DETERMINATION OF THE OPTICAL CONSTANTS OF HIGHLY ABSORBING MATERIALS

FEB 80 K D MOELLER, V P TOMASELLI

DAAK10-77-C-0121

ARCSL-CR-80024

END

6-80
DETERMINATION OF THE OPTICAL CONSTANTS OF HIGHLY ABSORBING MATERIALS IN THE INFRARED REGION

Final Report
1 May 1978 - 30 June 1979

by
K. D. Moeller
V. P. Tomaselli

February 1980

FAIRLEIGH DICKINSON UNIVERSITY
Teaneck, New Jersey 07666

Contract DAAK10-77-C-0121

Approved for public release; distribution unlimited.
The behavior of electromagnetic waves in ideal lossless dielectrics is used to generate expressions for the reflection coefficients. Strongly absorbing dielectrics are considered and methods for evaluating their optical constants are presented. The effect of polarized infrared radiation on measured reflected intensities is detailed. Anisotropic materials and their particular measurement problems are discussed. Application to powder spectroscopy of highly absorbing materials is made. A summary of experimental results is presented.
PREFACE

This report describes the effort in the infrared spectral region. It covers the period 1 May 1978 through 30 June 1979 and was performed under Contract DAAK10-77-C-0121 by the Physics Department of the Fairleigh Dickinson University in Teaneck, New Jersey. The research was conducted jointly by K. D. Moeller and V. P. Tomaselli.

The research was sponsored by the Army Smoke Research Program, Chemical Systems Laboratory, Aberdeen Proving Ground, Maryland 21010.

The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial hardware or software. This report may not be cited for purposes of advertisement.

Reproduction of this document in whole or in part is prohibited except with permission of the Commander/Director, Chemical Systems Laboratory, ATTN: DRDAR-CLJ-R, Aberdeen Proving Ground, Maryland 21010. However, Defense Technical Information Center and the National Technical Information Service are authorized to reproduce the document for United States Government purposes.
## CONTENTS

1. INTRODUCTION ........................................ 7
2. SOLUTION TO THE WAVE EQUATION FOR A LOSSLESS DIELECTRIC ................. 9
3. FRESNEL'S FORMULAE ................................... 11
   3.1 \( \vec{E} \) Perpendicular to Plane of Incidence .................. 11
   3.2 \( \vec{E} \) Parallel to Plane of Incidence ........................ 14
4. DETERMINATION OF REFRACTIVE INDEX .................................. 14
5. DISPERSION MODEL OF A DIELECTRIC .................................. 15
6. STRONGLY ABSORBING DIELECTRIC MEDIA .............................. 17
   6.2 Ellipsometry ........................................... 22
7. EFFECT OF POLARIZATION PROPERTIES ON MEASURED REFLECTANCES .......... 24
   7.1 Unpolarized Light. Two Angles of Incidence ...................... 24
   7.2 One Component of Polarized Light. Two Angles of Incidence ........ 27
   7.3 Both Components of Polarized Light. One Angle of Incidence ........ 28
   7.4 Ratio of Polarized Light Components. Two Angles of Incidence; No Standard .......... 28
   7.5 Sample in Sample Beam, Reference in Reference Beam. Unpolarized Light .............. 29
   7.6 Sample in Sample Beam, Reference in Reference Beam. One Component of Polarized Light .. 29
   7.7 Samples in Both Beams. Polarizers in Both Beams ................. 29
8. ANISOTROPIC CRYSTALS ........................................ 30
   8.1 Measurements on Anisotropic Crystals ......................... 31
CONTENTS (Contd)

9. APPLICATIONS TO POWDER SPECTROSCOPY ........ 31
   9.1 Highly Absorbing Materials .................. 33
10. EXPERIMENTAL RESULTS ........................ 34
   10.1 Quantitative Absorption Measurements on Tri-n-Butyl Phosphate ........... 34
   10.2 Infrared Reflection Methods for Powders .... 34

DISTRIBUTION LIST ................................. 37

LIST OF FIGURES

Figure

   1 Fresnel Formula Figure ...................... 11
   2 Permittivity and Resonance Frequency Relationships .......... 16
   3 Intersection of the Three Isoreflectance Curves .. 21
   4 I Values at Different Angles ................ 22
   5 Schematic Diagram of Optical Path of Spectrophotometer with Reflection Unit, Showing Polarization Components ........ 25
1. INTRODUCTION.

