.710	.47362	19.014	9.00544	4.170E-10

TEMP= 726. C, 1000/TEMP= 1.000 PRESS= 1.1E-05 MM HG

FREQ	CP	DS	KPK	KZPK	SIG
100745.0	17.711	.11172	10.983	1.22316	6.177E-00
50322.0	18.611	.13425	11.523	1.54708	4.323E-00
20319.0	20.103	.17484	12.446	2.17825	2.436E-00
10032.0	21.525	.20706	13.327	2.83955	1.337E-00
4984.0	23.333	.25468	14.446	3.87937	1.011E-00
1992.0	26.484	.34481	16.397	5.65414	6.237E-09
993.6	29.619	.44652	18.338	8.18872	4.370E-09
497.7	33.365	.59724	20.657	12.33773	3.411E-09
192.2	40.460	.87451	25.050	21.90713	2.333E-09
99.5	46.950	1.33330	29.069	38.75777	2.142E-09

TEMP= 863. C, 1000/TEMP= .860 PRESS= 1.1E-05 MM HG

FREQ	CP	DS	KPK	KZPK	SIG
100745.0	19.992	.15806	12.578	1.95662	1.033E-07
50322.0	21.375	.19092	13.234	2.52661	7.064E-00
20319.0	23.619	.25175	14.823	3.68158	4.133E-00
10032.0	25.822	.31099	15.988	4.97214	2.771E-00
4984.0	28.579	.40420	17.695	7.15239	1.980E-00
1992.0	33.736	.57668	20.887	12.04571	1.333E-00
993.6	38.734	.79259	23.982	19.00812	1.049E-00

THESIS TABLES

C2D DATA

6R-AL2O3

TEMP= 22. C, 1000/TEMP= 3.387 PRESS= 3.1E-05 MM HG

FREQ	CP	DS	KPK	K2PK	SIG
100745.0	15.459		9.737		
50322.0	15.468	.00001	9.743	.00009	2.791E-12
20319.0	15.472	.00006	9.746	.00059	6.786E-12
10032.0	15.474	.00006	9.747	.00058	3.269E-12
4984.0	15.475	.00007	9.747	.00077	2.152E-12
1992.0	15.476	.00009	9.748	.00097	1.074E-12
993.6	15.477	.00010	9.748	.00106	5.881E-13
497.7	15.477	.00010	9.749	.00106	2.951E-13

TEMP= 127. C, 1000/TEMP= 2.499 PRESS= 2.6E-05 MM HG

FREQ	CP	DS	KPK	K2PK	SIG
100745.0	15.658		9.862		
50322.0	15.670	.00012	9.870	.00119	3.332E-11
20319.0	15.676	.00018	9.874	.00180	2.038E-11
10032.0	15.678	.00019	9.875	.00188	1.049E-11
4984.0	15.681	.00024	9.877	.00246	6.815E-12
1992.0	15.684	.00034	9.879	.00344	3.811E-12
993.6	15.688	.00046	9.881	.00461	2.547E-12
497.7	15.692	.00059	9.884	.00590	1.632E-12

TEMP= 214. C, 1000/TEMP= 2.052 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPK	K2PK	SIG
100745.0	15.817	.00015	9.963	.00150	6.428E-11
50322.0	15.828	.00040	9.970	.00401	1.122E-10
20319.0	15.838	.00075	9.976	.00750	6.468E-11
10032.0	15.847	.00110	9.982	.01101	6.139E-11
4984.0	15.856	.00149	9.987	.01493	4.134E-11
1992.0	15.871	.00222	9.996	.02220	2.457E-11
993.6	15.886	.00300	10.007	.03002	1.657E-11
497.7	15.908	.00408	10.020	.04009	1.130E-11
192.2	15.944	.00576	10.043	.05790	6.135E-12
99.5	15.988	.00865	10.071	.08618	4.120E-12

TEMP= 258. C, 1000/TEMP= 1.882 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPK	K2PK	SIG
100745.0	15.903	.00060	10.017	.00605	3.115E-10
50322.0	15.922	.00110	10.029	.01110	3.100E-10
20319.0	15.940	.00186	10.040	.01876	2.118E-10
10032.0	15.955	.00246	10.050	.02480	1.312E-10
4984.0	15.973	.00332	10.061	.03349	9.275E-11
1992.0	16.006	.00494	10.082	.04980	5.512E-11
993.6	16.039	.00675	10.103	.06826	3.788E-11
497.7	16.089	.00945	10.134	.09583	2.649E-11
192.2	16.176	.01441	10.189	.14688	1.588E-11
99.5	16.303	.01990	10.269	.20436	1.129E-11

TEMP= 305. C, 1000/TEMP= 1.567 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPK	KZPK	SIG
100745.0	16.162	.00382	10.180	.03897	2.181E-09
50322.0	16.206	.00548	10.207	.05599	1.585E-09
20319.0	16.265	.00879	10.245	.09013	1.017E-09
10032.0	16.327	.01258	10.284	.12917	7.199E-10
4984.0	16.420	.01812	10.342	.18743	5.189E-10
1992.0	16.613	.02858	10.464	.29912	3.310E-10
993.6	16.851	.03881	10.614	.41205	2.274E-10
497.7	17.211	.04977	10.841	.53956	1.491E-10
192.2	17.882	.06150	11.263	.69277	7.397E-11
99.5	18.410	.06965	11.556	.80770	4.464E-11

TEMP= 435. C, 1000/TEMP= 1.412 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPK	KZPK	SIG
100745.0	16.577	.01158	10.442	.12097	6.771E-09
50322.0	16.672	.01529	10.501	.16065	4.491E-09
20319.0	16.833	.02367	10.602	.23096	2.833E-09
10032.0	17.018	.03240	10.719	.34736	1.935E-09
4984.0	17.289	.04296	10.890	.48786	1.295E-09
1992.0	17.805	.05581	11.215	.62598	6.327E-10
993.6	18.511	.06255	11.554	.72199	3.881E-10
497.7	18.877	.06619	11.890	.77708	2.151E-10
192.2	19.675	.06150	12.353	.78224	1.131E-10
99.5	20.515	.06467	12.758	.82159	6.575E-11

TEMP= 530. C, 1000/TEMP= 1.245 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPK	KZPK	SIG
100745.0	17.002	.02347	10.709	.25139	1.437E-09
50322.0	17.196	.03316	10.831	.35921	1.000E-09
20319.0	17.603	.04933	11.008	.54795	6.171E-10
10032.0	18.045	.05881	11.368	.65356	3.721E-10
4984.0	18.593	.06573	11.711	.76390	2.131E-10
1992.0	19.397	.06972	12.217	.85163	9.421E-11
993.6	20.037	.06985	12.821	.85161	4.801E-11
497.7	20.875	.06768	13.023	.85149	2.407E-11
192.2	21.490	.06230	13.536	.84333	1.000E-11
99.5	22.080	.06385	13.907	.88614	5.000E-12

TEMP= 673. C, 1000/TEMP= 1.058 PRESS= 1.4E-05 MM HG

FREQ	CP	DS	KPK	KZPK	SIG
100745.0	17.844	.05198	11.240	.58431	3.121E-09
50322.0	18.358	.06310	11.564	.72973	2.041E-09
20319.0	19.158	.07223	12.067	.87170	9.842E-10
10032.0	19.806	.07333	12.476	.91492	5.890E-10
4984.0	20.481	.07346	12.901	.94776	2.824E-10
1992.0	21.377	.07230	13.485	.97366	1.077E-10
993.6	22.039	.07223	13.882	1.00281	5.331E-11
497.7	22.681	.07515	14.287	1.07371	2.381E-11
192.2	23.670	.08956	14.909	1.33537	1.421E-11
99.5	24.250	.10845	15.274	1.65662	7.157E-12

