CHARACTERIZATION OF THE TEMPERATURE DEPENDENCE OF THE OPTICAL PROPERTIES OF SPINEL

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CHARACTERIZATION OF THE TEMPERATURE DEPENDENCE OF THE OPTICAL PROPERTIES OF SPINEL

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ABSTRACT

CHARACTERIZATION OF THE TEMPERATURE DEPENDENCE OF THE OPTICAL PROPERTIES OF SPINEL

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Characterization of the temperature dependence of the fundamental optical properties (resonance position, plasma frequency, and damping constant) of magnesium-aluminum-oxide (Spinel) is obtained through the use of a nonlinear curve-fit to a classical oscillator model and the implementation of a microrefrigeration system with a temperature range of 100°C to -190°C. The computer code implementing this nonlinear curve-fit is presented. The code was first successfully tested on two material models and then on the reststrahlen spectra of Spinel.

The reststrahlen spectra of Spinel was analyzed from -30°C to 80°C. Two of the five resonances of Spinel showed a quadratic dependence on temperature while the others exhibited a linear dependence. The plasma frequencies and damping constants all showed a linear dependence on temperature.
Three of the five damping constants of Spinel compared favorably to a theoretical quantum mechanical calculation.

A description of the microrefrigeration system is given. The system suffered from a manufacturing design flaw which caused an oily substance to be deposited onto the sample. This problem was fixed by redesigning the refrigeration stage prior to use.
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CHAPTER I
INTRODUCTION

With the advent of modern infrared devices and technology comes the need for comprehensive characterization of the fundamental optical properties (real and imaginary parts to the relative dielectric constant, real and imaginary parts to the index of refraction, and the corresponding oscillator parameters) including temperature-related effects. Much of this characterization work has employed techniques such as electro-reflectance, derivative spectroscopy, Raman scattering, and luminescence methods. One method which has not received such attention is Fourier Transform Infrared (FTIR) spectrophotometry. This technique is applicable to either opaque or transparent materials with the use of reflection or transmission measurements.

For highly absorbing materials there are two techniques which use normal incidence reflectance measurements to extract these optical properties: Kramers-Kronig analysis and a direct fit to a classical oscillator model. While the Kramers-Kronig method expresses an exact relationship between the amplitude and phase of the reflected light, it requires that the reflectance at all frequencies be known. Since measuring the
reflectance at all frequencies is an impossibility, an extrapolation, which introduces error, is required.

The classical oscillator fit, on the other hand, requires no extrapolation beyond the measured region. It is, however, only a semi-empirical model of the complex dielectric constant. This is not a hindrance in the one-phonon region of the reflectance spectra as the classical oscillator fit has been shown to provide excellent agreement with a broad range of experimental methods (derivative spectroscopy, Raman scattering, etc.).

The objective of this thesis is to institute a curve-fitting technique for the extraction of the fundamental oscillator parameters - resonance position, plasma frequency, and damping constant - and to use this technique to study the temperature dependence of these parameters for Spinel. In order to fulfill this objective, a classical oscillator model was used in a nonlinear curve-fitting computer program\(^1\) to extract the best fitting parameters from specular reflectance measurements.

The curve-fitting program has been implemented and successfully tested on theoretically generated reflectance curves as well as the experimental data obtained from MgAl\(_2\)O\(_4\) (Spinel). Several resonances of Spinel showed excellent agreement with published results and theoretical quantum mechanical calculations while others deviated considerably.
To measure the temperature dependence of the oscillator parameters a Joule-Thomson microrefrigeration system, capable of a temperature range from -190°C to 100°C, was used. During the initial tests of this system, a manufacturing design flaw was discovered and fixed. By using the microrefrigeration system with a specular reflectance attachment, temperature dependent reflectance data from Spinel was obtained.
CHAPTER II
CLASSICAL OSCILLATOR MODEL

Frequency dependent transmittance or reflectance is the quantity most often measured in spectrophotometry. However, the fundamental optical properties of a material (resonance position, resonance strength, and resonance width) are more closely related to the complex dielectric constant. Thus, a relationship between the measured quantities and the dielectric constant must be obtained if spectrophotometry is to be used to investigate the fundamental properties of materials. In doing so, an understanding of the Maxwell equations for the interaction of electromagnetic radiation with matter is essential.

In this chapter, Maxwell equations will be used to develop a wave equation applicable to dielectric materials. In addition, a possible solution to this equation will be used to obtain the complex index of refraction, $N$, for such a wave. The link between the experimentally observable reflectance and transmittance and the complex dielectric function will then be established through the use of several material models.
WAVE EQUATION

In order to obtain a fundamental understanding of the interaction of light and matter one must first start with the macroscopic Maxwell equations.

\[ \mathbf{\nabla} \cdot \mathbf{D} = 0 \]
\[ \mathbf{\nabla} \cdot \mathbf{B} = 0 \]
\[ \mathbf{\nabla} \times \mathbf{E} = -\mu \frac{\partial \mathbf{H}}{\partial t} \]
\[ \mathbf{\nabla} \times \mathbf{H} = \varepsilon \mathbf{E} + \sigma \frac{\partial \mathbf{E}}{\partial t} \]

where \( \mu, \varepsilon, \) and \( \sigma \) are respectively the magnetic permeability, dielectric constant of the material, and electrical conductivity.

By taking the curl of equation 2.3 and inserting equations 2.1 and 2.4, the electromagnetic wave equation is found to be

\[ \nabla^2 \mathbf{E} = \sigma \frac{\partial \mathbf{E}}{\partial t} + \varepsilon \frac{\partial^2 \mathbf{E}}{\partial t^2} \]

One possible solution to this wave equation is a plane wave, propagating in the positive \( \hat{u} \) direction, of the form

\[ \mathbf{E}(\mathbf{u}, t) = E_o e^{i(\omega t - \mathbf{k} \cdot \mathbf{u})} \]

where \( E_o \) is the amplitude of the wave and \( \kappa = \omega / \nu \) is defined as the wavevector. By inserting equation 2.6 into the wave equation and using the definition of the wavevector, it is clear that

\[ \frac{1}{\nu^2} = \varepsilon \sigma - i \frac{\sigma \mu}{\omega} \]

gives the velocity of the wave in a material.
It is also typical to define the velocity of a wave in a material as a function of the speed of light, \( c \), in a vacuum and the index of refraction, \( N \), of the material

\[
v = \frac{c}{N}
\]  

(2.8)

By comparing equations 2.7 and 2.8, the index of refraction becomes

\[
N^2 = c^2 \mu (\epsilon - i \frac{\sigma}{\omega}) = (n - ik)^2
\]  

(2.9)

where \( n \) and \( k \) are the real and imaginary parts of \( N \). Using equations 2.8 and 2.9 and assuming \( u \) has only an \( x \) component, the solution to the wave equation can be rewritten as

\[
\vec{E}(x,t) = E_0 e^{-\frac{kx}{c}} e^{-i\omega\left(\frac{nx}{c} - t\right)}
\]  

(2.10)

Written in this manner, it is simple to see that the complex part of the index of refraction gives rise to an exponential absorption term where \( k \) is the extinction coefficient.

Clearly then, knowledge of the real and imaginary parts of the complex index of refraction as a function of frequency provides information on the more fundamental property, the dielectric constant of the material.

**Fresnel Equations for Planar Interfaces**

Now that a specific solution to the wave equation has been found in terms of the complex index of refraction and the complex index of refraction is related to the dielectric function of the material, a relationship between the reflectance or transmittance and the complex index of refraction is desired. By finding this relationship, a means
of investigating the dielectric function of a material through
the use of either reflectance or transmittance will be
established.

The determination of reflectance or transmittance of the
electric and magnetic field components at a planar interface
first requires the setup of the interface geometry. Figure
2.1 illustrates that geometry for a wave propagating at an
angle θ to the normal of the interface between material 0 and
1. This wave will then give rise to a transmitted and a
reflected wave at the interface, each respectively propagating
at an angle of θ' and θ". Figure 2.1 also shows that the E
and B vectors are typically resolved into two orthogonal
components relative to the plane of incidence: the s-
polarization in which the E field is perpendicular to the
plane of incidence, and the p-polarization in which the E
field is parallel to the plane of incidence.

Using this geometry and applying the boundary conditions
(normal and tangential components of the E and B vectors are
continuous across the interface) the Fresnel equations for the
amplitude reflection at a planar interface may be written as

\[
\begin{align*}
R_p &= \frac{E'_p}{E_p} = \frac{N_1 \cos \theta - N_0 \cos \theta'}{N_1 \cos \theta + N_0 \cos \theta'} \\
R_s &= \frac{E'_s}{E_s} = \frac{N_0 \cos \theta - N_1 \cos \theta'}{N_0 \cos \theta + N_1 \cos \theta'}
\end{align*}
\]  

(2.11)

Where θ' is obtained from Snell's Law of refraction

\[
N_0 \sin \theta = N_1 \sin \theta' \tag{2.12}
\]
Figure 2.1 Interface geometry for the determination of the reflection coefficient: $^{[3]}$ (a) s-polarization component; (b) p-polarization component.
The power reflectance, which is the quantity measured by detectors, is found by taking the modulus of the reflection coefficients given in equation 2.11

\[ R_{p,s} = |r_{p,s}|^2 \]  \hspace{1cm} (2.13)

In the simplifying case when \( \theta = 0 \), then \( \theta' = 0 \) also and the two power reflectances of equation 2.11 become equal. Thus, the subscripts may be dropped.

For most measurements, \( N_0 \) is that of air; therefore, it can be considered a real function where \( n_0 = 1 \) and \( k_0 = 0 \) while \( N_1 \) is, in general, a complex function given by equation 2.9. Finally, the power reflectance from a dielectric interface in air at normal incidence is given by

\[ R = \frac{(1 - n_1)^2 + k_1^2}{(1 + n_1)^2 + k_1^2} \]  \hspace{1cm} (2.14)

**LORENTZ AND DRUDE MODELS**

In order to describe the fundamental properties of a material in terms of the complex index of refraction, a model describing the motion of charges in the material under the illumination of electromagnetic radiation is needed. One such model for a crystal dielectric assumes a linear, coupled chain of diatomic molecules with the incident electromagnetic field serving as the forcing function. The equation of motion of this type system will be a damped harmonic oscillator given by

\[ m \frac{\partial^2 \vec{X}}{\partial t^2} + m \Gamma \frac{\partial \vec{X}}{\partial t} + m \omega_0^2 \vec{X} = -e \vec{E} \]  \hspace{1cm} (2.15)

where \( m \) represents the reduced mass of the crystal lattice unit cell, \( \Gamma \) the damping constant, and \( \omega_0 \) the resonance
frequency of the system. This is the representative equation of motion for a Lorentz model crystal.

If the applied electromagnetic field is given by

$$\vec{E} = E_0 e^{i\omega t} \quad (2.16)$$

the atoms will respond to this electric field and a solution of the equation of motion for the Lorentzian model will be

$$\ddot{x} = \frac{-e\vec{E}}{m[\omega_0^2 - \omega^2 - i\omega\Gamma]} \quad (2.17)$$

which describes the motion of the atoms of a crystal under the influence of an electromagnetic field. A somewhat more useful equation is that which describes the polarization of a dielectric containing $M$ charges per unit cell. The polarization equation of a dielectric is

$$\vec{P} = -Me\vec{x} + e_0\varepsilon_\sigma \vec{E} \quad (2.18)$$

The second term of equation 2.18 accounts for the polarization of the background medium (i.e. the electron cloud). By substituting equation 2.17 into 2.18, the polarization of the crystal as a result of the applied field can be written as

$$\vec{P} = \frac{Me^2\vec{E}}{m[\omega_0^2 - \omega^2 - i\omega\Gamma]} + e_0\varepsilon_\sigma \vec{E} \quad (2.19)$$

Coupling this equation with the definition of the displacement vector

$$\vec{D} = e_0\vec{E} + \vec{P} = e_0\varepsilon_\sigma \vec{E} = e\vec{E} \quad (2.20)$$
yields the equation relating the relative dielectric function, \( \epsilon_r \), to the system parameters

\[
\epsilon_r = \epsilon_\infty + \frac{M\sigma^2}{m\epsilon_0 (\omega_0^2 - \omega^2 + i\omega\Gamma)} \tag{2.21}
\]

Equation 2.21 shows that \( \epsilon_r \) is, in general, complex. Thus, \( \epsilon_r \) may be written in a form similar to equation 2.9

\[
\epsilon_r = \epsilon_1 - i\epsilon_2 \tag{2.22}
\]

Now, by relating the real and imaginary parts of equations 2.21 and 2.22 the quantities are produced

\[
\epsilon_1 = \epsilon_\infty (1 + \frac{\omega_p^2 (\omega_0^2 - \omega^2)}{[(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2]}) \tag{2.23}
\]

\[
\epsilon_2 = \frac{\epsilon_\infty \omega_p^2 \omega \Gamma}{[(\omega_0^2 - \omega^2)^2 + \omega^2\Gamma^2]}
\]

where \( \omega_p \) is called the plasma frequency and is given by

\[
\omega_p = \sqrt{\frac{M\sigma^2}{m\epsilon_0 \epsilon_\infty}} \tag{2.24}
\]