The description of the interaction of light with matter, as formulated from Maxwell's electromagnetic theory uses microscopic parameters to characterize the specific properties of a material involved in the process. These parameters (notably the dielectric constant) are related to the optical constants, the refractive index $n$ and the absorption coefficient $k$ of the material in question. In a simplified picture, the index $n$ characterizes the refraction properties of the material, since it is the ratio of the velocity of the wave inside to that outside of the material, and the absorption coefficient $k$ describes the attenuation of the wave as it penetrates the medium.

The optical constants can be obtained by an analysis of reflection and transmission data. One determines $n$ and $k$ using polarized light measurements, since the reflection and transmission properties of the material are, in general, different for light polarized parallel to or perpendicular to the plane of incidence. For crystals with optical axes, the optical constants depend upon the orientation of the surface relative to plane of incidence. This latter effect is lost in polycrystalline materials where only average optical constants can be obtained. Reducing the size of the domains of the polycrystalline sample results, eventually, in an amorphous material where the long range order of the atoms has disappeared and only short range order of the molecular type prevails.

Powders have the nonoriented properties of the polycrystalline materials but, in addition, the powder particles are now embedded in a dielectric which might be air, KBr, other materials, or, in the limiting case, a vacuum. The discontinuity of the optical constants at the surface of the
powder particles introduces alterations in the transmitted or reflected light. One effect is that light is scattered out of the direction of the reflected or transmitted light beams. This scattered light is unavailable for analysis; its absence introduces an error in the determination of the optical constants. This effect is particularly troublesome if the absolute values of reflected and transmitted intensities are required. Nevertheless, using the pellet method, in which the powder is embedded in KBr and the optical constants are obtained from transmission and reflection data, surprisingly good results have been obtained. In this work, the "lost" light is simply disregarded in determining the optical constants. Observations of the transmitted and reflected light from powder samples have also shown, in some instances, new spectral features when compared to the bulk materials. Careful investigation has shown that these features depend on the size, shape and nature of the dielectric in which the powder particles are embedded. The most interesting change occurs with the optically active transverse mode frequency in, for example, alkali halide crystals. The frequency of this mode shifts to higher values if the size of the crystallite is reduced.2

Theoretically, one can account for these phenomena using the phonon concept. One considers finite atomic chains but omits the application of cyclic boundary conditions used in large crystals. An alternate approach, the continuum theory, first formulated by Frohlich3, considers

1F. E. Volz, Appl. Optics 12, 564 (1973)
the polarizations in the mixed medium. The effect of particle shape was considered for spherical and cylindrical geometries. The latter can be extended to the case of fibers. The general approach to dielectric constant studies also provides the possibility of studying metal particles embedded, either in their own oxide layers, or in a dielectric matrix. Before turning to the more detailed discussion of powder samples we will discuss the determination of optical constants of amorphous bulk materials.

2. SOLUTION TO THE WAVE EQUATION FOR A LOSSLESS DIELECTRIC

We start with Maxwell's equations written as

\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \]  

\[ \nabla \times \mathbf{B} = \mu_0 \frac{\partial \mathbf{D}}{\partial t} \]  

\[ \nabla \cdot \mathbf{B} = \rho \]  

\[ \nabla \cdot \mathbf{D} = 0 \]

where \( \mathbf{E} \) is the electric field vector, \( \mathbf{D} \) is the displacement vector defined by \( \mathbf{D} = \varepsilon \mathbf{E} \) where \( \varepsilon \) is the permittivity, \( \mathbf{B} \) is the magnetic induction vector, \( \mu_0 \) the permeability of free space and \( \rho \) is the charge density (zero in our case).

From Eqn.(1) and Eqn.(2) we obtain

\[ \nabla \times \nabla \times \mathbf{E} = -\nabla \times \mathbf{B} = -\mu_0 \mathbf{D} \]

\[ \nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\mu_0 \mathbf{D} \]

\[ \nabla^2 \mathbf{E} = \mu_0 \varepsilon \mathbf{E} \]  

This is the wave equation for the dielectric medium with permittivity \( \varepsilon \). It reduces to the vacuum equation for \( \varepsilon + \varepsilon_0 \).