THESIS TABLES

C2B DATA

GR-AL2O3

CON

TEMP= 992. C, 1000/TEMP= .790 PRESS= 1.4E-05 MM HG

FREQ	CP	DS	KPK	K2PK	SIG
100745.0	20.281	.10689	12.964	1.38575	7.71E-09
50322.0	21.487	.12711	13.554	1.72046	4.11E-09
20319.0	22.938	.17189	14.448	2.48367	2.13E-09
10032.0	24.180	.21779	15.230	3.31716	1.54E-09
4984.0	26.049	.29555	16.408	4.64549	1.342E-09
1992.0	29.794	.45457	18.767	8.53104	9.441E-09
993.6	33.884	.63689	21.343	13.59376	7.503E-09

TEMP= 1020. C, 1000/TEMP= .773 PRESS= 1.4E-05 MM HG

FREQ	CP	DS	KPK	K2PK	SIG
100745.0	20.475	.13409	12.897	1.72944	9.679E-09
50322.0	21.610	.16545	13.612	2.25224	6.296E-08
20319.0	23.496	.23082	14.799	3.41617	3.856E-08
10032.0	24.898	.28942	15.685	4.53907	2.529E-08
4984.0	27.432	.39154	17.279	6.76561	1.873E-08
1992.0	32.693	.60417	20.593	12.44203	1.376E-08
993.6	38.080	.83889	23.986	20.12228	1.110E-08

TEMP= 848. C, 1000/TEMP= .891 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPK	K2PK	SIG
100745.0	18.099	.07555	11.400	.8142	4.821E-09
50322.0	18.756	.08252	11.614	.97500	2.725E-09
20319.0	19.694	.09245	12.405	1.14689	1.294E-09
10032.0	20.405	.10021	12.652	1.25511	7.179E-09
4984.0	21.262	.11513	13.392	1.54191	4.25E-09
1992.0	22.638	.14402	14.259	2.05370	2.27E-09
993.6	23.830	.18222	15.010	2.73533	1.51E-09
497.7	25.429	.24287	16.017	3.69041	1.7E-09
192.2	27.761	.35028	17.486	6.12518	8.5E-10
99.5	30.350	.51680	19.117	9.87977	3.461E-10

THESIS TABLES

C5A DATA

6N-AL2O3+0.01 MgO

TEMP= 15. C, 1000/TEMP= 3.458 PRESS= 3.5E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.525	.00020	9.959	.00200	1.120e-10
50322.0	15.539	.00040	9.940	.00400	1.119e-10
20319.0	15.547	.00044	9.934	.00444	5.023e-11
10032.0	15.552	.00043	9.937	.00429	2.333e-11
4984.0	15.555	.00041	9.939	.00416	1.134e-11
1992.0	15.557	.00037	9.960	.00376	4.172e-12
993.6	15.560	.00035	9.962	.00356	1.987e-12
497.7	15.563	.00030	9.964	.00307	6.501e-13

TEMP= 40. C, 1000/TEMP= 3.193 PRESS= 3.7E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.569	.00020	9.968	.00200	1.124e-10
50322.0	15.585	.00035	9.978	.00351	9.126e-11
20319.0	15.594	.00040	9.984	.00405	4.500e-11
10032.0	15.599	.00043	9.987	.00433	2.401e-11
4984.0	15.603	.00041	9.989	.00416	1.136e-11
1992.0	15.606	.00036	9.991	.00366	4.074e-12
993.6	15.608	.00035	9.993	.00357	1.873e-12
497.7	15.609	.00031	9.994	.00310	5.442e-13

TEMP= 252. C, 1000/TEMP= 1.904 PRESS= 3.9E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.980	.00060	10.231	.00618	3.461e-11
50322.0	16.002	.00115	10.245	.01185	3.319e-10
20319.0	16.017	.00205	10.254	.02104	2.375e-10
10032.0	16.030	.00310	10.263	.03191	1.770e-10
4984.0	16.050	.00485	10.275	.04988	1.361e-10
1992.0	16.098	.00861	10.306	.08879	9.820e-11
993.6	16.165	.01268	10.349	.13132	7.240e-11
497.7	16.271	.01727	10.417	.17991	4.974e-11

TEMP= 392. C, 1000/TEMP= 1.503 PRESS= 4.2E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.268	.00654	10.415	.06820	3.617e-09
50322.0	16.332	.01006	10.456	.10524	2.942e-09
20319.0	16.455	.01615	10.535	.17018	1.921e-09
10032.0	16.596	.02048	10.625	.21766	1.213e-09
4984.0	16.775	.02389	10.740	.25661	7.105e-10
1992.0	17.044	.02589	10.912	.26238	3.127e-10
993.6	17.253	.02585	11.046	.26159	1.578e-10
497.7	17.454	.02503	11.174	.27975	7.735e-11
192.2	17.741	.02264	11.358	.25716	2.745e-11
99.5	17.900	.02288	11.460	.26226	1.449e-11

THESIS TABLES

C5A DATA

6R-AL2O3+0.01 MOO COI

TEMP= 466. C, 1000/TEMP= 1.352 PRESS= 2.97-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.600	.01682	10.828	.17881	1.000E-05
50322.0	16.762	.02183	10.731	.23438	6.302E-10
20319.0	17.033	.02696	10.909	.29404	3.001E-11
10032.0	17.260	.02792	11.050	.30663	1.000E-11
4984.0	17.492	.02781	11.199	.31140	8.024E-10
1992.0	17.781	.02613	11.384	.29752	3.292E-10
993.6	17.982	.02474	11.512	.28483	1.572E-10
497.7	18.170	.02359	11.633	.27445	7.508E-11
192.2	18.400	.02203	11.780	.25958	2.771E-11
99.5	18.550	.02390	11.876	.26396	1.569E-11

TEMP= 567. C, 1000/TEMP= 1.190 PRESS= 3.0E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	17.158	.02568	10.985	.28222	1.579E-05
50322.0	17.396	.02747	11.137	.30801	8.555E-09
20319.0	17.704	.02793	11.335	.31669	3.574E-09
10032.0	17.923	.02668	11.475	.30832	1.700E-09
4984.0	18.131	.02581	11.608	.29939	8.290E-10
1992.0	18.388	.02529	11.772	.29783	3.293E-10
993.6	18.572	.02623	11.890	.31190	1.721E-10
497.7	18.752	.02956	12.006	.33494	9.014E-11
192.2	19.030	.03776	12.183	.40014	4.913E-11
99.5	19.300	.05601	12.356	.69219	3.020E-11

TEMP= 658. C, 1000/TEMP= 1.073 PRESS= 4.1E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	17.719	.02861	11.344	.32458	1.010E-05
50322.0	17.971	.02858	11.506	.32887	9.194E-05
20319.0	18.276	.02804	11.701	.32609	3.703E-05
10032.0	18.501	.02798	11.845	.33154	1.647E-05
4984.0	18.710	.02890	11.979	.34628	9.508E-10
1992.0	18.981	.03406	12.152	.41395	4.501E-10
993.6	19.213	.04322	12.301	.53137	2.958E-10
497.7	19.508	.05922	12.490	.73974	2.040E-10
192.2	20.050	.09110	12.836	1.18946	1.240E-10
99.5	20.660	.13979	13.227	1.84914	1.022E-10

TEMP= 762. C, 1000/TEMP= .966 PRESS= 4.2E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	18.335	.03374	11.738	.39018	2.217E-05
50322.0	18.627	.03401	11.925	.40569	1.134E-05
20319.0	18.984	.03565	12.154	.43343	4.592E-05
10032.0	19.238	.03882	12.317	.47819	2.685E-05
4984.0	19.507	.04764	12.489	.59507	1.647E-05
1992.0	19.950	.07091	12.772	.90379	1.002E-05
993.6	20.425	.10253	13.077	1.34091	7.401E-10
497.7	21.077	.15130	13.494	2.04174	5.645E-10
192.2	22.280	.25207	14.264	3.59385	3.010E-10
99.5	23.620	.41003	15.122	6.20079	3.427E-10