The development thus far has been for a two-bodied repetitive system - a diatomic lattice with only one allowed resonance. This is very rarely the case for dielectrics. Therefore, a more general solution would be one in which a multitude of resonances are allowed. The solution of the equation of motion of the charges as a whole will then become a summation of the individual solutions. Thus, the real and imaginary components of the relative dielectric function for an isotropic material can be written as
\[
\epsilon_1 = \epsilon_m \left( 1 + \sum_j \frac{\omega_{p_j}^2 (\omega_j^2 - \omega^2)}{[(\omega_j^2 - \omega^2)^2 + \omega^2 \Gamma_j^2]} \right)
\]

\[
\epsilon_2 = \sum_j \frac{\epsilon_m \omega_{p_j} \omega \Gamma_j}{[(\omega_j^2 - \omega^2)^2 + \omega^2 \Gamma_j^2]}
\]

By looking at equation 2.9 and remembering that the dielectric function \(\epsilon\) is defined as \(\epsilon_0 \epsilon_r\), it appears as if an advantageous definition of the complex index of refraction would be

\[
N^2 = \epsilon_r
\]

It is now possible to write the real and imaginary components of the relative dielectric function in terms of the real and imaginary parts of the complex index of refraction

\[
\begin{align*}
\epsilon_1 &= n^2 - k^2 \\
\epsilon_2 &= 2nk
\end{align*}
\]

Solving equation 2.27 for \(n\) and \(k\) yields

\[
\begin{align*}
n^2 &= \frac{1}{2} \left[ \sqrt{(\epsilon_1^2 + \epsilon_2^2)} + \epsilon_1 \right] \\
k^2 &= \frac{1}{2} \left[ \sqrt{(\epsilon_1^2 + \epsilon_2^2)} - \epsilon_1 \right]
\end{align*}
\]

A somewhat similar development is followed for the Drude model of metals except that the restoring force, \(m \omega_0^2 x\), is not included in the equation of motion since it is assumed that the system consists of free electrons propagating in a lattice of bound metal atoms. With this change, the complex relative dielectric function becomes

\[
\epsilon_r = \epsilon_m \left( 1 + \frac{\omega_p^2}{[\omega^2 - i \omega \Gamma]} \right)
\]
Separating the real and imaginary parts leaves the quantities

\[
\begin{align*}
\epsilon_1 &= \epsilon_\infty (1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2}) \\
\epsilon_2 &= \frac{\epsilon_\infty \omega_p^2 \Gamma}{\omega [\omega^2 + \Gamma^2]}
\end{align*}
\]  

(2.30)

There are no summations in these equation since there can be only one lattice resonance in a pure metallic material.

Now, by using equations 2.14 and 2.28, a measurement of reflectance as a function of frequency in the region of the lattice absorption can be used to determine the fundamental material properties: relative dielectric function, \(\epsilon_r\); plasma frequency, \(\omega_p\); damping constant, \(\Gamma\); and the resonance frequency, \(\omega_j\).

**TEMPERATURE DEPENDENCE**

The above development, while it has been shown to adequately describe the reflectance from dielectric materials, is only a classical approximation to the dielectric function of the material - it assumes a coulomb potential with only first and second order effects and neglects anharmonic contributions i.e. the oscillators reside near the minimum of the coulomb potential well, and it also neglects the light's magnetic field \((-ev \times B)\) interaction with the electrons. The latter assumption is valid as long as the speed \((v)\) of the electron is not relativistic since the magnetic field \((B = E/c)\) is many orders of magnitude smaller than the electric field. Even with these assumptions, the classical Lorentz
model is useful since it describes a relatively simple relationship between the fundamental optical parameters of a material.

To be complete, however, the relative dielectric function must take into account the fact that the oscillator resonance frequencies (which is related to the phonon density of states) is not a discrete function, but rather is semi-continuous, extending from $\omega = 0$ to the highest allowable longitudinal optic mode frequency. Thus, the optical parameters of a material should no longer be temperature independent. Many authors have attempted to describe the dielectric function, and consequently the optical parameters of a material, through the use of the phonon density of states function.\textsuperscript{[4-8]} It is worth noting, however, that at frequencies close to the resonance frequencies, $\omega_j$, all of the attempts reduce to equations similar to the classical development.\textsuperscript{[9]} Therefore, equation 2.25 can be used to describe the relative dielectric function as long as the parameters are modified to include a temperature dependence and a frequency cutoff to the damping constant\textsuperscript{[10]}

$$
\varepsilon_r(\omega, T) = \varepsilon_\infty(T) \left(1 + \sum_j \frac{\omega_j^2(T)}{[\omega_j^2(T) - \omega^2 + i\omega \Gamma_j(\omega, T)]}\right) (2.31)
$$

Generally, for frequencies below approximately 1.1 times the highest allowable transverse optical phonon mode the frequency dependence of the damping constant will be a
constant. Above that frequency it will be an exponentially decaying function with increasing frequency, and will be different for each material.\textsuperscript{[11]}

The temperature dependence of the plasma frequency and resonance frequency of ionic materials have been measured and fit to linear equations at high temperatures.\textsuperscript{[12]} In addition, the damping constant has been successfully fit with a quadratic temperature dependence.\textsuperscript{[13,14]}
CHAPTER III

EXPERIMENTAL SETUP

The frequency-dependent reflectance of a dielectric material can be used to characterize the fundamental optical properties \( (n, k, \varepsilon_r, \omega_j, \omega_p, \Gamma, \text{and } \varepsilon_m) \) of the material as outlined in Chapter II. It was also shown that these fundamental parameters are functions of temperature. Several authors\textsuperscript{[15-18]} have attempted to characterize this temperature dependence on a wide range of materials. Most prior work emphasized high temperature measurements with little attention to the region below room temperature.

This chapter will describe the experimental method and equipment used to investigate these parameters and their temperature dependence in the range of interest. Included in the discussion will be descriptions of the modifications used to fix a design flaw in a microrefrigeration stage and the vacuum system required to run the refrigeration system. The software written to do the curve fitting of the data will be tested on several theoretically generated spectra as well as used on the reflectance data from Spinel.
FTIR SYSTEM

The spectrophotometric capabilities of the spectrophotometer laboratory at the University of Dayton encompasses a large range of wavelengths from the ultraviolet (UV) to the far infrared (IR). This range of wavelengths is covered by two spectrophotometers, a Beckman model 5270 which is a double monochromator dispersive machine and covers the UV (0.2 microns) to the near IR (2.5 microns), and a Nicolet 740SX Fourier Transform Infrared (FTIR) spectrophotometer which covers a range from the near IR (0.8 microns) to the far IR (250 microns). The latter machine was used to obtain the reflectance spectra of Spinel. Figure 3.1 shows the beam path of the Nicolet Spectrophotometer.

In the Nicolet system, a source is focused onto a variable diameter aperture and then collimated and sent into a Michelson Interferometer where it is modulated according to the pathlength difference between the two mirrors. The modulated beam is then focused by an off-axis parabolic mirror and sent through the sample compartment where a detector collects the signal from the sample. The spot size in the main sample compartment is controllable through the use of the variable aperture and is given by 1.57d, where d is the diameter of the aperture. An auxiliary experiment compartment is accessible through the use of a flipper mirror.

A tungsten lamp and a globar source are available to facilitate the use of the system across the full range of
Figure 3.1 Optical layout of the Nicolet 740SX spectrophotometer.\textsuperscript{[19]}
wavenumbers (15,000 cm\(^{-1}\) to 50 cm\(^{-1}\)). The wide range of wavenumbers also requires a change in the interferometer beamsplitter. There are three beamsplitters available: quartz (15,000 cm\(^{-1}\) to 3,800 cm\(^{-1}\)), germanium on a potassium bromide (KBr) substrate (5,800 cm\(^{-1}\) to 400 cm\(^{-1}\)), and a proprietary solid substrate (800 cm\(^{-1}\) to 50 cm\(^{-1}\)). Finally, five detectors are available for use across the full wavenumber range: silicon (15,000 cm\(^{-1}\) to 8,900 cm\(^{-1}\)), lead selenide (PbSe) (11,000 cm\(^{-1}\) to 3,900 cm\(^{-1}\)), mercury-cadmium-telluride (MCT) (5,800 cm\(^{-1}\) to 800 cm\(^{-1}\)), deuterium triglyceride sulfide (DTGS) with a KBr window (5,000 cm\(^{-1}\) to 400 cm\(^{-1}\)), and a DTGS with a polyethylene window (800 cm\(^{-1}\) to 50 cm\(^{-1}\)). With the appropriate choice of source, beamsplitter, and detector, the entire infrared spectrum is obtained.

In order to control the operation of the Nicolet spectrophotometer, a Nicolet 660 data system is used. The Nicolet data system controls the resolution of the instrument (16 cm\(^{-1}\) to 0.3 cm\(^{-1}\)) by adjusting the number of data points taken, the number of Fourier transform points of the signal versus mirror displacement, and the length of the mirror movement.

Since the system is a single beam instrument, atmospheric components can, if careful measures are not taken, show up in the spectra. In order to eliminate these absorptions from the spectra, a Balston air dryer is used to purify the purge air of the spectrophotometer. The air dryer eliminates nearly all
hydrocarbons and CO₂, while it reduces the moisture in the air to a dew point of -100°C.

MICROREFRIGERATION SYSTEM

A microrefrigeration system was purchased from MMR Technologies in order to add the capability to study temperature-dependent data. The system as received consisted of an ultra high purity gas filter, a microrefrigeration stage, a vacuum chamber jacket with two 25 mm diameter sapphire windows as well as two KBr windows, and a temperature indicator/controller. The vacuum chamber and microrefrigeration stage, as received from MMR, are shown in Figure 3.2.

The system works on the principle of Joule-Thomson cooling. When a high pressure gas such as nitrogen passes from a restricted tube into a larger diameter tube, a small amount of cooling takes place in the gas. The system designed by MMR works by passing high-purity nitrogen gas through fine capillary tubes embedded in a quartz extension of the microrefrigeration stage base, until it reaches the position of the sample mount where it is allowed to expand and cool, eventually condensing a drop or two of liquified nitrogen near the sample. Since the process does not provide a large amount of cooling capacity (maximum of 250 mW) the quartz extension, on which the sample is mounted, must be housed inside a vacuum, which serves to keep the atmospheric heat conduction.
Figure 3.2 Microrefrigeration stage and vacuum chamber prior to modifications.[20]
to a minimum. In addition, the sample must be small (maximum size of 20 mm in diameter and 5 mm in thickness).

The system requires a vacuum of 5 millitorr to operate at peak efficiency. Figure 3.3 shows the vacuum system designed for the refrigeration system. While this design was not capable of producing the 5 millitorr needed for optimum efficiency of the refrigeration system, it was capable of producing 10 millitorr at a slight loss in the microrefrigerator cool down rate.

The temperature range of the device is nominally -190°C to 100°C but is dependent upon the vacuum obtained inside the vacuum chamber and the amount of heat dissipation required by the sample. A resistor heater maintains the temperature stability of the sample at ±0.1°C and a diode temperature sensor maintains the temperature accuracy to better than ±2°C.

The cooling gas is typically commercial grade nitrogen which is purified to 99.998% by an ultra-high-purity filter. Without this filter the fine capillary tubes inside the microrefrigerator stage would become plugged by frozen or liquified contaminates.

During the initial setup and trial of the refrigeration system, an unknown material was found to have been deposited on the surface of the sample. This material was later identified as the vacuum epoxy potting compound which is used to seal the quartz extension into the base of the
Figure 3.3 10 millitorr vacuum system designed for use with the MMR microrefrigeration system. The liquid nitrogen cold trap was used to prevent back-streaming of pump oil into the refrigeration system.
microrefrigeration stage.\textsuperscript{[21]} The potting compound was believed to be degrading under the influence of the vacuum.

In order to check if this degradation was a one-time failure or a serious design flaw in the refrigeration system, MMR sent two additional microrefrigeration stages. After initial tests, both stages showed no degradation of their potting compounds. It was only after several cycles of the system that degradation was observed in both additional stages. This indicated that the potting compound was incompatible with vacuum service.

The solution we used was to seal the potting compound from the vacuum. Two considerations were explored in picking the proper sealing compound. First, it must provide an effective seal between the vacuum and the potting compound so that no potting compound can enter into the vacuum chamber. Second, since the base of the microrefrigerator does fluctuate in temperature by a small amount, the sealing compound must either remain pliable throughout this range of temperatures and pressures or it must match the thermal expansion properties of the quartz extension. A Polymeric Systems, Inc. silicon RTV sealant (PSI 601 Clear) was selected. This sealant should remain pliable throughout large temperature and pressure ranges and minimize the chance of the quartz extension being broken by a sealant which may have expanded at a faster rate than the quartz.
In order to seal the potting compound from the vacuum inside the vacuum chamber, a 1\(\frac{3}{4}\) x 1\(\frac{3}{4}\) x \(\frac{1}{4}\) inch thick aluminum plate was fabricated with a \(\frac{3}{4}\) x \(\frac{3}{4}\) inch wide hole milled out of the center of the plate and four 4-40 socket-head screw holes in the corners. The plate was then bonded to the microrefrigerator base using Epi-Seal General Purpose Adhesive. The center hole allowed the quartz extension of the microrefrigeration stage to pass through to the vacuum chamber while also providing a well that surrounded the potting compound and allowed it to be covered with the silicon RTV sealant.