As solutions to the wave equation we will consider only plane waves propagating in the x direction.
\[ E = A \, e^{i(Kx - \omega t)} \] (6)

where \( K = \frac{2\pi}{\lambda} \) is the wave vector and \( \omega = 2\pi v = 2\pi c/\lambda \) is the angular frequency. Insertion of Eqn. (6) into the wave equation gives

\[-K^2 = -\mu_0 \varepsilon \omega^2 \] (7)

The wave equation for any disturbance \( y(x,t) \) can be written as

\[ \frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2} \] (8)

where \( v \) is the velocity of the wave. Eqn. (5) with \( E(x,t) \) has the form of Eqn. (8). Consequently, we can take

\[ \mu_0 \varepsilon = 1/v^2 \]

and, using the definition of the refractive index, \( n = c/v \) get

\[ n^2 = \frac{c^2 \mu_0 \varepsilon}{\varepsilon_0} \] (9)

The permittivity \( \varepsilon \) can be expressed as the product of the dielectric constant \( \kappa \) and the permittivity of free space \( \varepsilon_0 \),

\[ \varepsilon = \kappa \varepsilon_0 \] (10)

Introducing Eqn. (10) into Eqn. (9) gives

\[ n^2 = \frac{c^2 \mu_0 \varepsilon_0 \kappa}{\varepsilon_0} \]

and, since \( \mu_0 \varepsilon_0 = 1/c^2 \), we have finally

\[ n = \sqrt{\kappa} \] (11)

The refractive index, for a non-magnetic material \((\mu = \mu_0)\), is equal to the square root of the dielectric constant.

Another useful relation is

\[ \frac{K^2}{\omega^2} = \frac{n^2}{c^2} = \mu_0 \varepsilon \] (12)
3. FRESNEL'S FORMULAE
To obtain Fresnel's formulae, we consider the behavior of the electric and magnetic field vectors at the interface separating the media with refractive indices \( n_1 \) and \( n_2 \). The boundary conditions require that the tangential components of both \( \vec{E} \) and \( \vec{B} \) are continuous at the interface. We will adopt the notation of Fig. 1.

![Figure 1. Fresnel Formula Figure](image)

3.1 \( \hat{E} \) Perpendicular to Plane of Incidence
We represent the incident, reflected, and transmitted plane waves by

\[
E_\perp = A \ e^{i(K_1 x - \omega t)} \quad (13a)
\]
\[
E'_\perp = A' \ e^{i(K_1 x' - \omega t)} \quad (13b)
\]
\[
E''_\perp = A'' \ e^{i(K_2 x'' - \omega t)} \quad (13c)
\]

where \( K_1 \) and \( K_2 \) are, respectively, the wave vectors outside and inside the dielectric. Note that the angular frequency \( \omega \) is the same for both media. From the boundary condition on \( \hat{E} \) we obtain

\[
\vec{E} + \vec{E}' = \vec{E}'' \quad (14)
\]

Since the phase factors are equal at the boundary, we have
The result
\[ A + A' = A'' \] (15)

The first Maxwell equation relates the \( \hat{E} \) and \( \hat{B} \) vector as follows:
\[ \nabla \times \hat{E} = -\frac{\partial}{\partial t} (B_x \hat{i} + B_y \hat{j} + B_z \hat{k}) \] (16)

From the \( y \) and \( z \) components of the electric field
\[ E_y = A e^{i(Kx-\omega t)} \] (17a)
\[ E_z = A e^{i(Kx-\omega t)} \] (17b)

which are also propagating in the \( x \) direction, we get, using Eqn. (16)
\[ \frac{\partial B_z}{\partial t} = -\frac{\partial E_y}{\partial x} \] and \[ \frac{\partial B_y}{\partial t} = \frac{\partial E_z}{\partial x} \] (18)

Integration results in
\[ B_z = -iK \int E_y \, dt = -iKA e^{iKx} \int e^{-i\omega t} \, dt \]
\[ = -\frac{iK}{\omega} A e^{i(Kx-\omega t)} = \frac{K}{\omega} E_y = \frac{n}{c} E_y \] (19)

and correspondingly
\[ B_y = -\frac{n}{c} E_z \] (20)

where \( n \) is either \( n_1 \) or \( n_2 \).