THESIS TABLES

CSA DATA

6N-AL2O3+0.01 MgO CO

TEMP= 629. C, 1000/TEMP= 1.108 PRESS= 4.4E-05 mm HG
 FREQ CP DS KPR K2PR SIG
 100745.0 17.565 .02800 11.245 .31496 1.762E-06

TEMP= 640. C, 1000/TEMP= 1.095 PRESS= 4.4E-05 mm HG
 FREQ CP DS KPR K2PR SIG
 100745.0 17.651 .02841 11.301 .32107 1.797E-06

TEMP= 638. C, 1000/TEMP= .899 PRESS= 4.0E-05 mm HG
 FREQ CP DS KPR K2PR SIG
 100745.0 18.724 .04211 11.968 .50464 2.825E-06

TEMP= 638. C, 1000/TEMP= .899 PRESS= 1.0E-05 mm HG
 FREQ CP DS KPR K2PR SIG
 100745.0 18.686 .03979 11.963 .47115 2.864E-06

TEMP= 671. C, 1000/TEMP= .874 PRESS= 4.3E-05 mm HG
 FREQ CP DS KPR K2PR SIG
 100745.0 20.132 .05208 12.889 .67135 3.757E-06

TEMP= 682. C, 1000/TEMP= .865 PRESS= 4.3E-05 mm HG
 FREQ CP DS KPR K2PR SIG
 100745.0 20.208 .05500 12.938 .71170 3.903E-06

TEMP= 933. C, 1000/TEMP= .829 PRESS= 4.3E-05 mm HG
 FREQ CP DS KPR K2PR SIG
 100745.0 20.820 .08623 13.329 1.14955 6.433E-06

TEMP= 946. C, 1000/TEMP= .820 PRESS= 4.3E-05 mm HG
 FREQ CP DS KPR K2PR SIG
 100745.0 21.089 .10356 13.502 1.39039 7.826E-06

TEMP= 990. C, 1000/TEMP= .791 PRESS= 4.3E-05 mm HG
 FREQ CP DS KPR K2PR SIG
 100745.0 21.819 .16723 13.969 2.33626 1.567E-07

TEMP= 1003. C, 1000/TEMP= .783 PRESS= 4.3E-05 mm HG
 FREQ CP DS KPR K2PR SIG
 100745.0 22.016 .20874 14.095 2.94243 1.646E-07

THESES TABLES C5A DATA 6R-AL2O3+0.01 RGO CO
 TEMP= 832. C, 1000/TEMP= .904 PRESS= 4.0E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	18.713	.03999	11.911	.47920	2.682E-05
50322.0	19.058	.04710	12.202	.57475	1.600E-10
20319.0	19.529	.06410	12.503	.70134	9.04E-15
10032.0	19.965	.08497	12.782	1.00817	6.055E-20
4984.0	20.578	.12210	13.174	1.60175	4.454E-25
1992.0	21.764	.20059	13.934	2.79514	3.055E-30
993.6	23.098	.29579	14.786	4.37446	2.41E-35
497.7	25.040	.44006	16.031	7.05514	1.95E-40
192.2	28.660	.71258	18.477	13.16656	1.405E-45
99.5	33.300	1.10813	21.319	23.62529	1.305E-50

TEMP= 152. C, 1000/TEMP= 2.352 PRESS= 3.9E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.742	.00030	10.078	.00304	1.704E-10
10032.0	15.769	.00042	10.096	.00425	2.370E-11
993.6	15.781	.00054	10.104	.00552	3.047E-12

TEMP= 300. C, 1000/TEMP= 1.744 PRESS= 4.0E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.046	.00141	10.273	.01449	8.110E-10

TEMP= 336. C, 1000/TEMP= 1.641 PRESS= 4.1E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.112	.00231	10.316	.02390	1.337E-09

TEMP= 371. C, 1000/TEMP= 1.552 PRESS= 4.4E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.188	.00423	10.364	.04385	2.454E-09

TEMP= 368. C, 1000/TEMP= 1.559 PRESS= 4.0E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.172	.00372	10.354	.03859	2.168E-09

TEMP= 375. C, 1000/TEMP= 1.542 PRESS= 4.4E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.205	.00463	10.375	.04808	2.691E-09

TEMP= 393. C, 1000/TEMP= 1.501 PRESS= 4.2E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.267	.00654	10.414	.06820	3.817E-09

TEMP= 625. C, 1000/TEMP= 1.113 PRESS= 4.4E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	17.537	.02790	11.228	.31333	1.702E-09

THESIS TABLES

CSA DATA

6K-AL2O3+0.1MGU

TEMP= 354. C, 1000/TEMP= 1.594 PRESS= 1.7E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 16.035 .00342 10.100 .03439 1.936E-09

TEMP= 162. C, 1000/TEMP= 2.298 PRESS= 1.4E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 15.480 .00050 9.750 .00491 2.748E-10

TEMP= 251. C, 1000/TEMP= 1.907 PRESS= 1.4E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 15.797 .00090 9.950 .00902 5.049E-10

TEMP= 283. C, 1000/TEMP= 1.798 PRESS= 1.4E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 15.876 .00151 10.000 .01511 6.431E-10

TEMP= 397. C, 1000/TEMP= 1.492 PRESS= 1.4E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 16.194 .00705 10.200 .07193 4.028E-09

TEMP= 441. C, 1000/TEMP= 1.400 PRESS= 1.5E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 16.273 .01118 10.250 .11462 6.415E-09

TEMP= 319. C, 1000/TEMP= 1.688 PRESS= 1.3E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 15.956 .00231 10.050 .02328 1.303E-09

TEMP= 508. C, 1000/TEMP= 1.280 PRESS= 1.3E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 16.670 .01763 10.500 .16912 1.035E-09

TEMP= 539. C, 1000/TEMP= 1.231 PRESS= 1.3E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 16.988 .02558 10.700 .27380 1.532E-06

TEMP= 594. C, 1000/TEMP= 1.153 PRESS= 1.4E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 17.305 .02629 10.900 .28661 1.604E-06

TEMP= 460. C, 1000/TEMP= 1.363 PRESS= 1.4E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 16.353 .01460 10.300 .15046 8.421E-09

TEMP= 713. C, 1000/TEMP= 1.014 PRESS= 1.4E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 17.781 .03385 11.199 .37912 2.121E-06

TEMP= 814. C, 1000/TEMP= .919 PRESS= 1.5E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 18.416 .03939 11.599 .45593 2.557E-06

TEMP= 903. C, 1000/TEMP= .850 PRESS= 1.5E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 19.051 .06014 11.999 .72170 4.039E-06

TEMP= 999. C, 1000/TEMP= .786 PRESS= 1.5E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 21.428 .13570 13.496 1.83152 1.029E-07

TEMP= 1030. C, 1000/TEMP= .767 PRESS= 1.7E-05 MM HG
 FREQ CP DS KPR K2PR SIG
 100745.0 22.513 .32057 14.180 4.54577 2.544E-07

THESIS TABLES

C4A DATA

6N-AL2O3+1.0 MGU

TEMP= 53. C, 1000/TEMP= 3.065 PRESS= 2.0E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.125		9.474		
50322.0	15.134	.00015	9.480	.00143	4.001E-11
20319.0	15.138	.00020	9.483	.00192	2.175E-11
10032.0	15.141	.00024	9.485	.00228	1.272E-11
4984.0	15.145	.00026	9.486	.00255	7.069E-12
1992.0	15.145	.00029	9.487	.00283	3.137E-12
993.6	15.147	.00032	9.488	.00311	1.717E-12
497.7	15.148	.00034	9.489	.00330	9.141E-13

TEMP= 54. C, 1000/TEMP= 3.056 PRESS= 2.1E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.125		9.475		
50322.0	15.133	.00010	9.479	.00095	2.667E-11
20319.0	15.139	.00020	9.483	.00192	2.175E-11
10032.0	15.141	.00024	9.485	.00228	1.272E-11
4984.0	15.143	.00026	9.486	.00255	7.069E-12
1992.0	15.145	.00028	9.487	.00274	3.032E-12
993.6	15.147	.00031	9.488	.00301	1.665E-12
497.7	15.148	.00034	9.489	.00330	9.141E-13