The microrefrigeration stage top plate was purposely made wider than the microrefrigeration base so that an improved vacuum seal could be obtained. In order to do so, a vacuum chamber top plate, identical to the microrefrigeration stage top plate except for an additional 1-inch diameter O-ring groove on one face of the plate, was fabricated and bonded, to the top of the vacuum chamber, using the same general purpose adhesive. The vacuum chamber and the microrefrigeration stage could then be sealed together by tightening the socket-head screws with the O-ring providing the vacuum seal. An extra \(\frac{1}{2}\)-inch needed to be cut from the top of the vacuum chamber so the sample would still be visible through the two windows of the vacuum chamber. Figure 3.4 shows the two top plate components and Figure 3.5 shows the assembly of the redesigned refrigerator system.
Figure 3.4 Top plates designed for the refrigerator system.
Figure 3.5  Final assembly of the redesigned MMR refrigerator system. After bonding the top plates to the appropriate component, the RTV sealant well was filled with RTV and the top plates were combined by tightening 4 socket-head screws.
After these modifications were made, the system was checked without a sample in place by drawing a vacuum in the vacuum chamber and cooling the sample pad to -150°C. The system was allowed to stabilize at this temperature for one hour and was then warmed by turning off the flow of nitrogen to the system. When the sample pad reached ambient temperatures, it was again cooled to -150°C and allowed to remain at that temperature for one hour before the nitrogen gas was again turned off and the system warmed to ambient temperatures.

The pressure in the vacuum chamber was brought up to atmospheric and the microrefrigeration stage was removed. The sample pad was then inspected with a low-power stereoscopic microscope to look for signs of oily deposits. No deposits were observed and the RTV sealant appeared to have held. This temperature cycling was repeated again with a small silicon sample mounted on the sample pad. Again, no deposits were seen on the sample or on the sample pad. Thus, the potting compound problem was solved.

**REFLECTION ATTACHMENT**

The reflection attachment used to obtain the spectra from Spinel was a modified variable angle attachment supplied by Harrick Scientific Corp. The modifications were two-fold; the sample mount was changed to operate in a fixed angle mode (approximately 12.5° angle of incidence), and the sample mount
was redesigned to accommodate the microrefrigeration system at the sample position. Figure 3.6 shows the variable angle reflection attachment supplied by Harrick and the modified, fixed angle reflection attachment.

In the unmodified variable angle mode, the device used a thin, rectangular mirror and sample to retroreflect the beam without affecting the focal position or the f-number of the spectrometer. In the modified fixed angle mode, a thin sample is used in place of both the mirror and the sample. This substitution must be done such that the focal position and f-number of the spectrometer is unchanged. This only occurs when the sample is placed at a fixed angle of 12.5°.

The sample holder was originally designed to hold samples of less than 4 mm in thickness. The microrefrigeration system's vacuum chamber jacket, however, is 19 mm in width. In order to accommodate this larger size, a new sample holder was fabricated from an aluminum block and dowel rod. The new sample holder accounted for the fact that the 5 mm thick KBr window of the microrefrigeration system will translate the focus of the beam 1.72 mm toward the detector by moving the position of the sample back by 1.72 mm with respect to the rest of the reflection attachment.

**COMPUTER SOFTWARE**

The relationship between the reflectance and the complex index of refraction is given in Chapter II by equation 2.14
Figure 3.6 Beam path in the Harrick reflection attachment for the Nicolet spectrophotometer: \[^{[22]}\] (a) unmodified variable angle mode; (b) modified for fixed angle operation.
and, through the use of equations 2.25 and 2.28, to the fundamental material parameters - resonance position, damping constant, and plasma frequency. Therefore, the fundamental parameters of a material can be extracted by using a computer program which curve-fits equations 2.25, 2.28 and 2.14 to the measured reflectance as a function of frequency. A nonlinear curve fitting computer program (CURVEFIT) which fits equations 2.28, 2.25, and 2.14 to the measured reflectance as a function of frequency was written in Fortran-77 for use on a VAX 11/780. The Fortran code and flowchart is given in the Appendix.

The program was written to accept files given as a column of wavenumber and reflectance pairs where the reflectance is given in percent. There should be no header information in the input file and the data should end with -999.99 in each column which will cause the program to stop reading into the data array.

The Nicolet data is stored, however, in a proprietary manner so it required a conversion program supplied by Nicolet. The output of this conversion is shown in Figure 3.7 and consists of general file information including the data range, x and y multiplication factors for the converted data, an x increment for the converted data, and the number of data points.

The data itself was written as an array consisting first of a wavenumber and then eight reflectance values which were
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## JCAMP-DX = 4.10  
## DATA TYPE = INFRARED SPECTRUM  
## XUNITS = 1/CM  
## YUNITS = TRANSMITTANCE  
## XFACTOR = 1  
## YFACTOR = .001  
## FIRSTX = 7900.036  
## LASTX = 8192  
## NPOINTS = 8192  
## DELTAX = .964478  
## FIRSTY = .109  
## XYDATA

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Figure 3.7 Output of a reflectance data file from the Nicolet supplied conversion program. The "?" which appear in the data are out-of-range values and result because the wavenumber value is outside the usable range of the detector.
multiplied by 1/YFACTOR to do away with the decimal values. This enables the array to use only integer values. The first reflectance value (column 2) refers to the wavenumber written to its left (column 1). The reflectance value in the next column corresponds to the wavenumber written in column 1 plus the quantity of DELTAX given in the header information. This process is continued for each additional reflectance value in the line.

Occasionally a value of "?" is found in the reflectance values. This corresponds to a data point greater than 200 and is ignored by the conversion program. It should also be noted that the converted file contains all the wavenumbers from 0 to approximately 8000.

Since this file format cannot be read into CURVEFIT the program PREKRM\textsuperscript{24} was used to convert the file format to a linear column of wavenumber and reflectance pairs between prespecified wavenumber limits. The output from this program is then read into CURVEFIT.

After the input file has been read into the wavenumber-reflectance array of CURVEFIT, the user is given a choice of a Lorentz or Drude model fit to the data. Once that choice is made, CURVEFIT asks for the initial guesses to the oscillator parameters ($\omega_j$, $\Gamma_j$, $\omega_p$, and $\epsilon_0$) and their uncertainties. A maximum of 8 resonances can be fit to the measured reflectance.
These parameters are then used by the subroutine LEASTSQ in the appropriate equations to calculate the reflectance versus frequency based on the initial guesses. The normalized sum of the deviations (CHISQ) between the calculated and measured reflectance values versus frequency is the function that is minimized by the nonlinear curve fitting subroutine, STEPIT.\(^{[23]}\) STEPIT works by a direct search technique which does not calculate any derivatives and works well on functions with narrow valleys in the minimizing function. The only requirement is that the function to be minimized must be smooth and continuous.

After STEPIT has minimized the sum of the deviations between the calculated and measured reflectance values, the corresponding best fit oscillator parameters are written to a user specified output file (OUTFILE). The header of OUTFILE contains the best fit oscillator parameters and the body contains the real and imaginary parts to the index of refraction and the reflectance as a function of wavenumber. Figure 3.8 shows the data format of OUTFILE.

SOFTWARE TESTING

In order to tell if CURVEFIT was working properly, several tests were devised. The first two tests were curve fits to theoretically generated Lorentzian and Drude model reflection curves. These curves were generated using two pre-existing programs, LORGEN and DRDGEN.\(^{[25]}\) Both of these
FINAL CHISQUARE = 0.59593
HIGH FREQUENCY DIELECTRIC CONSTANT = 2.552

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Figure 3.8  A typical OUTFILE generated by the program CURVEFIT. Resonance position, damping constant, plasma frequency, and wavenumber are all given in units of cm$^{-1}$. 
programs allow the user to input a set of oscillator parameters which the programs use to calculate the reflectance spectrum across the specified frequency range.

The first test of CURVEFIT was a theoretically generated Drude model reflectance curve with a plasma frequency ($\omega_p$) of 1000 cm$^{-1}$, a damping constant ($\Gamma$) of 50 cm$^{-1}$, and a high frequency dielectric constant ($\epsilon_{\infty}$) of 3.0. The generated reflectance curve was input into CURVEFIT and the result, along with the input curve, is shown in Figure 3.9. Very few deviations can be observed between the two curves. The initial guesses for the three parameters used by CURVEFIT were $\omega_p = 800$ cm$^{-1}$, $\Gamma = 30$ cm$^{-1}$, and $\epsilon_{\infty} = 2.5$.

Excellent agreement was obtained between the input and output reflectance curves and the input and output oscillator parameters. Table 3.1 shows a comparison between the input and output parameters of the fit.

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<th>$\epsilon_{\infty}$</th>
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As shown in the table, there is virtually no deviations between the input and output parameters. What little
Figure 3.9 Generated Drude model reflectance curve using: \( \omega_p = 1000 \text{ cm}^{-1}, \Gamma = 50 \text{ cm}^{-1}, \epsilon_e = 3.0 \); and the corresponding output from CURVEFIT. The two curves are virtually indistinguishable.
deviation there is can mostly be attributed to round-off errors in both the Drude generation program and CURVEFIT.

The standard deviation between the two reflectance curves, $2.9 \times 10^{-4}$, also shows that the fitted reflectance curve had very little measurable deviation. This shows CURVEFIT's ability to fit the oscillator parameters of Drude type materials.

The second test of CURVEFIT was a theoretically generated Lorentzian reflectance curve with five resonances. This test was made more difficult in order to simulate actual material reflectance spectra i.e. MgAl$_2$O$_4$ (Spinel). The oscillator parameters used to generate the theoretical reflectance curve are listed in Table 3.2. This theoretical reflectance curve was used as the input for CURVEFIT. The CURVEFIT output and the theoretical reflectance curve are shown in Figure 3.10.

Excellent agreement was again obtained between the input and output reflectance curves as well as between the input and

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<td>800</td>
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Table 3.2 Values used to theoretically generate a five resonance Lorentzian reflectance curve.
Figure 3.10 Theoretically generated reflectance curve from a Lorentzian model with five resonances and the corresponding output from CURVEFIT. The two curves are virtually indistinguishable.
output oscillator parameters. The standard deviation between the two reflectance curves was 2.9x10^4, suggesting that a very close fit was obtained. Table 3.3 lists the deviations between the output oscillator parameters and those listed in Table 3.2.

Table 3.3 Deviations between the input oscillator parameters listed in Table 3.2 and the output parameters from CURVEFIT.

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<th>( \Gamma ) (cm(^{-1}))</th>
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The small deviations shown in Table 3.3 are again attributed to round-off errors in LORGEN and CURVEFIT. According to these two tests, CURVEFIT shows an excellent ability to extract oscillator parameters from the reflectance spectra of a Drude or Lorentzian-type material.

**REFLECTANCE SPECTRA OF SPINEL**

After showing CURVEFIT's ability to extract the fundamental oscillator parameters from a reflectance spectra and making the modifications to the refrigerator system, the temperature dependent reflectance spectra of Spinel was
analyzed. There were several reasons for picking Spinel as the material to be studied. First, it was readily available in a sufficiently good condition. Second, it showed multiple resonances in the mid-IR region (400 cm$^{-1}$ to 4000 cm$^{-1}$) where the DTGS detector and germanium on KBr substrate beamsplitter could be used. The DTGS detector is a room temperature detector with very low noise levels across the detection range. Third, the resonances were at higher frequencies than the transmittance cutoff of the KBr windows on the microrefrigeration vacuum chamber jacket, which ensures high throughput and low reflectance losses at the windows. Finally, the sample was nonhygroscopic and extremely resistant to scratches.

The sample was provided by Coors and was fabricated by hot pressing. The sample was 5 mm thick and 70 mm in diameter. In order for the sample to fit inside the refrigeration system it was cut to a square with dimensions of 13mm x 13mm x 2.5mm thick. After cutting, the front surface of the sample was polished with the back surface left in an optically rough form.

The refrigeration system and the Harrick reflection attachment in its fixed angle modified arrangement were placed in the main sample compartment of the Nicolet spectrophotometer. A small square aluminum mirror was first mounted on the microrefrigeration sample pad with a small amount of Dow Corning vacuum grease. With the KBr windows in
place, a 100% background scan was taken, which provided the reference to be used in the ratio to the sample scans.

After removing the aluminum mirror and cleaning the vacuum grease from the sample pad with freon, the Spinel sample was mounted to the microrefrigeration stage's sample pad with a thin film of Nuclear Systems Inc. thermal grease to ensure a good thermal contact between the sample pad and the sample.

The vacuum system was connected to the vacuum chamber jacket and the pressure was allowed to reach 10 millitorr. The nitrogen inlet gas to the microrefrigeration stage was adjusted to 1700 psi which gave an outlet flow from the microrefrigeration stage of 3 cubic feet per hour (CFH).

A reflectance spectra was taken first at 20°C. The sample was then cooled to 10°C and allowed to stabilize for two minutes before the next spectra was taken. This process was repeated at intervals of 10°C until the sample reached -40°C when an attempt to further cool the sample resulted in a drastic drop in the outlet flow of the nitrogen gas to near 0 CFH and a rise in temperature. The nitrogen gas flow to the microrefrigerator was turned off and the system was allowed to warm until it reached 20°C. The sample was then heated by increments of 10°C and a reflectance spectra was taken at each temperature up to 80°C.

The nitrogen gas was turned on and the system was allowed to cool. It was noted that the outflow from the
microrefrigerator stage was again 3 CFH and that the refrigerator was cooling properly. The system was cooled to -40°C before the outflow of nitrogen gas again dropped to 0 CFH. This indicated that the high-purity filter material had become contaminated with a material which liquifies or solidifies at approximately -40°C. With the small capillary tubes of the microrefrigerator stage plugged by this contaminate, the pressure drop at the sample pad was insufficient to produce any significant cooling. As a consequence, lower temperatures will not be obtainable until a replacement filter medium is received from MMR Technologies.

The reflectance spectra was then ratioed to that of the aluminum mirror. The resulting spectra did not go to zero at frequencies slightly higher than the highest allowable longitudinal optic mode (approximately 870 cm⁻¹) as expected but instead was around 2.4%. Therefore, a bias term must have entered into the sample and background spectra prior to ratioing.

Since a portion of the reflectivity of the KBr window will be added to both the background and sample spectrums, any frequency where the sample would have had zero reflectance will be artificially higher by an amount proportional to the reflectance of the KBr window (the reflectivity of the KBr window from both front and back surfaces, assuming no absorption, will be approximately 8% but not all of this will
reach the detector since the signal will not match the f-number of the system). A correction term for the reflectivity of the KBr was determined and subtracted from both of the unratioed aluminum and sample spectra. In addition, since the aluminum mirror used for the background spectra was assumed to have a reflectivity of 98.5%, a correction for this was also made. The governing equation used to compensate for these two effects is

\[ R_s = \left[ \frac{(R_s^*) - R_{KBr}}{(R_{Al}^*) - R_{KBr}} \right] 0.985 \]  

(3.1)

where \( R_s^* \), \( R_{Al}^* \), and \( R_{KBr} \) are the unadjusted sample and aluminum mirror reflectances and the collected portion of the reflectance from the KBr window respectively. After performing this correction, the spectra were ratioed again and all approached zero around 900 cm\(^{-1}\). The spectra from -30°C to 80°C are shown in Figure 3.11.

The spectra were then converted using the Nicolet-supplied conversion program and the PREKRM program from 400 cm\(^{-1}\) to 900 cm\(^{-1}\). Each spectra was input into CURVEFIT and an oscillator fit to the reflectance spectra was produced. Figure 3.12 shows the reflectance spectra at 0°C and the fitted spectra produced by CURVEFIT while Figure 3.13 shows the real and imaginary parts of the associated complex index of refraction. The two spectra differ in two main places, around 500 cm\(^{-1}\) and around 700 cm\(^{-1}\). However, the standard
Figure 3.11 Temperature dependent reflectance spectra of Spinel from -30°C to 80°C.
Figure 3.12 Reflectance spectra of Spinel at 0°C (input) and the fitted output from CURVEFIT.
Figure 3.13 The real and imaginary parts to the complex index of refraction obtained from the fit to the 0°C reflectance spectra shown in Figure 3.12.
deviation between the two spectra was 0.5 which indicates a good fit.
CHAPTER IV
REFLECTANCE SPECTRA ANALYSIS

In this chapter we will analyze the oscillator parameters obtained by the nonlinear curve-fit minimization procedure applied to the data shown in Figure 3.11. The slope of the temperature-dependent resonance position will be compared to other experimental results while the data for the normalized damping constant will be compared to a theoretical model. Finally, the data for the normalized plasma frequency will be presented and compared with respect to two other authors' results.

ERROR ANALYSIS

For this type of analysis, there are three main sources of error which can enter the final values of the parameters: the precision of the spectrophotometer, the absolute reflectance of the aluminum mirror, and the background reflectance contribution from the KBr window. Since the precision of the Nicolet spectrophotometer is extremely high, it was assumed that no uncertainty enters the parameters from the Nicolet. Therefore, the largest errors should result from the assumption that the aluminum mirror's reflectance was
98.5% and the assumption that the reflectance from the KBr window was 2.4%. In addition, a somewhat smaller source of error can appear from the sensitivity of the curve-fit to the initial guesses for the parameters.

In order to obtain the magnitude of the errors in the oscillator parameters, fits to three additional cases (besides $R_{Al} = 98.5\%$ and $R_{KBr} = 2.4\%$) pertaining to the assumed reflectances from the aluminum mirror and KBr window were performed. The three cases were: $R_{Al} = 98.5\%$ and $R_{KBr} = 1.4\%$, $R_{Al} = 97.5\%$ and $R_{KBr} = 2.4\%$, and finally $R_{Al} = 97.5\%$ and $R_{KBr} = 1.4\%$. The largest deviations from the three cases above and the original case was taken as the associated error for the parameter. The results of this error analysis are shown in Figures 4.1 through 4.8.

**RESONANCE POSITION**

The resonance position as a function of temperature for all five resonances is shown in Figures 4.1 through 4.5. Two of the resonances (582 cm$^{-1}$ and 808 cm$^{-1}$) show quadratic dependence while the other three show linear dependence. Therefore, the resonances at 582 cm$^{-1}$ and 808 cm$^{-1}$ were fit to an equation of the form $\omega_j = n*T^2 + m*T + b$ while the other resonances were fit to the equation $\omega_j = m*T + b$ where $n$, $m$, $T$, and $b$ are the quadratic and linear slopes, temperature, and intercept, respectively. The results of
Figure 4.1  Temperature dependence of the 494 cm\(^{-1}\) resonance of Spinel. Dashed line is a linear regression fit to the data.
Figure 4.2  Temperature dependence of the 520 cm$^{-1}$ resonance of Spinel. Dashed line is a linear regression fit to the data.
Figure 4.3 Temperature dependence of the $582 \text{ cm}^{-1}$ resonance of Spinel. Dashed line is a second order regression fit to the data.
Figure 4.4  Temperature dependence of the 678 cm\(^{-1}\) resonance of Spinel. Dashed line is a linear regression fit to the data.
Figure 4.5  Temperature dependence of the 808 cm\(^{-1}\) resonance of Spinel. Dashed line is a second order regression fit to the data.
these fits, and the standard deviations, are listed in Table 4.1.

**Table 4.1** Temperature dependent slope and the standard deviation of the fit for the resonances of Spinel.

<table>
<thead>
<tr>
<th>RESONANCE (cm$^{-1}$)</th>
<th>m</th>
<th>STANDARD DEV.</th>
<th>n</th>
<th>STANDARD DEV.</th>
</tr>
</thead>
<tbody>
<tr>
<td>494</td>
<td>-6.0x10$^{-3}$</td>
<td>5.2x10$^{-3}$</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>520</td>
<td>-1.4x10$^{-2}$</td>
<td>4x10$^{-3}$</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>582</td>
<td>-7.9x10$^{-3}$</td>
<td>6x10$^{-4}$</td>
<td>-2.2x10$^{-4}$</td>
<td>9x10$^{-5}$</td>
</tr>
<tr>
<td>678</td>
<td>-3.3x10$^{-2}$</td>
<td>4x10$^{-3}$</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>808</td>
<td>-4.0x10$^{-3}$</td>
<td>1.6x10$^{-3}$</td>
<td>-8.4x10$^{-5}$</td>
<td>2x10$^{-6}$</td>
</tr>
</tbody>
</table>

The standard deviation is low with respect to the slope for all the resonances except 494 cm$^{-1}$. The standard deviation of this resonance is large enough and the slope small enough that it must be considered a constant.

M. E. Thomas has reported values for the temperature dependent slopes of the resonance positions for Spinel in a computer code used to predict the optical properties of materials.$^{[26]}$ This program assumes a linear dependence on temperatures above 295 K and no dependence below that temperature. While this simplifies the program, the expected behavior should be a linear dependence at "high temperatures" followed by a quadratic dependence at lower temperatures and finally a region where there is roughly no temperature dependence.$^{[27]}$ The data in Figures 4.1 through 4.5 shows that
the three regions can occur at different temperatures for each resonance as opposed to the single abrupt cutoff of 295 K modeled by Thomas.

The resonances that exhibited quadratic temperature behavior and the one that showed no temperature dependence will have slopes that differ from Thomas' values. Therefore, no comparison will be made on those resonances. The other two resonances (520 cm\(^{-1}\) and 678 cm\(^{-1}\)) are compared in Table 4.2 to Thomas' values.

**Table 4.2** Comparison of the linear temperature dependence of the 520 cm\(^{-1}\) and 678 cm\(^{-1}\) resonance positions and the values given by M. E. Thomas in the computer code OPTPROP.

<table>
<thead>
<tr>
<th>RESONANCE POSITION (cm(^{-1}))</th>
<th>CURVEFIT DATA</th>
<th>OPTPROP DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td>520</td>
<td>-1.364 \times 10^{-2}</td>
<td>-1.40 \times 10^{-2}</td>
</tr>
<tr>
<td>678</td>
<td>-3.341 \times 10^{-2}</td>
<td>-7.12 \times 10^{-3}</td>
</tr>
</tbody>
</table>

The 520 cm\(^{-1}\) resonance agrees remarkably well with Thomas' data; however, the 678 cm\(^{-1}\) resonance has a considerably higher temperature dependence. This is attributed to the impurity resonance which causes the deviation in the fit around 700 cm\(^{-1}\). A sixth resonance was initially added to the curve-fit in an attempt to account for the impurity resonance but without success. Therefore, the resonances (678 cm\(^{-1}\) and the impurity) as a sum will show a different temperature dependence than the individual resonance.
DAMPING CONSTANT

In analyzing the temperature dependence of the oscillator parameters, the plasma frequency and damping constant are best done after they have been normalized. The normalized damping constant is simply $\Gamma/\omega_j$ and the normalized plasma frequency is given by

$$\omega_{pN} = \frac{\omega_{pV}/\epsilon_m}{\omega_j} \tag{4.1}$$

The normalized damping constant for all five resonances is shown in Figure 4.6. The data shows very little scatter except for the damping constant of the 582 cm$^{-1}$ resonance. This resonance is heavily damped and, furthermore, is close to two strong resonances which tend to overwhelm it. Under these circumstances, the 582 cm$^{-1}$ resonance is extremely difficult to fit properly. Therefore, the amount of scatter seen in the data is not unexpected.

The damping constant was initially fit to a linear equation of the form $\Gamma = m*T + b$ where $m$, $T$, and $b$ are as defined previously. The values of the slope and the standard deviation from this regression fit are given in Table 4.3.

The damping constant of the 494 cm$^{-1}$ and 520 cm$^{-1}$ resonance shows no temperature dependence, as the standard deviation of both approaches or surpasses the value of the slope. The scatter seen in the damping constant of the 582 cm$^{-1}$ resonance did not, however, adversely affect the fit
Figure 4.6 Temperature dependence of the normalized damping constant of Spinel. Dashed lines are linear regression fits to the data.
Table 4.3  Temperature dependent slope and the standard deviation of the regression fit to the damping constant of Spinel.

<table>
<thead>
<tr>
<th>RESONANCE (cm(^{-1}))</th>
<th>SLOPE (m)</th>
<th>STANDARD DEVIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>494</td>
<td>-6.482 \times 10^{-7}</td>
<td>7.225 \times 10^{-6}</td>
</tr>
<tr>
<td>520</td>
<td>-1.040 \times 10^{-5}</td>
<td>7.75 \times 10^{-6}</td>
</tr>
<tr>
<td>582</td>
<td>1.537 \times 10^{-4}</td>
<td>2.51 \times 10^{-5}</td>
</tr>
<tr>
<td>678</td>
<td>4.166 \times 10^{-5}</td>
<td>3.00 \times 10^{-6}</td>
</tr>
<tr>
<td>808</td>
<td>3.572 \times 10^{-5}</td>
<td>7.45 \times 10^{-6}</td>
</tr>
</tbody>
</table>

as the standard deviation is a factor of ten below the value of the slope.

Jasperse et. al.\(^{[28]}\) used a quantum mechanical derivation by Maradudin and Wallis for the normalized damping constant of an ionic crystal as a function of temperature and found that, when evaluated at the resonance position, it reduces to the form

\[
\frac{\Gamma(\omega, T)}{\omega_j} \bigg|_{\omega = \omega_j} = \frac{A}{\omega_j^4} \left[ (e^{\frac{\hbar \omega_j}{kT}} - 1)^{-1} + \frac{1}{2} \right]
\] (4.2)

where \(\hbar\), and \(k\), are Plank's and Boltzmann's constants and \(A\) is a material and resonance dependent constant. They have shown this equation to fit experimental data from MgO and LiF in the high temperature limit (\(\hbar \omega_j < kT\)). However, they observe large discrepancies in the low temperature limit (\(\hbar \omega_j \gg kT\)).