TEMP= 130. C, 1000/TEMP= 2.480 PRESS= 1.9E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.263	.00005	9.561	.00048	2.685E-11
50322.0	15.272	.00020	9.566	.00192	5.363E-11
20319.0	15.279	.00034	9.571	.00330	3.732E-11
10032.0	15.283	.00043	9.573	.00412	2.501E-11
4984.0	15.286	.00047	9.575	.00458	1.261E-11
1992.0	15.290	.00054	9.578	.00524	5.106E-12
993.6	15.294	.00062	9.580	.00599	3.310E-12

TEMP= 266. C, 1000/TEMP= 1.854 PRESS= 2.0E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.493	.00050	9.705	.00486	2.738E-10
50322.0	15.511	.00095	9.716	.00929	2.597E-10
20319.0	15.525	.00148	9.725	.01442	1.623E-10
10032.0	15.537	.00194	9.732	.01894	1.055E-10
4984.0	15.550	.00257	9.741	.02565	6.936E-11
1992.0	15.573	.00371	9.755	.03624	4.010E-11
993.6	15.596	.00502	9.769	.04911	2.711E-11
497.7	15.625	.01383	9.787	.13542	3.744E-11

THESIS TABLES

C4A DATA

6R-AL2O3+1.0 RGO CON

TEMP= 17. C, 1000/TEMP= 5.446 PRESS= 1.7E-05 MM HG

FREQ	CP	DS	KPR	KZPR	SIG
100745.0	15.052		9.429		
50322.0	15.061	.00011	9.434	.00104	2.919E-11
20319.0	15.052	.00016	9.429	.00153	1.730E-11
10032.0	15.065	.00021	9.437	.00198	1.108E-11
4984.0	15.068	.00022	9.438	.00216	5.991E-12
1992.0	15.069	.00023	9.439	.00225	2.497E-12
993.6	15.070	.00026	9.440	.00253	1.393E-12
497.7	15.072		9.441		

TEMP= 368. C, 1000/TEMP= 1.559 PRESS= 1.5E-05 MM HG

FREQ	CP	DS	KPR	KZPR	SIG
100745.0	15.717	.00292	9.845	.02876	1.610E-09
50322.0	15.753	.00432	9.868	.04270	1.191E-09
20319.0	15.798	.00670	9.896	.06635	7.450E-10
10032.0	15.843	.00922	9.924	.09159	5.104E-10
4984.0	15.905	.01325	9.963	.13206	3.857E-10
1992.0	16.035	.02071	10.045	.20010	2.302E-10
993.6	16.200	.02792	10.148	.28333	1.504E-10
497.7	16.435	.03513	10.295	.36176	1.000E-10
192.2	16.872	.04036	10.589	.42659	4.555E-11

TEMP= 456. C, 1000/TEMP= 1.371 PRESS= 1.4E-05 MM HG

FREQ	CP	DS	KPR	KZPR	SIG
100745.0	16.032	.00987	10.043	.09915	5.549E-09
50322.0	16.115	.01388	10.095	.14021	3.919E-09
20319.0	16.261	.02184	10.186	.22249	2.511E-09
10032.0	16.431	.02869	10.292	.29531	1.645E-09
4984.0	16.679	.03618	10.446	.37804	1.046E-09
1992.0	17.109	.04213	10.717	.48155	4.997E-10
993.6	17.471	.04302	10.944	.47086	2.599E-10
497.7	17.823	.04140	11.164	.46232	1.270E-10
192.2	18.272	.03844	11.446	.44000	4.850E-11

TEMP= 18. C, 1000/TEMP= 5.434 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPR	KZPR	SIG
100745.0	15.061	.00014	9.434	.00133	7.447E-11
50322.0	15.070	.00035	9.440	.00332	9.250E-11
20319.0	15.078	.00058	9.445	.00556	6.282E-11
10032.0	15.084	.00075	9.449	.00710	3.982E-11
4984.0	15.088	.00089	9.451	.00847	2.347E-11
1992.0	15.096	.00108	9.456	.01026	1.136E-11
993.6	15.104	.00128	9.461	.01212	6.694E-12
497.7	15.112	.00149	9.466	.01413	3.908E-12
192.2	15.129	.00192	9.477	.01821	1.945E-12

THESIS TABLES

C4A DATA

CH-AL2O3+1.0 MGU CO

TEMP= 135. C, 1000/TEMP= 2.450 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.265	.00070	9.574	.00675	3.779E-10
50322.0	15.306	.00125	9.588	.01206	3.372E-10
20319.0	15.322	.00162	9.598	.01560	1.781E-10
10032.0	15.336	.00195	9.607	.01879	1.047E-10
4984.0	15.351	.00227	9.616	.02185	6.051E-11
1992.0	15.372	.00262	9.629	.02532	2.882E-11
995.6	15.392	.00290	9.641	.02797	1.544E-11
497.7	15.409	.00318	9.652	.03074	8.501E-12
192.2	15.439	.00345	9.671	.03346	3.572E-12
99.5	15.469	.00398	9.690	.03656	2.131E-12

TEMP= 260. C, 1000/TEMP= 1.875 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	15.515	.00171	9.719	.01664	9.316E-10
50322.0	15.543	.00251	9.736	.02449	6.848E-10
20319.0	15.574	.00335	9.755	.03270	3.692E-10
10032.0	15.599	.00391	9.771	.03823	2.150E-10
4984.0	15.627	.00458	9.789	.04468	1.242E-10
1992.0	15.668	.00567	9.815	.05272	6.186E-11
995.6	15.706	.00675	9.838	.06047	3.681E-11
497.7	15.750	.00836	9.866	.06849	2.281E-11
192.2	15.828	.01076	9.914	.10671	1.139E-11

TEMP= 452. C, 1000/TEMP= 1.379 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.019	.00896	10.034	.06997	5.035E-09
50322.0	16.093	.01258	10.081	.12862	3.345E-09
20319.0	16.222	.01970	10.162	.20029	2.250E-09
10032.0	16.373	.02658	10.257	.27269	1.511E-09
4984.0	16.599	.03419	10.398	.35551	9.781E-10
1992.0	17.005	.04113	10.652	.43818	6.889E-10
995.6	17.360	.04282	10.874	.46571	2.570E-10
497.7	17.714	.04180	11.096	.46890	1.202E-10
192.2	18.150	.03671	11.389	.41737	4.458E-11
99.5	18.450	.03432	11.557	.39673	2.193E-11

TEMP= 527. C, 1000/TEMP= 1.249 PRESS= 1.2E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.297	.01793	10.208	.18307	1.924E-09
50322.0	16.454	.02536	10.307	.26140	7.300E-09
20319.0	16.767	.03657	10.503	.38414	4.338E-09
10032.0	17.090	.04163	10.705	.44570	2.484E-09
4984.0	17.458	.04385	10.936	.47965	1.328E-09
1992.0	17.941	.04252	11.236	.47793	5.269E-10
995.6	18.287	.04014	11.455	.45983	2.530E-10
497.7	18.605	.03732	11.654	.43503	1.202E-10
192.2	18.990	.03267	11.895	.38867	4.150E-11
99.5	19.260	.03124	12.064	.37693	2.083E-11

THESIS TABLES

C4A DATA

GR-AL2O3+1.0% MgO CO

TEMP= 733. C, 1000/TEMP= .993 PRESS= 1.1E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	17.639	.04694	11.049	.51674	2.903e-08
50322.0	18.071	.04840	11.320	.54799	1.532e-08
20319.0	18.619	.04835	11.663	.56404	6.337e-09
10032.0	19.008	.04644	11.907	.55396	3.002e-09
4984.0	19.377	.04635	12.136	.56262	1.557e-09
1992.0	19.844	.05039	12.430	.62647	6.333e-10
993.6	20.228	.05961	12.671	.75340	4.189e-10
497.7	20.721	.07565	12.986	.98195	2.715e-10
192.2	21.700	.09811	13.593	1.33373	1.424e-10
99.5	22.770	.12248	14.262	1.74705	9.657e-11