The damping constant data shown in Figure 4.6 was fit to equation 4.2. The constant \(A\) in the equation was obtained by inserting the normalized damping constant data into equation
4.2 for each resonance and temperature. The value of A at every temperature was averaged to give a single resultant value for each resonance. The results of the theoretical fit are shown in Figure 4.7.

Good agreement was obtained for the 582 cm\(^{-1}\), 678 cm\(^{-1}\), and 808 cm\(^{-1}\) resonance. However, the two resonances that showed no temperature dependence deviate considerably from equation 4.2. These deviations could be a result of the fact that the data collected from Spinel does not satisfy the high temperature limit condition, nor can it be classified in the low temperature limit. In addition, Maradudin and Wallis have stated that a potential source of error may result from their simplistic assumption of the anharmonic crystalline potential interactions and their assumption of a "nearest neighbor, central force, interionic potential function"\(^{[29]}\) in deriving the equation for the temperature dependence of the damping constant. While these errors may be small for diatomic ionic crystals, they may become significant when the structure of the material becomes more complex as it is for Spinel.

**PLASMA FREQUENCY**

The normalized plasma frequency for all five resonances is shown in Figure 4.8. It appears that the 50°C value for the plasma frequency of both the 494 cm\(^{-1}\) and the 520 cm\(^{-1}\) resonances deviated further than expected from their respective regression fit. Since these resonances reside very
Figure 4.7 Theoretical fit to the damping constant using equation 4.2 and the resonance position data shown in figures 4.1 through 4.5.
close to each other in the spectra seen in Figure 3.11, and since the data points lie on opposite sides of their respective regression fit, it is believed that the plasma frequencies for these two resonances were coupled by CURVEFIT during the fitting process.

The plasma frequency, like the damping constant, was fit to a linear equation of the form \( \omega_p = m \cdot T + b \). The slope and standard deviation of the regression fit are given in Table 4.4. The data shows that the plasma frequency fit for two resonances, 582 cm\(^{-1}\) and 808 cm\(^{-1}\), is essentially temperature independent. Both had standard deviations on the order of the value for the slope. The other three resonances, however, show a linear temperature-dependence.

It should be noted here that the two resonances which have temperature independent damping constants exhibit temperature-dependent plasma frequencies. In addition, the two resonances which have temperature independent plasma frequencies exhibit two of the three temperature-dependent damping constants. This is a trend which may signify that CURVEFIT has compensated for a change in one parameter by adjusting a second.

Although there is very little theoretical work available on the temperature dependence of the plasma frequency, the present experimental results agree - that the plasma frequency has a linear temperature dependency - with work done by Jasperse et. al.\(^{[30]}\) and Thomas.\(^{[31]}\) Both authors, however,
Figure 4.8  Temperature dependence of the normalized plasma frequency of Spinel. Dashed lines are linear regression fits to the data.
Table 4.4 Temperature dependent slope and the standard deviation of the regression fit to the plasma frequency of Spinel.

<table>
<thead>
<tr>
<th>RESONANCE (cm(^{-1}))</th>
<th>SLOPE (m)</th>
<th>STANDARD DEVIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>494</td>
<td>$-1.160 \times 10^{-3}$</td>
<td>$1.45 \times 10^{-4}$</td>
</tr>
<tr>
<td>520</td>
<td>$-8.137 \times 10^{-4}$</td>
<td>$1.558 \times 10^{-4}$</td>
</tr>
<tr>
<td>582</td>
<td>$-1.937 \times 10^{-5}$</td>
<td>$4.811 \times 10^{-5}$</td>
</tr>
<tr>
<td>678</td>
<td>$-6.147 \times 10^{-4}$</td>
<td>$8.43 \times 10^{-5}$</td>
</tr>
<tr>
<td>808</td>
<td>$-3.951 \times 10^{-5}$</td>
<td>$3.178 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

found positive slopes for the temperature-dependence of the plasma frequency. The trends observed in our data (Figure 4.8) show negative slopes for the temperature-dependence of the plasma frequencies.
CHAPTER V
SUMMARY

In Chapter II a review of the classical theoretical development leading to a relationship between the relative dielectric constant, complex index of refraction, and finally the reflectance as a function of frequency was presented. Chapter II also showed that the relative dielectric constant should include frequency and temperature dependence. The governing equation was given as

\[ \varepsilon_r(\omega, T) = \varepsilon_\infty(T) \left( 1 + \sum_j \frac{\omega^2_j(T)}{\omega^2_j(T) - \omega^2 + i\omega\Gamma_j(\omega, T)} \right) \quad (5.1) \]

In order to investigate the temperature dependence associated with the reststrahlen spectra of Spinel a Joule-Thomson microrefrigeration stage was used. In prior work, a design flaw which caused a potting compound to soften and vaporize under the influence of a vacuum had been observed. This flaw had to be fixed before the refrigeration system could be used in this investigation. The solution was to seal the potting compound from the vacuum by use of a silicon RTV sealant. In the process the improved vacuum seal between the vacuum chamber and refrigeration stage was improved to provide
easier use. If the system is to be used in the future, a similar modification to the bottom of the vacuum chamber jacket should be made.

Equation 5.1 was the basis of a nonlinear curve fitting computer program, CURVEFIT. The program reads in wavenumber-reflectance pairs and then minimizes the normalized square of the deviations between the measured and calculated reflectance values. The output from the program contains the best fit oscillator parameters (resonance position, plasma frequency, and damping constant) as well as the calculated index of refraction as a function of frequency.

The program was successfully tested through the use of the Drude and Lorentzian theoretical models. The standard deviation from the fits was $2.9 \times 10^{-4}$ which verified an extremely close fit between measured and calculated reflectance. The errors on the oscillator parameters were, in general, no greater than 0.0015% for either the Lorentzian or Drude models. These validation tests confirmed the program's utility in extracting oscillator parameters from reflectance curves with a high degree of precision under optimum conditions (no noise and purely Lorentzian-type or Drude-type oscillators).

The residual errors observed in the validation tests are believed to be the result of round-off in both the reflectance generation programs and CURVEFIT itself. One possible method for lowering the errors is to allow CURVEFIT to do a full fit
to the reflectance. The program initially starts with an increment to each parameter in the fitting equation equal to the uncertainty entered by the user in the initial guesses. As the function to be minimized becomes smaller, the parameter increments are decreased until some minimum specified value is reached which causes the program to stop. Currently, the minimum value is $1 \times 10^{-10}$ times the user specified uncertainty for each parameter. This limits the running time of the program. By entering zero for the estimated uncertainty for all initial guesses, the program will continue until a full fit is obtained.

The program was applied to the reflectance spectrum of Spinel to investigate the temperature dependence of the oscillator parameters. The reflectance spectra from Spinel was obtained from -30°C to 80°C and analyzed by CURVEFIT. The full temperature range of the microrefrigeration system (-190°C to 100°C) was not used because of a contamination in the ultra-high purity nitrogen gas filter. This problem will be fixed when a replacement filter is received from MMR Technologies. Future work may then concentrate on lower temperatures.

Several trends were observed in the resonance position. All five resonances exhibited negative temperature slopes. However, three distinct dependencies were observed: quadratic, linear, and constant (temperature independent). Literature sources have verified a linear temperature dependence on ionic
materials at "high temperatures" and have also suggested that the dependence should become roughly temperature independent at some lower temperature. From a strictly semi-classical model, temperature dependence of the resonance position arises from anharmonic contributions to the potential energy and from the volume expansion of the crystal. The directions of the temperature-dependence from the two components are often in opposite directions. Additionally, both components should approach zero as the temperature approaches zero. This would suggest, at the very least, a change in slope for the temperature-dependence of the resonance position.

This work has shown that a transition between the linear and the temperature independent regions can occur at room temperatures or higher depending on the individual resonance oscillation. It is interesting to note that the two resonances which exhibited quadratic temperature dependence were the two weakest resonances.

The slopes of the two resonances which showed linear temperature dependence were compared to literature values. One resonance differed by only 2.5% while the other was off by a factor of 5. It is believed that this resonance suffered from the presence of a nearby impurity resonance which was not accounted for in the spectral fit. An attempt was made, without success, to account for this resonance by adding a sixth oscillator during the curve-fitting of the spectra. Future work may again attempt to account for this impurity
through the addition of a sixth resonance to the spectral fit or by stripping out this component from the spectra through the use of a curve-stripping routine.

The normalized damping constant data showed that two constants exhibited virtually temperature independent trends. The other three normalized damping constants were initially fit to linear equations with positive slopes. These three resonances agreed with the classical result - as the temperature decreases, the phonon density of states (which is related to the resonance width) should become narrower. In addition, all three agreed reasonably well with prior theoretical quantum mechanical work which modeled the temperature dependence of the normalized damping constant of an ionic cubic crystal as

\[
\frac{\Gamma(\omega, T)}{\omega_j} \mid_{\omega - \omega_j} = \frac{A}{\omega_j^4} \left[ (e^{\frac{\hbar \omega_j}{kT}} - 1)^{-1} + \frac{1}{2} \right]
\]

(5.2)

The two resonances that were temperature independent deviated considerably from equation 5.2.

This deviation could be a result of the assumed sodium-chloride-like unit cell used in the development of the crystalline potential for equation 5.2. Spinel has a much more complex unit cell which will add higher order terms to the potential. Furthermore, there are several sources of error in the assumptions which were used in developing the crystalline potential for equation 5.2 (central force,
nearest-neighbor, interionic potential). Finally, this equation has been shown to provide excellent agreement with experimental results in the high temperature limit but deviates considerably in the low temperature limit. The data for Spinel satisfies neither of these two conditions.

The normalized plasma frequencies of all five oscillators also showed linear dependence with positive slopes, except for two which were temperature independent. This is contrary to published results on LiF and MgO which have negative slopes. However, from a classical view, when the reflectance increases and the width of the resonance decreases, the plasma frequency (strength) should increase in a manner which allows the integrated area of the resonance to remain constant.

As mentioned in Chapter III, assuming a 2.4% reflectance from the KBr window and a 98.5% reflectance from the aluminum mirror, while providing close values for use in the ratio between the sample and reference, is a primary source of error. A future modification to the system should be the inclusion of a VW reflectance attachment for determination of the absolute reflectance of the reference mirror. In addition, changing the angle of the sample mount with respect to the vacuum chamber windows will eliminate the contribution to the reflectance values from the KBr windows.

Finally, it was noted that the 50°C data point for the plasma frequency of two close resonances appeared to have been coupled by CURVEFIT. This coupling caused one value to be
artificially high at the expense of the other which was artificially low. Even though these two resonances are similar in strength and reside within 30cm$^{-1}$ of each other, this may signify a wider co-dependence between variables and future work should address this potential problem. One possible solution would be to measure the low frequency and high frequency dielectric constants with the difference serving to define the summation of all the oscillator plasma frequencies. This number could be added as a constraint to equation 2.25 ($\Sigma\omega_p = \epsilon(0)-\epsilon(\infty)$).
Figure A.1 Flowchart of the program CURVEFIT.
PROGRAM CURVEFIT

**THIS PROGRAM CALCULATES THE BEST FIT TO THE**
**REFLECTANCE DATA OF A CLASSICAL LORENTZIAN OR**
**DRUDE MODEL. IT STARTS WITH INITIAL GUESSES**
**TO THE OPTICAL PARAMETERS THEN, THROUGH A**
**NONLINEAR CURVE FITTING ROUTINE, STEPIT,**
**FINDS THE BEST VALUES TO APPROXIMATE THE**
**REFLECTANCE CURVE.**

**VARIABLE DECLARATION**

CHARACTER*40 INFILE, OUTFILE
REAL WVNM(5000), REFL(5000), GAMMA(6)
REAL PLASM(6), RESON(6), EINF, CHISQ, KKK(5000)
REAL R(5000), UNC(4), MASK(20), X(20), XMAX(20)
REAL XMIN(20), DELTAX(20), DELMIN(20)
REAL NNN(5000), IWRT, ERR(20, 20)
INTEGER M, NPTS, LORENTZ, NV, NTRACE, MATRIX
COMMON/GUESS/PLASMA, RESON, GAMMA, EINF, M, LORENTZ, UNC
COMMON/OUT/WVNM, REFL, R, NPTS, NNN, KKK
COMMON/STEPIT/NV, NTRACE, MATRIX, CHISQ, MASK, X,
+ XMAX, XMIN, DELTAX, DELMIN, ERR, IWRT

READ IN DATA

WRITE (*,100)
100 FORMAT (// 'ENTER THE INPUT FILE NAME: ')
READ (*,110) INFILE
110 FORMAT (A40)
OPEN (UNIT=10, STATUS='OLD', FILE=INFILE)
I=1
120 READ (10,*) WVNM(I), REFL(I)
IF (WVNM(I) .EQ. -999.99 .AND. REFL(I) .EQ. -999.99)
+ GOTO 200
I = I + 1
GOTO 120
200 CLOSE (UNIT=10)

DECREASE I BY 1 TO ACCOUNT FOR -999.99, -999.99

I = I - 1
NPTS=I
WRITE (*,210)
210 FORMAT (// 'PLEASE ENTER THE NAME YOU WISH TO USE AS THE'
+ OUTPUT')
READ (*,220) OUTFILE
220 FORMAT (A40)
OPEN (UNIT=11, STATUS='NEW', FILE=OUTFILE)
C--------------------------------
C    CALLING ALL SUBROUTINES
C-------------------------------
    CALL GUESS
    CALL ENCODE
    CALL LEASTSQ
    CALL STEPIT(LEASTSQ)
    CALL OUTPUT(X,M,LORENTZ,OUTFILE)
    CLOSE (UNIT=11, STATUS='KEEP')
C
    STOP
    END
SUBROUTINE GUESS

*****************************************************************************

* THIS SUBROUTINE ASKS THE USER FOR THE TYPE OF *
* MODEL TO BE EMPLOYED, LORENTZIAN OR DRUDE, THEN *
* ASKS FOR ALL INITIAL GUESSES TO THE NECESSARY *
* VARIABLES TO IMPLEMENT THAT MODEL, i.e. NUMBER *
* OF OSCILLATORS, PLASMA FREQUENCY OF ALL *
* OSCILLATORS, etc. *
*****************************************************************************

VARIABLE DECLARATION

REAL PLASMA(6), RESON(6), GAMMA(6), EINF, UNC(4)
INTEGER M, LORENTZ
COMMON/GUESS/PLASMA, RESON, GAMMA, EINF, M, LORENTZ, UNC

C ASK FOR THE INITIAL GUESSES

WRITE (*,230)
230 FORMAT ('WILL YOU BE USING A LORENTZIAN OSCILLATOR MODEL?' )
READ (*,240) LORENTZ
240 FORMAT (A40)
IF (LORENTZ .EQ. 1) GOTO 300

C ENTER THE INITIAL DRUDE MODEL GUESSES AND THEIR ACCOMPANYING UNCERTAINTIES

WRITE (*,250)
250 FORMAT ('THEN YOU WILL BE USING THE DRUDE MODEL.')
WRITE (*,260)
260 FORMAT ('ENTER INITIAL GUESS FOR THE DAMPING CONSTANT' )
READ*, GAMMA, UNC(1)
WRITE (*,270)
270 FORMAT ('ENTER INITIAL GUESS FOR THE PLASMA FREQUENCY')
READ*, PLASMA, UNC(2)
WRITE (*,280)
280 FORMAT ('ENTER INITIAL GUESS FOR THE HIGH FREQUENCY DIELECTRIC CONSTANT')
READ*, EINF, UNC(3)
GOTO 400
C----------------------------------------
C  DETERMINE THE NUMBER OF
C  LORENTZIAN OSCILLATORS
C----------------------------------------
300     WRITE (*,310)
310     FORMAT (/'HOW MANY OSCILLATORS WILL YOU BE
+      FITTING? '/'(THE MAXIMUM IS 6)'/)
          READ*, M
C----------------------------------------
C  ENTER THE INITIAL LORENTZIAN MODEL GUESSES
C  AND THEIR ACCOMPANYING UNCERTAINTIES
C----------------------------------------
320     WRITE (*,320)
330     CONTINUE
335     WRITE (*,335)
340     CONTINUE
350     WRITE (*,355)
360     CONTINUE
370     WRITE (*,375)
380     RETURN
END

C
WRITE (*,310)
FORMAT (/'HOW MANY OSCILLATORS WILL YOU BE
+      FITTING? '/'(THE MAXIMUM IS 6)'/)
READ*, M

WRITE (*,320)
FORMAT (/'ENTER THE RESONANCE FREQUENCY FOR
+      OSCILLATOR #'/)
DO 330 I = 1, M
   PRINT*, I,'') '
   READ*, RESON(I)
330 CONTINUE
WRITE (*,335)
FORMAT (/'ENTER THE UNCERTAINTY FOR THESE
+      RESONANCES. '/)
READ*,UNC(1)
WRITE (*,340)
FORMAT (/'ENTER THE DAMPING CONSTANT FOR
+      OSCILLATOR #'/)
DO 350 J = 1, M
   PRINT*, J,'') '
   READ*, GAMMA(J)
350 CONTINUE
WRITE (*,355)
FORMAT (/'ENTER THE UNCERTAINTY FOR THESE
+      DAMPING CONS. '/)
READ*,UNC(2)
WRITE (*,360)
FORMAT (/'ENTER THE PLASMA FREQUENCY FOR
+      OSCILLATOR #'/)
DO 370 K = 1, M
   PRINT*, K,'') '
   READ*, PLASMA(K)
370 CONTINUE
WRITE (*,375)
FORMAT (/'ENTER THE UNCERTAINTY FOR THESE PLASMA
+      FREQS. '/)
READ*,UNC(3)
WRITE (*,380)
FORMAT (/'ENTER THE HIGH FREQUENCY DIELECTRIC
+      CONSTANT FOLLOWED BY THE
+      UNCERTAINTY.'/)  
READ*, EINF,UNC(4)
RETURN
SUBROUTINE ENCODE

* THIS SUBROUTINE PLACES ALL NECESSARY INFORMATION INTO THE VARIABLES REQUIRED BY THE "STEPIT" SUBROUTINE. i.e. Assigns the STEPIT VARIABLES X(I) TO THE CORRECT OSCILLATOR VARIABLES. *

VARIABLE DECLARATION

INTEGER M, NV, I, LORENTZ, NTRACE, MATRIX
REAL X(20), XMAX(20), XMIN(20), DELMIN(20), MASK(20)
REAL PLASMA(6), GAMMA(6), EINF, UNC(4), CHISQ
REAL ERR(20, 20), IWRT, RESON(6), DELTAX(20)
COMMON/STEPIT/NV, NTRACE, MATRIX, CHISQ, MASK, X, XMAX, XMIN,
+ DELTAX, DELMIN, ERR, IWRT
COMMON/GUESS/PLASMA, RESON, GAMMA, EINF, M, LORENTZ, UNC

PLACE THE DRUDE MODEL PARAMETERS INTO THE PROPER VARIABLES FOR STEPIT TO USE

IF (LORENTZ .EQ. 1) GOTO 100
X(1) = GAMMA
X(2) = PLASMA
X(3) = EINF
DO 50 I=1, 3
   XMAX(I)=5.e8
   XMIN(I)=1.e-5
   DELTAX(I)=UNC(I)
   DELMIN(I)=UNC(I) * 1.E-10
50 CONTINUE
NV = 3
GOTO 300

PLACE THE LORENTZIAN MODEL PARAMETERS INTO THE PROPER VARIABLES FOR STEPIT TO USE

DO 200 I = 1, M
   X(I) = RESON(I)
   X(M + I) = GAMMA(I)
   X(2*M + I) = PLASMA(I)
   DELTAX(I) = UNC(1)
   DELMIN(I) = UNC(1) * 1.E-10
   DELTAX(M + I) = UNC(2)
   DELMIN(M + I) = UNC(2) * 1.E-10
   DELTAX(2*M + I) = UNC(3)
   DELMIN(2*M + I) = UNC(3) * 1.E-10
XMAX(I) = 5.e8
XMAX(M+I) = 5.e8
XMAX(2*M+I) = 5.e8
XMIN(I) = 1.
XMIN(M+I) = 1.e-5
XMIN(2*M+I) = 1.e-5

CONTINUE
X(3*M + 1) = EINF
NV = 3*M +1
DELTAX(NV) = UNC(4)
DELMIN(NV) = UNC(4) * 1.E-10
XMAX(NV) = 1.e8
XMIN(NV) = 0.0

C-----------------------------
C SET THE STEPIT PARAMETERS WHICH
C WILL ENSURE EACH VARIABLE WILL BE
C MINIMIZED
C-----------------------------

NTRACE = 1
MATRIX = 107
DO 400  I=1,NV
       MASK(I)=0
400  CONTINUE
RETURN
END
SUBROUTINE LEASTSQ

****************************************************************************
*                  THIS SUBROUTINE COMPUTES THE VALUES FOR THE REAL  *
* AND IMAGINARY COMPONENTS TO THE DIELECTRIC                           *
*                        CONSTANT FROM THE VALUES OF THE OPTICAL          *
*                  PARAMETERS READ IN. IT THEN COMPUTES THE              *
*            CORRESPONDING VALUE OF REFLECTANCE. FINALLY, IT            *
*                  COMPUTES THE "CHISQ" FROM THE MEASURED AND           *
*                CALCULATED REFLECTANCE VALUES. THIS IS THE VALUE        *
*                    WHICH THE SUBROUTINE "STEPIT" MINIMIZES.             *
**************************************************************************

VARIABLE DECLARATION

REAL   E1(5000),E2(5000),PLASMA(6),RESON(6),GAMMA(6)
REAL   EINF,REFL(5000),R(5000),CHISQ,SUM1,SUM2,SUM3
REAL   TOP2,BOT,NNN(5000),KKK(5000),WVNM(5000)
REAL   X(20),XMAX(20),XMIN(20),DELTAX(20),DELMIN(20)
REAL   ERR(20,20),UNC(4),IWRT,MASK(20)
INTEGER M,NPTS,LORENTZ,NV,NTRACE,MATRIX
COMMON/GUESS/PLASMA,RESON,GAMMA,EINF,M,LORENTZ,UNC
COMMON/STEPIT/NV,NTRACE,MATRIX,CHISQ,MASK,X,XMAX,XMIN
+    DELMIN,DELTAX,ERR,IWRT
COMMON/OUT/WVNM,REFL,R,NPTS,NNN,KKK

Determine what model is being used and compute
SUMMATIONS IF NECESSARY FOR E1 AND E2.
IF LORENTZ=Yes, use the Lorentzian model.
IF IT DOESN'T, USE THE DREUDE MODEL.

IF (LORENTZ .EQ. 1) GOTO 120
   GAMMA = X(1)
   PLASMA = X(2)
   EINF = X(3)

DRUDE MODEL CALCULATIONS FOR THE DIELECTRIC
FUNCTION, REAL AND IMAGINARY PARTS TO THE
INDEX OF REFRACTION, AND THE CALCULATED REFLECTANCE

SUM3=0.
DO 100 J = 1, NPTS
   E1(J)=EINF * (1 - (PLASMA**2/(GAMMA**2 +
                    WVNM(J)**2))
   E2(J)=PLASMA**2 * GAMMA * EINF/
             (WVNM(J) * (WVNM**2 + GAMMA**2))
   NNN(J) = SQRT((SQRT(E1(J)**2 + E2(J)**2))/2.
             + E1(J)/2.)
   KKK(J) = SQRT((SQRT(E1(J)**2 + E2(J)**2))/2.
             - E1(J)/2.)

81
\[ R(J) = \frac{100 \times ((1. - NNN(J)) \times NNN(J) + KKK(J) \times KKK(J))}{((1. + NNN(J)) \times NNN(J) + KKK(J) \times KKK(J))} \]

\[ \text{SUM3} = (\text{REFL}(J) - R(J)) \times 2 + \text{SUM3} \]

100 CONTINUE
GOTO 500

C-------------------------------------------------------------------------------
C LORENTZIAN MODEL CALCULATIONS FOR THE DIELECTRIC
C FUNCTION, REAL AND IMAGINARY PARTS TO THE
C INDEX OF REFRACTION, AND THE CALCULATED REFLECTANCE
C-------------------------------------------------------------------------------

120 DO 150 I = 1, M
   RESON(I) = X(I)
   GAMMA(I) = X(M+I)
   PLASMA(I) = X(2*M+I)
150 CONTINUE
   EINF = X(3*M+I)
   SUM3 = 0.