TEMP= 660. C, 1000/TEMP= 1.071 PRESS= 1.1E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	17.007	.03838	10.653	.46693	2.285e-08
50322.0	17.376	.04297	10.864	.46777	1.307e-08
20319.0	17.878	.04490	11.199	.50289	5.676e-09
10032.0	18.243	.04343	11.426	.49641	2.758e-09
4984.0	18.593	.04226	11.647	.49227	1.363e-09
1992.0	19.032	.04153	11.922	.49516	5.479e-10
993.6	19.357	.04272	12.125	.51607	2.859e-10
497.7	19.685	.04658	12.331	.57445	1.570e-10
192.2	20.170	.05593	12.634	.70656	7.545e-11
99.5	20.680	.07353	12.954	.95253	5.265e-11

TEMP= 975. C, 1000/TEMP= .801 PRESS= 1.3E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	19.651	.08261	12.310	1.01695	5.651e-08
50322.0	20.315	.10517	12.725	1.33340	3.741e-08
20319.0	21.578	.14914	13.516	2.01592	2.275e-08
10032.0	22.878	.18478	14.331	2.64832	1.475e-08
4984.0	24.444	.23484	15.312	3.59609	9.357e-09
1992.0	26.943	.35059	16.677	5.91716	6.544e-09
993.6	29.308	.50673	18.359	9.30345	5.131e-09
497.7	32.402	.75749	20.257	15.37502	4.251e-09
192.2	39.070	1.27524	24.474	31.21040	5.332e-09
99.5	48.660	1.69946	30.461	51.80177	2.863e-09

TEMP= 673. C, 1000/TEMP= 1.056 PRESS= 1.1E-05 MM HG

FREQ	CP	DS	KPR	K2PR	SIG
100745.0	16.661	.04321	10.437	.45106	2.524e-08
50322.0	17.070	.04851	10.693	.51672	1.450e-08
20319.0	17.625	.04998	11.040	.55166	6.229e-09
10032.0	18.020	.04725	11.288	.53339	2.972e-09
4984.0	18.392	.04505	11.521	.51908	1.437e-09
1992.0	18.850	.04322	11.808	.51043	5.648e-10
993.6	19.192	.04312	12.022	.51843	2.861e-10
497.7	19.518	.04459	12.226	.54522	1.307e-10
192.2	19.940	.05112	12.490	.63858	6.816e-11
99.5	20.350	.06965	12.747	.86766	4.907e-11

Appendix II-4 An estimate of the accuracy of conductivity measurements.

In deriving an estimate of the accuracy of electrical conductivity measured with the G.R. 1650 capacitance measuring assembly the following assumptions have been made.

t_0 = representative room temperature sample thickness,	$t_0 = 0.1$ cm
d_0 = representative room temperature guarded electrode diameter,	$d_0 = 1.5$ cm
α = coefficient of linear expansion,	$\alpha = 10^{-5} \text{ } ^\circ\text{C}^{-1}$
$\Delta\theta$ = maximum used temperature variation,	$\Delta\theta = 10^3 \text{ } ^\circ\text{C}$

The errors associated with these quantities are:

$$\Delta t_0 = .0003 \text{ cm}$$

$$\Delta d_0 = .008 \text{ cm}$$

$$\Delta\alpha = 10^{-5} \times .25 \text{ } ^\circ\text{C}^{-1}$$

$$\Delta(\Delta\theta) = 10^3 \times .02 \text{ } ^\circ\text{C}$$

Δt_0 was obtained by summing the micrometer error and parallelism error

Δd_0 was obtained in the following manner.

The effective diameter of the guard electrode is given by:

$$\frac{D_2 + D_1}{2} - 2\delta$$

$$\text{where } \delta = \text{gap error} = t_0 \frac{2}{\pi} \log_e \cosh (\pi/4 g/t)$$

and g = gap size = a maximum of 0.040 cm.

The error in the effective diameter

$$\Delta d_0 \approx \frac{\Delta D_2 + \Delta D_1}{2} + 2\delta$$

and since $\delta \ll 1$ this yields $\Delta d_0 \approx 0.008$ cm.

The error $\Delta\alpha$ was obtained as follows:

Since the spread of reported results for α are scattered 25% about the value used ($0.8 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$) then

$$\frac{\Delta\alpha}{\alpha} \approx 25\% \rightarrow \Delta\alpha \approx .25 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$$

The error $\Delta(\Delta\theta)$ was obtained by considering that the thermocouple calibrated to 1% was accurate to this extent at other than calibration pts.

$$\frac{\Delta T}{T} = 1\%$$

$$\Delta\theta = T_1 - T_2$$

$$\Delta(\Delta\theta) = 2\Delta T = 0.02 \times 10^3 \text{ } ^\circ\text{C}$$

Now, the following errors were inherent in bridge measurements:

$$\Delta C_m = 0.2\% \quad C_m = \text{measured series capacity}$$

$$\Delta D = 0.1\% \quad D = \text{measured dissipation factor}$$

$$\Delta f = 0.1\% \quad f = \text{measured frequency}$$

Here, ΔC_m was obtained from the G.R. 1650 specifications and represents the M.P.E. in C_m (which occurs for high C and high f).

ΔD was also obtained from the G.R. 1650 specifications.

Δf as used here represents the maximum possible error in frequency measurements for $f \geq 5 \times 10^2 \text{ cps}$.

$\Delta f = 0.2\%$ for $f = 10^2 \text{ cps}$ due to the fact that the accuracy of the instrument used to calibrate the generator was limited to $\pm .1\%$ at 10^2 cps .

It should be noted that both, ΔC_m , and, ΔD , as quoted here were checked by calibrating both the bridge capacitance and dissipation factor (see appendix II-2).

The following equations have been used in deriving a value for the ac electrical conductivity:

The vacuum capacitance, $C_{vac} = \frac{10^7}{4\pi c^2} \frac{d^2}{t}$ (MKS units)

where $d^2 = d_0^2 (1 + 2 \alpha \Delta\theta)$

$t = t_0 (1 + \alpha \Delta\theta)$

$c = \text{velocity of light}$

The parallel capacitance, $C_p = C_m / (1 + D^2)$

where $C_m = \text{measured capacitance}$

$D = \text{dissipation factor}$

The dielectric constant, $k' = C_p / C_{vac}$

The dielectric loss, $k'' = k' D$

The ac conductivity, $\sigma = \omega \epsilon'' = 2\pi f \epsilon_0 k''$

where $\epsilon_0 = \frac{10^7}{4\pi c^2}$

$\therefore \Delta C_{vac} / C_{vac} \approx 2.6\%$

$\Delta C_p / C_p \approx 0.4\%$

$\Delta k' / k' \approx 3.0\%$

$\Delta k'' / k'' \approx 3.1\%$

$\Delta \sigma / \sigma \approx 3.2\%$

For $D \geq 0.1$, the error in conductivity measured with the procedure described in Section II was inaccurate by less than 3% for temperatures in the range 200°C to 1000°C, and for frequencies of the applied field in the range 5×10^2 to 10^5 cps.

For $D \leq 0.1$ the accuracy is reduced due to the basic uncertainty in dissipation factor readings. The errors in k'' and σ may be calculated by adding the values quoted in Figure 2.9 and 3.4%. The accuracy of k'

is independent of the magnitude of $\tan \delta$.

A considerable increase in experimental accuracy can be obtained by the precise measurement of sample thicknesses and diameters. The faces can be polished to a $2\text{-}\mu$ in. finish (Paladino and Kingery¹²). The parallelism can be kept within 2×10^{-5} in.

With these improvements, the dimension accuracy is limited by the uncertainty of the expansion coefficient but even then it should be possible to obtain a conductivity value accurate to within 1% at 1000°C .

Appendix II-5 Summary of additional 3-terminal measurements
with specimen C4A (1.0% MgO) using pure platinum
electrodes†.

Mean Temperature (°C)	Temperature/gradient (°C)	Cp (pf)	Tan δ	k'	k''	σ ($\text{-}^1\text{cm}^{-1}$)
356.	14.	14.828	.00221	9.8	.022	1.22×10^{-9}
523.	5.	15.265	.01380	10.1	.139	7.78×10^{-9}
715.	0.	16.717	.04271	11.0	.472	2.64×10^{-8}
737.	3.	16.967	.04432	11.2	.497	2.78×10^{-8}
817.	14.	17.440	.04261	11.5	.491	2.75×10^{-8}
820.	14.	17.461	.04251	11.5	.490	2.74×10^{-8}
814.	12.	17.396	.04049	11.5	.465	2.60×10^{-8}
888.	25.	17.858	.04835	11.8	.570	3.19×10^{-8}
895.	10.	17.874	.04996	11.8	.590	3.30×10^{-8}
949.	22.	18.205	.06890	12.0	.829	4.64×10^{-8}
990.	20.	18.815	.09671	12.4	1.202	6.73×10^{-8}

† For these measurements; $P = 2.6 \times 10^{-5}$ mm Hg
V applied = 30 volts, and frequency = 100745 cps.

Appendix III-1 Error in the trap depth energy (equation 3.7) due to overlap effects.

The trap depth energy, E , as given by equation 3.7 is proportional to $T^*T'/(T^*-T')$ so that

$$\frac{\Delta E}{E} = \frac{\Delta T^*}{T^*} + \frac{\Delta T'}{T'} + \frac{\Delta(T^* - T')}{T^* - T'}$$

When there are no overlap effects $\Delta(T^*-T') \rightarrow 0$ since the difference in temperatures can be measured quite accurately, however, when there are overlap effects then the values of T^* and T' are affected, in general, quite differently so that $\Delta(T^*-T') = \Delta T^* + \Delta T' \approx 2\Delta T'$ and

$$\therefore \frac{\Delta E}{E} \approx \frac{2\Delta T'}{T'} + \frac{2\Delta T'}{T^*-T'}$$

Now, typically the difference, (T^*-T') , varies from 10° to 50° so that even if T^* and T' are only affected to the extent that $\Delta T' \approx 2.0^\circ$, and this is highly optimistic, then at best $\frac{\Delta E}{E} \approx \frac{400}{50} = 8\%$

but at worst

$$\frac{\Delta E}{E} \approx 40\%$$

Consequently, overlap effects if present can lead to a derived value of E which is grossly inaccurate.

Appendix III-2

The error in the predicted first order decay time constant due to an error in the temperature.

The predicted decay time constant is given by:

$$\tau = \exp(E/kT)/s$$

For an error ΔT in T there will be an error $\Delta\tau$ in τ which is given by:

$$\frac{\Delta\tau}{\tau} = \frac{E}{kT} \frac{\Delta T}{T}$$

For $E/kT \approx 20$, a typical value encountered in the present studies, and for $\Delta T/T \approx 1\%$ (in these studies $\Delta T \approx 3^\circ$), then $\Delta\tau/\tau \approx 20\%$. The error in T is due to the drift of temperature when decay is measured as well as to the basic temperature measurement inaccuracy.

Appendix III-3

Tabulated results of decay studies.

Table III-A

Decay Data Sample C3A (150 ± 3°C)

Time Seconds t	Measured Intensity Arbitrary Units $I_M \pm \Delta I_M$	Calculated Intensity (from R.M.S. 1st Order Fit) $I_1 \pm \frac{(I_M - I_1)}{I_M}$	Calculated Intensity (from R.M.S. 2nd Order Fit) $I_2 \pm \frac{(I_M - I_2)}{I_M}$
0	33.2 ± .5	33.1 + .00	39.4 - .19
60	29.5	29.7 - .01	33.1 - .12
120	26.5	26.7 - .01	28.2 - .06
180	24.0	24.0 + .00	24.3 - .01
240	21.5	21.6 + .00	21.1 + .02
300	19.5	19.4 + .01	18.6 + .05
360	17.5	17.4 + .00	16.4 + .06
420	15.7	15.7 + .00	14.7 + .07
480	14.2	14.1 + .01	13.2 + .07
540	12.6	12.7 + 0.00	11.9 + .06
600	11.6	11.4 + 0.02	10.8 + .07
660	10.2	10.2 + .00	9.8 + .04
720	9.2	9.2 + .00	9.0 + .03
780	8.2	8.3 - .01	8.2 - .00
840	7.4	7.4 + .00	7.6 - .03
900	6.6	6.7 - .01	7.0 - .06
960	6.0	6.0 + .00	6.5 - .08

$$\begin{aligned}
 \sum_{i=1}^n (\text{deviations})_i &= 1.0 \times 10^{-5} &= 6 \times 10^{-7} \\
 \sum (\text{deviations squared})_i &= 8.6 \times 10^{-4} &= 1.3 \times 10^{-3}
 \end{aligned}$$

 τ (1st order) = 562 seconds = best fit τ (2nd order) = 658 seconds

Table III-B
Decay Data Sample C5A (123.5 ± 3°C)

Time Seconds t	Measured Intensity Arbitrary Units $I_M \pm \Delta I_M$	Calculated Intensity (from R.M.S. 1st Order Fit) $I_1 \pm \frac{(I_M - I_1)}{I_M}$	Calculated Intensity (from R.M.S. 2nd Order Fit) $I_2 \pm \frac{(I_M - I_2)}{I_M}$
0	35.0 ± .5	31.6 + .10	32.8 + .06
30	31.5	29.9 + .05	30.5 + .03
60	28.5	28.2 + .01	28.4 + .00
90	25.8	26.6 - .03	26.6 - .03
120	24.5	25.1 - .03	24.9 - .02
150	23.0	23.7 - .03	23.4 - .02
180	21.6	22.4 - .04	22.0 - .02
210	20.5	21.2 - .03	20.7 - .01
240	19.5	20.0 - .03	19.5 + .00
270	18.3	18.9 - .03	18.5 - .01
300	17.3	17.8 - .03	17.5 - .01
330	16.4	16.8 - .03	16.6 - .01
360	15.5	15.9 - .03	15.8 - .02
390	14.9	15.0 - .01	15.0 - .01
420	14.4	14.2 + .02	14.3 + .01
450	13.7	13.4 + .02	13.6 + .01
480	13.2	12.6 + .04	13.0 + .02
510	12.6	11.9 + .05	12.4 + .02

$$\sum_{i=1}^n d_i =$$

$$6 \times 10^{-6}$$

$$6 \times 10^{-7}$$

$$\sum d_i^2 =$$

$$3 \times 10^{-2}$$

$$8 \times 10^{-5}$$

$$\tau \text{ (1st order)} = 523 \text{ seconds}$$

$$\tau \text{ (2nd order)} = 814 \text{ seconds} = \text{best fit}$$

Table III-C
Decay Data Sample C5A (181.1 ± 3°C)