200 DO 400 J = 1, NPTS
   SUM1 = 0.
   SUM2 = 0.

C-----------------------------------------------------------------------------
C COMPUTE SUMMATIONS OVER ALL OSCILLATORS AND
C CALCULATE THE REAL AND IMAGINARY PARTS OF THE
C DIELECTRIC FUNCTION, INDEX OF REFRACTION, AND
C REFLECTANCE AT EACH WAVENUMBER
C-----------------------------------------------------------------------------

300 DO 300 I = 1, M
   TOP1 = PLASMA(I) \times RESON(I) - WVNM(J) \times WVNM(J)
   BOT = (RESON(I) \times RESON(I) - WVNM(J) \times WVNM(J)) \times 2
   SUM1 = TOP1 / BOT + SUM1
   TOP2 = PLASMA(I) \times WVNM(J) \times GAMMA(I)
   SUM2 = TOP2 / BOT + SUM2
300 CONTINUE
E1(J) = EINF \times (1. + SUM1)
E2(J) = EINF \times SUM2
NNN(J) = \sqrt{((\sqrt{E1(J) \times E1(J) + E2(J) \times E2(J)}) / 2 + E1(J) / 2.)}
KKK(J) = \sqrt{((\sqrt{E1(J) \times E1(J) + E2(J) \times E2(J)}) / 2 - E1(J) / 2.)}
R(J) = 100 \times ((1. - NNN(J)) \times NNN(J) + KKK(J) \times KKK(J))
+/ ((1. + NNN(J)) \times NNN(J) + KKK(J) \times KKK(J))
SUM3 = (REFL(J) - R(J)) \times 2 + SUM3

400 CONTINUE

C-----------------------------------------------------------------------------
C CALCULATE THE STANDARD DEVIATION - THIS IS THE
C FUNCTION THAT STEPIT WILL MINIMIZE
C-----------------------------------------------------------------------------

500 CHISQ = SUM3 / NPTS
RETURN
END
SUBROUTINE OUTPUT(X,M,LORENTZ,OUTFILE)

C *************************************************************
C * OUTPUTS THE BEST FITTING OSCILLATOR PARAMETER DATA INTO A FILE NAMED BY "OUTFILE" *
C *************************************************************

C VARIABLE DECLARATION
C
CHARACTER OUTFILE
REAL NNN(5000),REFL(5000),WVNM(5000)
REAL KKK(5000),R(5000),X(20)
INTEGER M,NPTS,LORENTZ
COMMON/OUT/WVNM,REFL,R,NPTS,NNN,KKK

C OUTPUT LORENTZIAN OSCILLATOR PARAMETERS
C----------------------------------------------

IF (LORENTZ .EQ. 1) THEN
  WRITE(11,50)X(3*M+1)
  50 FORMAT(1X,'HIGH FREQUENCY DIELECTRIC CONSTANT = ',F7.4)
  WRITE(11,100)
  100 FORMAT(4X,'RESON(1/CM)',2X,'DAMP. CONST.',2X,'PLASMA FREQ. ')
    DO 130 I = 1,M
      WRITE(11,120)X(I),X(M+I),X(2*M+1)
      120 FORMAT(1X,I2,' :' ,2X,F7.2,3X,F6.2,3X,F8.1)
    CONTINUE
C-------------------------------
C OUTPUT DRUDE PARAMETERS
C----------------------------------------------
ELSE
  WRITE(11,150)
  150 FORMAT(4X,'DAMP. CONST.',2X,'PLASMA FREQ.',
      2X,'H.F.DIELECT.CONST. ')
  WRITE(11,160)X(1),X(2),X(3)
  160 FORMAT(4X,F6.2,3X,F8.1,3X,F5.2)
ENDIF
C-------------------------------
C OUTPUT N AND K AND THE REFLECTANCE AS A FUNCTION OF WAVENUMBER
C--------------------------------------------------------------------------
WRITE(11,170)
  170 FORMAT(3X,'WVNM',4X,'N',4X,'K',4X,'CALC. REFL.'
DO 200 I=1,NPTS
    WRITE(11,180)WVNM(I),NNN(I),KKK(I),R(I)
  180 FORMAT(F8.2,2X,F8.4,2X,F8.4,2X,F5.2)
CONTINUE
RETURN
END
SUBROUTINE STEPIT(FUNK)

CCOPYRIGHT 1965 -- J. P. CHANDLER, PHYSICS DEPT.,
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C
CSTEPIT 5.1 ... STEPIT WITH /JVARY/. SEPTEMBER 2, 1966.
CAVAILABLE FROM .... QUANTUM CHEMISTRY PROGRAM EXCHANGE
CI.U. CHEMISTRY DEPT.,
BLOOMINGTON INDIANA.
C

COMMON/STEPIT/NV,NTRACE,MATRIX,CHISQ,MASK(20),X(20)
+ XMAX(20),XMIN(20),DELTAX(20),DELMIN(20)
+ ERR(20,20),IWRT
DIMENSION VEC(20),TRIAL(20),XSAVE(20),CHI(20)
DIMENSION DX(20),SECOND(2,2),OLDVEC(20),SALVO(20)
DIMENSION CHIOSC(15),XOSC(20,15)

I=0
J=0
MOSQUE=4
NVMAX=20
KW=6
REWIND KW
RATIO=5.0
COLIN=0.99
NCOMP=5
ACK=2.0
SIGNIF=2.E8
HUGE=1.E38

IWRT=0
JVARY=0
40 IF(NV)290,290,50
50 NACTIV=0
DO 150 I=1,NV
 IF(MASK(I))150,60,150
60 IF(SIGNIF*ABS(DELTAX(I))-ABS(X(I)))70,70,100
70 IF(X(I))90,80,90
80 DELTAX(I)=0.01
GO TO 100
90 DELTAX(I)=0.01*X(I)
100 IF(DELMIN(I))120,110,120
110 DELMIN(I)=DELTAX(I)/SIGNIF
120 IF(XMAX(I)-XMIN(I))130,130,140
130 XMAX(I)=HUGE
XMIN(I)=-HUGE
140 NACTIV=NACTIV+1
X(I)=AMAX1(XMIN(I),AMIN1(XMAX(I),X(I)))
150 CONTINUE
COMPAR=0.0
IF(NACTIV-1)160,190,180
DO 170 J=1,NV
170 MASK(J)=0
GO TO 50
A=NACTIV
SUB=2.0/(A-1.0)
P=2.0*(1.0/SQRT(A))/(1.0-0.5**SUB)-1.0
COMPAR=AMIN1(.999,ABS((1.0-(1.0-COLIN)**SUB)*(1.0+
+P*(1.-COLIN))))
IF(NTRACE)280,200,200
WRITE (KW,210)
210 FORMAT('1ENTER SUBROUTINE STEPIT. COPYRIGHT 1965'
+,'J.P. CHANDLER, PHYSICS DEPT.,'
+,'INDIANA UNIVERSITY.'// ' INITIAL ' +
+,'VALUES....'/)
WRITE (KW,220) (MASK(J),J=1,NV)
220 FORMAT('MASK = ',10(I6,6X)/4X,10I12)
WRITE (KW,230) (X(J),J=1,NV)
230 FORMAT('X = ',10E12.4/10X,10E12.4)
WRITE (KW,240) (XMAX(J),J=1,NV)
240 FORMAT('XMAX = ',10E12.4/(10X,10E12.4))
WRITE (KW,250) (XMIN(J),J=1,NV)
250 FORMAT('XMIN = ',10E12.4/(10X,10E12.4))
WRITE (KW,260) (DELTAX(J),J=1,NV)
260 FORMAT('DELTAX = ',10E12.4/(10X,10E12.4))
WRITE (KW,270) (DELMIN(J),J=1,NV)
270 FORMAT('DELMIN = ',10E12.4/(10X,10E12.4))
CALL FUNK
NF=1
JOCK=1
IF(NTRACE)320,300,300
WRITE (KW,310) NV,NACTIV,MATRIX,NCOMP,RATIO,ACK,COLIN,
+COMPAR,CHISQ
310 FORMAT('VARIABLES','ACTIVE.',10X,
+MATRIX =',14,10X,'NCOMP =',I2//' RATIO =',F5.1,10X,
+'ACK =',F5.1,10X,'COLIN =',F6.3,10X,'COMPAR =',
+F6.3//' CHISQ =',E15.8)
IF(NV)2150,2150,330
WRITE (KW,345)
345 FORMAT(10X,'TRACE MAP OF THE MINIMIZATION PROCESS')
C
DO 370 I=1,NV
DX(I)=DELTAX(I)
VEC(I)=0.
DO 370 J=1,NV
ERR(I,J)=0.
CHIOLD=CHISQ
NOSC=0
C MAIN DO LOOP FOR CYCLING THROUGH THE VARIABLES.
C FIRST TRIAL STEP WITH EACH VARIABLE IS SEPARATE.
C---------------------------------------------------------------
380 NCIRC=0
NZIP=0
390 NACK=0
   DO 1350 I=1,NV
   OLDVEC(I)=VEC(I)
   VEC(I)=0.0
   TRIAL(I)=0.0
   IF(MASK(I)) 400,410,400
   VEC(I)=-0.0
   GO TO 1350
400 NACK=NACK+1
   SAVE=X(I)
   IF (SIGNIF*ABS(DX(I))-ABS(X(I))) 580,580,420
410 NACK=NACK+1
   SAVE=X(I)
   IF (SIGNIF*ABS(DX(I))-ABS(X(I))) 580,580,420
420 X(I)=SAVE+DX(I)
   JVARY=0
   IF(JOCK) 440,440,430
430 JOCK=0
   JVARY=I
440 NFLAG=1
   IF(X(I)-XMIN(I)) 460,450,450
450 NFLAG=NFLAG+3
   IF(X(I)-XMAX(I)) 470,470,460
460 NFLAG=NFLAG+3
   IF(X(I)-XMAX(I)) 470,470,460
470 CALL FUNK
   NF=NF+1
   JVARY=I
   CHIME=CHISQ
   IF(CHISQ-CHIOLD) 620,480,490
480 NFLAG=NFLAG+1
490 X(I)=SAVE-DX(I)
   IF(X(I)-XMIN(I)) 590,500,500
500 IF(X(I)-XMAX(I)) 510,510,590
510 CALL FUNK
   NF=NF+1
   JVARY=I
   IF(CHISQ-CHIOLD) 610,520,530
520 NFLAG=NFLAG+1
530 IF(NFLAG-3) 540,580,590
540 IF((CHISQ-CHIME)*(CHIME-2.*CHIOLD+CHISQ)) 550,590,550
550 TRIAL(I)=.5*DX(I)*(CHISQ-CHIME)/(CHIME-2.*
   + CHIOLD+CHISQ)
   VEC(I)=TRIAL(I)/ABS(DX(I))
   X(I)=SAVE+TRIAL(I)
   IWRT=1
   CALL FUNK
   IWRT=0
   NF=NF+1
   IF(CHISQ-CHIOLD) 560,570,570
560   CHIOLD=CHISQ
     JOCK=1
     GO TO 600
570   TRIAL(I)=0.0
     VEC(I)=0.0
     GO TO 590
580   VEC(I)=-0.0
590   X(I)=SAVE
600   NCIRC=NCIRC+1
     IF(NCIRC=NACTIV)690,1430,1430
610   DX(I)=-DX(I)

C-----------------------------------------------
C A LOWER VALUE HAS BEEN FOUND. HENCE THIS VARIABLE
C WILL CHANGE.
C-----------------------------------------------
620   NCIRC=0
     DEL=DX(I)
630   CHIME=CHIOLD
     CHIOLD=CHISQ
     VEC(I)=VEC(I)+DEL/ABS(DX(I))
     TRIAL(I)=TRIAL(I)+DEL
     DEL=ACK*DEL
     SAVE=X(I)
     X(I)=SAVE+DEL
     IF(X(I)-XMIN(I))680,640,640
640   IF(X(I)-XMAX(I))650,650,680
650   CALL FUNK
     NF=NF+1
     IF(CHISQ-CHIOLD)630,660,660
660   CINDER=(0.5/ACK)*(ACK**2*CHIME-(ACK**2-1.0)*CHIOLD+
           CHISQ)/(ACK*CHIME-(ACK+1.0)*CHIOLD+CHISQ)
     X(I)=SAVE+CINDER*DEL
     IWRT=1
     CALL FUNK
     IWRT=0
     NF=NF+1
     IF(CHISQ-CHIOLD)670,680,680
670   CHIOLD=CHISQ
     TRIAL(I)=TRIAL(I)+CINDER*DEL
     VEC(I)=VEC(I)+CINDER*DEL/ABS(DX(I))
     GO TO 690
680   X(I)=SAVE
690   IF(NZIP=1)1340,700,700
700   IF(ABS(VEC(I))-ACK)750,710,710
710   DX(I)=ACK*ABS(DX(I))
     VEC(I)=VEC(I)/ACK
     OLDVEC(I)=OLDVEC(I)/ACK
     DO 720 J=1,MOSQUE
720   ERR(I,J)=ERR(I,J)/ACK
     IF(NTRACE)750,730,750
730   WRITE (KW,740) I,DX(I)
740   FORMAT(' STEP SIZE',I3,' INCREASED TO ',E12.5)
SUMO=0.0
SUMV=0.0
DO 760 J=1,NV
    SUMO=SUMO+OLDVEC(J)**2
    SUMV=SUMV+VEC(J)**2
END

IF(SUMO*SUMV)1340,1340,770

SUMO=SQRT(SUMO)
SUMV=SQRT(SUMV)
COSINE=0.0
DO 780 J=1,NV
    COSINE=COSINE+(OLDVEC(J)/SUMO)* (VEC(J)/SUMV)
END

IF(NZIP-l)1340,790,800
IF(NACK-NACTIV)1340,820,820
IF(NZIP-NCOMP)820,830,830
IF(COSINE-COMPAR)1340,830,830
C
SIMON SAYS, TAKE AS MANY GIANT STEPS AS POSSIBLE...
C

IF(NTRACE)860,860,840
WRITE(KW,850)CHIOLD,(VEC(J),J=1,I)
FORMAT('CHISQ =',E15.8,'NO. OF STEPS =',10F9.2/
       (42X,10F9.2))
NGIANT=0
NTRY=0
NRETRY=0
KL=1
NOSC=NOSC+1
IF(NOSC-MOSQUE)890,890,870
NOSC=MOSQUE
DO 880 K=2,MOSQUE
    CHIOSC(K-1)=CHIOSC(K)
    DO 880 J=1,NV
        XOSC(J,K-1)=XOSC(J,K)
    END
ERR(J,K-1)=ERR(J,K)
DO 900 J=1,NV
    XOSC(J,NOSC)=X(J)
ERR(J,NOSC)=VEC(J)/SUMV
    CHIOSC(NOSC)=CHIOLD
    IF(NOSC-3)960,910,910
C
SEARCH FOR A PREVIOUS SUCCESSFUL GIANT STEP IN A
DIRECTION MORE NEARLY PARALLEL TO THE DIRECTION OF THE
PROPOSED STEP THAN WAS THE IMMEDIATELY PREVIOUS ONE.
C
COXCOM=0.0
DO 920 J=1,NV
    COXCOM=COXCOM+ERR(J,NOSC)*ERR(J,NOSC-1)
NAH=NOSC-2
NTRY=0
DO 950 K=KL,NAH
    NRETRY=NAH-K
COSINE=0.0
DO 940 J=1,NV
940  COSINE=COSINE+ERR(J,NOSC)*ERR(J,K)
   IF(COSINE-COXCOM)950,950,970
950  CONTINUE
960  CHIBAK=CHI(I)
   GO TO 1020
970  NTTRY=1
   KL=K+1
   IF(NTRACE)1000,1000,980
980  NT=NOSC-K
   WRITE (KW,990) NT
   FORMAT(/1X,'******','5X,' POSSIBLE OSCILLATION WITH
+ PERIOD ','I2,' DETECTED.')
1000  DO 1010 J=1,NV
1010  SALVO(J)=TRIAL(J)
   TRIAL(J)=TRIAL(J)+ACK
   CHIBAK=CHIOLD+(CHIOSC(K)-CHIOLD)/ACK
   C
1020  DO 1040 J=1,NV
   XSAVE(J)=X(J)
   IF(MASK(J))1120,1110,1120
1030  X(J)=AMAX1(AMIN1(XSAVE(J)+CINDER*TRIAL(J),XMAX(J))+CINDER*TRIAL(J),XMIN(J))
1040  CONTINUE
   JOCK=0
   JVARY=0
   IWRT=1
   CALL FUNK
   IWRT=0
   NF=NF+1
   IF(CHISQ-CHIOLD)1050,1080,1080
1050  CHIBAK=CHIOLD
   CHIOLD=CHISQ
   NGIANT=NGIANT+1
   IF(NTRACE)1020,1020,1060
1060  WRITE (KW,1070) CHISQ,(X(J),J=1,NV)
1070  FORMAT(' CHISQ=','E15.8/' X(I)....'/(10(1X,E12.5))
   GO TO 1020
1080  IF(NRETRY)1100,1100,1090
1090  IF(NGIANT)1150,1150,1100
1100  CINDER=(0.5/ACK)*(ACK**2*CHIBAK-(ACK**2-1.0)*CHIOLD-
   CHISQ)/(ACK*CHIBAK-(ACK+1.0)*CHIOLD+CHISQ)
   DO 1120 J=1,NV
   IF(MASK(J))1120,1110,1120
1110  X(J)=AMAX1(AMIN1(XSAVE(J)+CINDER*TRIAL(J),XMAX(J)))
+ ,XMIN(J))
1120  CONTINUE
   JOCK=0
   JVARY=0
   IWRT=1
   CALL FUNK
IWRT=0
NF=NF+1

IF(CHISQ-CHIOLD)1280,1130,1130
IF(NGIANT)1170,1140,1170
IF(NTRY)1150,1170,1150
DO 1160 J=1,NV
TRIAL(J)=SALVO(J)
1160 X(J)=XSAVE(J)
GO TO 1190

DO 1180 J=1,NV
TRIAL(J)=TRIAL(J)/ACK
1180 X(J)=XSAVE(J)
GO TO 1190

IF(NTRACE)1240,1240,1200
1200 IF(NTRACE)1240,1240,1200
WRITE (KW,1210) CHIOLD,NGIANT
1210 FORMAT('/' CHISQ =',E15.8,' AFTER',I3,' + GIANSTEMPS. ')
WRITE (KW,1220) (X(J),J=1,NV)
1220 FORMAT( ' X(I)....'/(10(1X,E12.5)))
WRITE (KW,1230)
1230 FORMAT('/
1240 IF(NGIANT)1250,1250,1310
1250 IF(NRETRY)1260,1260,930
1260 IF(NTRY)1270,1330,1270
1270 NTRY=0
GO TO 960

CHIOLD=CHISQ
JOCK=1

IF(NTRACE)1310,1310,1290
1390 IF(NTRACE)1420,1390,1420
WRITE (KW,1220) (X(J),J=1,NV)
1420 IF(NTRACE)1420,1420,1400
WRITE (KW,1410)

C-------------------------------------------------------------
C ANOTHER CYCLE THROUGH THE VARIABLES HAS BEEN COMPLETED.
C PRINT ANOTHER LINE OF TRACES.
C-------------------------------------------------------------

IF(NTRACE)1370,1370,1360
1360 WRITE(KW,850) CHIOLD,(VEC(J),J=1,NV)
1370 CONTINUE
1380 IF(NZIP)1420,1390,1420
1390 IF(NTRACE)1420,1420,1400
1400 WRITE (KW,1220) (X(J),J=1,NV)
WRITE (KW,1410)
91

1410 FORMAT(' ', )
1420 NZIP=NZIP+1
GO TO 390

C-----------------------------------------------
C A MINIMUM HAS BEEN FOUND. PRINT THE REMAINING TRACES.
C-----------------------------------------------
1430 IF(NTRACE)1450,1450,1440
1440 WRITE (KW,850) CHIOLD,(VEC(J),J=1,I)
1450 IF(NTRACE)1470,1470,1460
1460 WRITE (KW,1220) (X(J),J=1,NV)
1470 CONTINUE

C-----------------------------------------------
C DECREASE THE SIZE OF THE STEPS FOR ALL VARIABLES.
C-----------------------------------------------
1480 NOSC=0
1500 NGATE=1
1520 DO 1520 J=1,NV
1530 IF(MASK(J))1520,1490,1520
1490 IF (AMAX1(VEC(J),SIGN(1.0,VEC(J)))) 1500,1520,1500
1500 IF (ABS(DX(J))-ABS(DELMIN(J))) 1520,1520,1510
1510 NGATE=0
1520 DX(J)=DX(J)/RATIO
1530 IF(NGATE)1530,1530,1600
1540 WRITE (KW,1550) (DX(J),J=1,NV)
1550 FORMAT(60(1X,' '/ STEP SIZES REDUCED TO ....'// + (10(1X,E12.5)))
1560 WRITE (KW,1560)
1570 GO TO 380
1580 WRITE (KW,1590) (DX(J),J=1,NV)
1590 FORMAT(/' SUBROUTINE STEPIT TERMINATED BY + OPERATOR.'// ' CURRENT STEP SIZE + VALUES....'//(10(1X,E12.5)))
1600 CHISQ=CHIOLD
1610 IF(NTRACE)1630,1610,1610
1610 WRITE (KW,1620) NF
1620 FORMAT(/'1X,I5,' FUNCTION COMPUTATIONS ' )
1630 CONTINUE
1640 IF (IABS(MATRIX-100)-50) 1650,1650,2190
1650 IF(NACTIV-NV)2190,1660,2190

C-----------------------------------------------
C COMPUTE THE STANDARD ERRORS AND THE CORRELATIONS.
C-----------------------------------------------
1660 FAC=RATIO**((MATRIX-100)
1670 DO 1680 I=1,NV
1680 DX(I)=ABS(FAC*DX(I))
1690 XSAVE(I)=X(I)
1700 JVARY=0
1710 DOE 1670 J=1,2
1720 X(I)=XSAVE(I)+DX(I)
CALL FUNK
NF=NF+1
JVARY=I
SECOND(1,J)=CHISQ
DX(I)=-DX(I)
X(I)=XSAVE(I)
ERR(I,I)=(SECOND(1,1)-2.0*CHIOLD+SECOND(1,2))/DX(I)**2
DO 1710 I=2,NV
IM=I-1
DO 1710 J=1,IM
X(I)=XSAVE(I)+DX(I)
JVARY=0
DO 1690 L=1,2
X(J)=XSAVE(J)+DX(J)
CALL FUNK
NF=NF+1
JVARY=J
SECOND(K,L)=CHISQ
X(J)=XSAVE(J)
DX(J)=-DX(J)
X(I)=XSAVE(I)
DO 1700 K=1,2
X(I)=XSAVE(I)+DX(I)
JVARY=0
DO 1690 L=1,2
X(J)=XSAVE(J)+DX(J)
CALL FUNK
NF=NF+1
JVARY=J
SECOND(K,L)=CHISQ
X(J)=XSAVE(J)
DX(J)=-DX(J)
X(I)=XSAVE(I)
ERR(I,J)=0.25*(SECOND(1,1)-SECOND(1,2)-SECOND(2,1)+
+SECOND(2,2))/ABS(DX(I)*DX(J))
DO 1710 J=1,I
IF(ERR(I,J))1780,1790,1780
CONTINUE
GO TO 1810
1790 WRITE (KW,1800)
FORMAT('////// THE ABOVE MATRIX CONTAINS ONE OR MORE
+ ZEROES. A LARGER VALUE OF (MATRIX) SHOULD BE
+ TRIED, TO SEE IF THEY ARE LEGITIMATE. ')
C---------------------------------------------
C INVERT THE MATRIX USING SYMINV2
C (COMM. OF THE A.C.M. 6, P. 67).
C---------------------------------------------
1810 DET=1.0
DETLOG=0.
DO 1820 J=1,NV
1820  SALVO(J)=1.0
1830  DO 1970  I=1,NV
1840  BIGAJJ=0.0
1850  DO 1850  J=1,NV
1860  IF (SALVO(J))1830,1850,1830
1870  IF (ABS(ERR(J,J))—BIGAJJ) 1850,1850,1840
1880  BIGAJJ=ABS(ERR(J,J))
1890  K=J
1900  CONTINUE
1910  IF(BIGAJJ)1870,1860,1870
1920  DET=0.0
1930  GO TO 1980
1940  SALVO(K)=0.0
1950  DET=DET*ERR(K,K)
1960  DETLOG=DETLOG+ALOG(ABS(ERR(K,K)))/2.303
1970  TRIAL(K)=1.0/ERR(K,K)
1980  ERR(K,K)=0.0
1990  XSAVE(K)=1.0
2000  M=K-1
2010  IF(M)1910,1910,1880
2020  DO 1900  J=1,M
2030  XSAVE(J)=ERR(K,J)
2040  TRIAL(J)=ERR(K,J)*TRIAL(K)
2050  IF(SALVO(J))1860,1900,1890
2060  TRIAL(J)=-TRIAL(J)
2070  ERR(K,J)=0.0
2080  M=K+1
2090  IF(M-NV)1920,1920,1960
2100  DO 1950  J=M,NV
2110  XSAVE(J)=ERR(J,K)
2120  IF(SALVO(J))1860,1930,1940
2130  XSAVE(J)=-XSAVE(J)
2140  TRIAL(J)=-ERR(J,K)*TRIAL(K)
2150  ERR(J,K)=0.0
2160  DO 1970  J=1,NV
2170  DO 1970  K=J,NV
2180  ERR(K,J)=ERR(K,J)+XSAVE(J)*TRIAL(K)
2190  IF(DET)2000,1980,2020
2200  WRITE (KW,1990)
2210  FORMAT(///' ERROR MATRIX IS SINGULAR. (MATRIX) SHOULD + PROBABLY BE INCREASED. '////)
2220  GO TO 2150
2230  WRITE (KW,2010)
2240  FORMAT(///' ERROR MATRIX IS NEGATIVE DEFINITE. + (MATRIX) SHOULD PROBABLY BE DECREASED. ')
2250  IF(NTRACE)2050,2030,2030
2260  WRITE (KW,2040) DET,DETLOG
2270  FORMAT(///' DETERMINANT OF ABOVE MATRIX = ' + ',E12.5,10X,'LOG10F(DET) = ',E12.5)
2280  IF(NTRACE)2050,2030,2030
2290  WRITE (KW,2050) DET,DETLOG
2300  FORMAT(///' DETERMINANT OF ABOVE MATRIX = ' + ',E12.5,10X,'LOG10F(DET) = ',E12.5)
ERR(J,I) = ERR(I,J)
IF(ERR(I,I)) 2070, 2070, 2090
WRITE (KW,2080) ERR(I,I)
FORMAT( ///' NEGATIVE OR ZERO MEAN SQUARE ERROR
+ ENCLOSED...',3X,E15.8/' (MATRIX)
+ SHOULD PROBABLY BE DECREASED.'///)
XSAVE(I) = SIGN (SQRT (ABS (ERR(I,I))),ERR(I,I))
WRITE (KW,2160) 2160, 2100, 2100
WRITE (KW,2210) (XSAVE(J),J=1,NV)
WRITE (KW,2120)
WRITE (KW,2110)
WRITE (KW,1740) (TRIAL(J),J=1,IM)
WRITE (KW,1620) NF
C IF((XSAVE(I) * XSAVE(J)) .NE. 0.) GO TO 2190
WRITE (KW,2180)
WRITE (KW,2220) CHISQ
2190 JVARY=0
IWRT=1
CALL FUNK
IWRT=0
WRITE (KW,2210) (X(J),J=1,NV)
WRITE (KW,2220) CHISQ
RETURN
END
Bibliography


[27] J. R. Jasperse et. al., 540, [12]


[29] Maradudin et. al., 894, [14]