Time Seconds t	Measured Intensity Arbitrary Units $I_M \pm \Delta I_M$	Calculated Intensity (from R.M.S. 1st Order Fit) $I_1 \pm \frac{(I_M - I_1)}{I_M}$	Calculated Intensity (from R.M.S. 2nd Order Fit) $I_2 \pm \frac{(I_M - I_2)}{I_M}$
0	85.0 ± .5	79.9 + .06	82.0 + .04
30	78.0	75.7 + .03	76.7 + .02
60	72.5	71.6 + .01	71.9 + .01
90	67.0	67.8 - .01	67.6 - .01
120	62.5	64.2 - .03	63.6 - .02
150	59.1	60.8 - .03	60.0 - .01
180	56.2	57.5 - .02	56.6 - .01
210	53.5	54.5 - .02	53.6 + .00
240	50.0	51.5 - .03	50.8 - .02
270	47.5	48.8 - .03	48.2 - .01
300	45.3	46.2 - .02	45.8 - .01
330	43.5	43.7 - .01	43.5 + .00
360	41.5	41.4 + .00	41.5 + .00
390	39.6	39.2 + .01	39.5 + .00
420	38.3	37.1 + .03	37.7 + .01
450	36.6	35.1 + .04	36.1 + .01

$$\sqrt[n]{\sum_{i=1}^n d_i} =$$

$$8 \times 10^{-6}$$

$$4 \times 10^{-7}$$

$$\sum d_i^2 =$$

$$1.0 \times 10^{-2}$$

$$1.0 \times 10^{-5}$$

$$\tau \text{ (1st order)} = 547 \text{ seconds}$$

$$\tau \text{ (2nd order)} = 886 \text{ seconds} = \text{best fit}$$

Table III-D¹
Decay Data Sample C5A (247.5 ± 5%)

Time Seconds t	Measured Intensity Arbitrary Units $I_M \pm \Delta I_M$	Calculated Intensity (from R.M.S. 1st Order Fit) $I_1 \pm \frac{(I_M - I_1)}{I_M}$	Calculated Intensity (from R.M.S. 2nd Order Fit) $I_2 \pm \frac{(I_M - I_2)}{I_M}$
0	56.0 ± 0.8	56.4 - .01	56.9 - .02
60	52.5	53.0 - .01	53.1 - .01
120	50.0	49.8 + .00	49.6 + .01
180	47.0	46.7 + .01	46.5 + .01
240	44.5	43.9 + .01	43.7 + .02
300	42.0	41.2 + .02	41.1 + .02
360	38.0	38.7 - .02	38.7 - .02
420	36.0	36.3 - .01	36.5 - .01

$$\sum_{i=1}^n d_i =$$

$$3 \times 10^{-6}$$

$$1 \times 10^{-7}$$

$$\sum d_i^2 =$$

$$1 \times 10^{-3}$$

$$1 \times 10^{-5}$$

$$\tau \text{ (1st order)} = 953 \text{ seconds}$$

$$\tau \text{ (2nd order)} = 1,691 \text{ seconds} = \text{best fit}$$

Values of I^* , T^* and T' were found from input experimental data in the following manner. To obtain T^* and T' six intensities, 3 to left and 3 to right of the maximum, were labelled during input by labelling the temperatures 1, thru, 6, at which the intensities were measured, as illustrated in Figure III-1.

Figure III-1. Illustration of the labelling system for interpolation program.

I^* , and T^* , were then interpolated using Bessel's method of central differences (see J. B. Scarborough "Numerical Analysis" Oxford Press 1960) in the following manner.

The interpolated value of I was calculated from:

$$\begin{aligned}
 I = & \frac{I_0 + I_1}{2} + vI_0 + \frac{(v^2 - \frac{1}{4})}{2} \frac{\Delta^2 I_{-1} + \Delta^2 I_0}{2} \\
 & + \frac{v(v^2 - \frac{1}{4})\Delta^3 I_{-1}}{3!} \\
 & + \frac{v(v^2 - \frac{1}{4})(v^2 - 9/4)}{4!} \frac{\Delta^4 I_{-2} \Delta^4 I_{-1}}{2}
 \end{aligned}$$

$$+ \frac{v(v^2 - \frac{1}{4})(v^2 - 9/4)}{5!} \Delta^5 I_{-2}$$

$$\text{where } v = \frac{T - T_0}{\Delta T} - \frac{1}{2}$$

$$\Delta T \equiv T_M - T_{M-1}$$

$$\text{and } \Delta^N I_M \equiv \Delta^{N-1} I_{M+1} - \Delta^{N-1} I_M$$

Now, starting with $T = T_0 + 0.1^\circ$ values of I were computed as T was incremented by 0.1° . The first computed value I (of $T = T_0 + 0.1$) was called I^* , the second computed value of I (of $T = T_0 + 0.2$) was compared with I^* . If it was greater it was then called I^* , if it was smaller the original choice was retained, and so on. For some value of $T = T_0 + x \cdot 0.1^\circ$, the value I^* was found and $\therefore T^* = T_0 + x \cdot 0.1^\circ$.

The same procedure was used to find T' only then $I' = I^*/2$ where I^* had been found by interpolation. The six temperatures were chosen by finding a value of I_0 in the input data which was just less than $I^*/2$ (which consequently gave T_0) in order to label the points.

Appendix III-5 Calculation of the number of luminous centers and an estimate of the number of traps.

The area under a glow curve peak, defined by the fitted theoretical curve, is a measure of the total quanta, N_q , emitted by a specimen. This area may be found by approximation by describing the peak visually by a triangle of height ($I^* - I_{\text{minimum}}$) and base Δt where $\Delta t = T/\beta$. The important number in the area approximation is I^* since it is orders of magnitude greater than all other quantities.

It is assumed that:

- 1) the manufacturer's specifications for the Photometer response is correct as quoted
- 2) the luminous efficiency of the specimens is constant (the estimate of the number of traps depends on $\eta = 1.0$)
- 3) the emission spectrum would be the same for all doped specimens as that obtained from sample C4A
- 4) the emission originates in the surface grains of a common uniform size of $\approx 30\mu$ (from optical studies)
- 5) the emitted photons are mono-energetic with energy $E = hc/\lambda$
- 6) the test specimen is a point source isotropic radiator
- 7) the solid angle subtended by the detector at the source is 3×10^{-3} steradians (the surface area of the detector is ≈ 1 sq. in. and it is $\approx 10''$ from the source).

With the 931 A tube used the dark current level was about 4×10^{-10} lumens. The maximum peak height recorded was 250 times the D.C. level reading and since the meter reading is directly proportional to the incoming flux, then the maximum flux was 10^{-7} lumens. For C5A, then, the maximum intensities of the 3 major peaks are

$I^*_1 = 1/6 \times 10^{-7}$ lumens, referring to the peak at 127.4°C

$I^*_2 = 1/12 \times 10^{-7}$ lumens, referring to the peak at 185°C

and

$I^*_3 = 1/30 \times 10^{-7}$ lumens, referring to the peak at 260°C

and the areas under these peaks are

$$A_1 \approx 10^{11} \text{ photons (2.22 eV)}$$

$$A_2 \approx 5 \times 10^{11}$$

$$A_3 \approx 2 \times 10^{11}$$

since 1 lumen $\approx 5 \times 10^{15}$ (2.22 eV) photons.

Now, since 10^{11} to 10^{12} photons have hit the detector, then 10^{14} to 10^{15} photons must have left the specimen. There are then 10^{14} to 10^{15} emission centers and at least 10^{14} to 10^{15} traps responsible for thermoluminescence, if each center emits but one photon and, as well, if each trap is operative but once for radiative transitions.

The photons detected may be reasonably assumed to have been emitted from the surface grains of the test specimens. Although atoms deeper in the sample may be emitting during glow curve experiments the light is quite likely scattered by grain boundaries and reabsorbed. It is reasonable then to see if all the phenomena can be due to the 2 ppm trace impurities in the specimens.

Impurity Effect: of the 2 ppm unknown impurity atoms about 8×10^{14} reside in grain layer. It is just barely possible that all the unknown impurity produces the observed effects, if a grain layer emits, but then the MgO glow curves should not be so much different from the pure Al_2O_3 curves.

The addition of even 10 ppm of Mg results in about 4×10^{15} Mg atoms in a grain layer, so that it is more likely the source of the effects may be traced to Mg either in a Spinel or a MgO or an Al_2O_3 phase and in any of these cases to the associated oxygen ion vacancies.

Appendix III-6 A calculation of the error in the trap depth energy;
 (a) due to errors in analysis and (b) due to
 experimental errors.

Errors in calculated trap depth energies arise due to computation as well as experimental inaccuracies. The errors that arise in computation can be ascertained by the analysis of theoretical glow curves and then the effect of these computational errors on the trap depth energy can be calculated. The experimental inaccuracy is known so that its effect can be estimated once the trap depth energy is expressed as a function of experimentally measured parameters. Such expressions were derived in Section III.

The formulae, equations (3.11) and (3.17) relate the thermal activation energy of a trap to two measured temperatures. The formulae are valid to $\pm 5\%$ as illustrated in Table 3.3. On the basis, then, of these expressions, the following estimate of error due to analysis and to experimental inaccuracy may be deduced:

$$\begin{aligned} \therefore E &\propto \frac{T^* T'}{T^* - T'} \\ \therefore \frac{\Delta E}{E} &= \frac{\Delta T'}{T'} + \frac{\Delta T^*}{T^*} + \frac{\Delta T^* \pm \Delta T'}{T^* - T'} \quad (A2) \\ \text{or } \frac{\Delta E}{E} &\lesssim \frac{2\Delta T}{T'} + \frac{\Delta T \pm \Delta T}{T^* - T'} \\ \therefore \Delta T' &\approx \Delta T^* = \Delta T \end{aligned}$$

We distinguish between the analysis of theoretical glow curves and experimental glow curves because the analysis varied for these respective types of curves.

a) The error in trap depth energy due to computation ascertained by the analysis of theoretical glow curves:

A theoretical glow curve may be generated when the two parameters E and T^* are inserted into the proper normalized expression I_N (equation 3.9 or equation 3.16). The temperature corresponding to the value $I_N = 0.5$ was found to the nearest 0.1°K ; that is, $\Delta T' = \pm 0.1^\circ\text{K}$. It is interesting to note that the program for interpolation (Appendix III-4) when applied to theoretical curves where the intensity was calculated in 2°K intervals yielded the same value of T' as that found by calculating the intensities, I_N , in 0.1°K steps and then simply reading the temperature T' which corresponded to $I_N = 0.5000$. In the case of analysis of theoretical curves, then, $\Delta T = \pm 0.1^\circ$ so that equation, A2, becomes

$$\frac{\Delta E}{E} \approx \frac{0.2}{T'} + \frac{0.2}{T^* - T'}$$

and for the worst possible case, which is T' about 300°K and $(T^* - T')$ about 10°K , yields a measure of the effect of analysis

$$\frac{\Delta E}{E} \approx 1.0\%$$

This error in E can be considerably reduced by calculating T^* and T' to the nearest 0.01°K , for then $\Delta E/E \approx 0.1\%$.

(b) The error in trap depth energy due to experimental inaccuracy estimated by the analysis of experimental glow curves:

The method of fitting a theoretical curve to experimental data has already been discussed (Section 3.8). It was shown that the energy, E , was to be considered as an adjustable parameter; in the sense that a value of E obtained from either equation (3.11) or (3.17) could be varied within the limits of experimental error associated with E as long as it was consistent with a choice of T' that was within the experimental error of $\pm 2^\circ\text{K}$ associated with the value of T' as read

from the experimental data. In this case, equation A2 becomes:

$$\frac{\Delta E}{E} \approx \frac{2\Delta T}{T'}$$

which for the worst possible case yields:

$$\frac{\Delta E}{E} \approx 2\%$$

Again, this error may be considerably reduced by simply measuring T^* and T' more accurately. For example, if the temperature was measured to $\pm .1^\circ\text{K}$ then, $\Delta E/E \approx 0.2\%$.

It is concluded that the effects of analysis and the effects of inaccurate temperature measurements on the value of E is negligible in comparison to the already approximate nature of E as given by:

$$E = \alpha \frac{kT^* T'}{T^* - T'}$$

where $\alpha = 1.46$ for 1st order

and $\alpha = 1.70$ for 2nd order

when $E/kT \geq 17.0$

and with the uncertainty $\pm 5\%$.

Appendix III-7

Derivation of the Randall and Wilkins's Relation.

The basic rate equation proposed by Randall and Wilkins was derived in section III. It was

$$I = -c \frac{dn}{dt} = cPn \quad (\text{III-1})$$

where I = glow intensity

C = geometry constant (and luminous efficiency)

dn/dt = rate of escape of electrons from traps

P = probability of escape ($s \exp(-E/kT)$)

n = number of electrons in traps at a time, t .

From III-1 it follows that if a sample is heated at a constant rate, β , then

$$-\frac{dn}{dT} \frac{dT}{dt} = -\beta \frac{dn}{dT} = Pn$$

so that

$$\int_{n_0}^n -\frac{dn}{n} = \int_0^T \frac{P}{\beta} dT$$

where n_0 = number traps regularly filled,

and, therefore,

$$n = n_0 \exp\left(-\int_0^T \frac{s}{\beta} \exp(-E/kT) dT\right) \quad (\text{III-2})$$

Replacing, n , in equation (III-1) by its value in (III-2) results in the Randall and Wilkins' Relation:

$$I = -C \frac{dn}{dt} = C s \exp(-E/kT) n_0 \exp\left(-\int_0^T \frac{s}{\beta} \exp(-E/kT) dT\right)$$

Sample Name	Heating Rate	λ (max) Observed	λ^* (max) Corrected	E optical = hc/λ^*	Temperature of maximum
	(°C/min)	(Å)	(Å)	(ev)	(°C)
G1B (6N Al_2O_3)	4.0	3350	Average		74
	4.0	3400	3325 $\pm$ 300	3.7 $\pm$ 0.4	96
	4.0	3300			116
	4.0	3200-3600	Not Resolvable		125 - 275
G4A (1.0% MgO)	10.0	3750			40
	10.0	3725	N.R.		53
	10.0	3700			68
	10.0	5200	5150 $\pm$ 200	2.4 $\pm$ 0.1	138
	10.0	5200			158
	4.0	5150			158
	4.0	5150			184
	10.0	5200	N.R.		188
	4.0	5150-5200			203 - 230
N.R.C. (3N ⁺ Al_2O_3)	8.3	3300			126
	8.3	3700			128
	8.3	3500	It is impossible to determine whether these are single or double peaks		140
	8.3	3800			142
	8.3	3550			153
	8.3	3800			155
	8.3	3500			170
	8.3	3750			172
	8.3	5500	N.R.		256

VITA

Name: Paul James Kelly

Personal: Born: 19th July, 1934 at Montreal, Quebec; married to Jacquelyn Dorothy McNeil, a registered nurse; 4 children.

Education: Primary - Lajoie, Montreal 1940-1947
Secondary - Loyola H. S., Montreal 1947-1951
Technical - Radio College of Canada 1952 - 1953
University - Sir George Williams 1956-1960
Major: Mathematics and Physics
Degree: B.Sc. 1960
Carleton University 1960-1962
Degree: M.Sc. (Physics) 1962

Bursaries: N.R.C.(1). Scholarships: S.G.W.U.(3), N.R.C.(3).
Awards: Malcolm Steiner Award S.G.W.U. (1959), Lt. Governor's Medal (Math and Physics) S.G.W.U. (1960).

Experience: Academic Year Employment:
Teaching: P.S.S.C. Physics (1962-63)
Demonstrating: Undergraduate Laboratories (1958-1964).

Summer Employment:
Carleton ('64, '63, '62, '61), mostly thesis work.
Steel Company of Canada Limited, Montreal, Quebec, (1960),
Metallurgical assistant under Dr. Wade.

Papers:
"The dielectric properties of sintered Al_2O_3 " (J. Hart and P. Kelly) presented to the October '63, N.R.C.-N.A.S. Convention; reported in Electro-Technology January '63 issue.
"Evaluation of the P.S.S.C. curriculum as a first year University course", (J. Hart and P. Kelly) presented at the C.A.P. meeting in Quebec June '63; reported in the C.A.P. bulletin May '63.