The \( B \) vector accompanying the \( \hat{E} \), \( \hat{E}' \) and \( \hat{E}'' \) vectors in the above figure are in the plane of the paper and have, at the boundary, the components
\[-B_\parallel \cos \theta, B'_\parallel \cos \theta', B''_\parallel \cos \theta''\]

Therefore the boundary condition on \( \hat{B} \) can be written as
\[-B_\parallel \cos \theta + B'_\parallel \cos \theta' = -B''_\parallel \cos \theta'' \] (21)
Using the relation between the $\mathbf{B}$ and $\mathbf{E}$ and the fact that the phase has to be the same for all terms on the boundary we get

\[-n_1 A \cos \theta + n_1 A' \cos \theta' = -n_2 A'' \cos \theta'' \]

Eqns. (15) and (22) can be written as

\[1 + \frac{A'}{A} = \frac{A''}{A} \quad (23)\]

and

\[1 - \frac{A'}{A} = \alpha \frac{A''}{A} \quad (24)\]

using

\[\alpha = \frac{n_2 \cos \theta''}{n_1 \cos \theta} \quad (25)\]

We now introduce the amplitude reflection coefficient

\[r_{E_\perp} = \frac{A'}{A} \quad (26)\]

and the amplitude transmission coefficient

\[t_{E_\perp} = \frac{A''}{A} \quad (27)\]

Eqns. (23) and (24) can now be written as

\[r_{E_\perp} - t_{E_\perp} = -1 \quad (28)\]

\[r_{E_\perp} + \alpha t_{E_\perp} = 1 \quad (29)\]

which are to be solved for $r_{E_\perp}$ and $t_{E_\perp}$. The result is

\[r_{E_\perp} = \frac{n_1 \cos \theta - n_2 \cos \theta''}{n_2 \cos \theta + n_2 \cos \theta''} \quad (30)\]

\[t_{E_\perp} = \frac{2n_1 \cos \theta}{n_1 \cos \theta + n_2 \cos \theta''} \quad (31)\]
3.2 Parallel to Plane of Incidence

In a similar way, the amplitude reflection coefficient $r_{E\parallel}$ and amplitude transmission coefficient $t_{E\parallel}$ for the case where the $\hat{E}$ is in the plane of incidence, are given by

$$r_{E\parallel} = \frac{n_1 \cos \theta'' - n_2 \cos \theta}{n_1 \cos \theta'' + n_2 \cos \theta}$$  \hspace{0.5cm} (32)

$$t_{E\parallel} = \frac{2n_1 \cos \theta}{n_1 \cos \theta'' + n_2 \cos \theta}$$  \hspace{0.5cm} (33)

4. Determination of Refractive Index

We consider an air-dielectric interface and take $n_1 = 1$ and $n_2 = n$. At normal incidence we have the amplitude ratios.

$$r = \frac{l - n}{1 + n}$$  \hspace{0.5cm} (34)

$$t = \frac{2n}{1 + n}$$  \hspace{0.5cm} (35)

However, experimentally, we measure, for example, the ratio

$$\frac{\text{reflected power flux}}{\text{incident power flux}} = R = \text{Reflectance}$$

Using Poynting's vector, the reflected power flux is given by

$$R = r^2 = \left(\frac{A'}{A}\right)^2$$  \hspace{0.5cm} (36)

Similarly, one obtains for the transmitted power flux

$$T = nt^2 = \frac{n_2}{n_1} \frac{\cos \theta''}{\cos \theta} \left(\frac{A''}{A}\right)^2$$  \hspace{0.5cm} (37)

At normal incidence, we can obtain the refractive index from one measurement of $R$, that is Eqns. (34) and (36) can be combined to give

$$n = \frac{1 - R}{1 + R} = \frac{1 - \sqrt{R}}{1 + \sqrt{R}}$$  \hspace{0.5cm} (38)
For non-normal incidence we can write the reflection coefficients as

\[
\begin{align*}
    r_E^\perp &= \frac{\cos \theta - n \sqrt{1 - (\sin \theta/n)^2}}{\cos \theta + n \sqrt{1 - (\sin \theta/n)^2}} \\
    r_E^\parallel &= \frac{-n \cos \theta + \sqrt{1 - (\sin \theta/n)^2}}{n \cos + \sqrt{1 - (\sin \theta/n)^2}}
\end{align*}
\]

(39) and

(40)

using the law of refraction. One sees again that a single measurement is sufficient to determine \( n \) if the angle of incidence is known and polarized light is used.

5. DISPERSION MODEL OF A DIELECTRIC

In another report we investigated the relationship between the refractive index and the parameters of an oscillator model having resonance frequencies \( \omega_{0i} \), mass \( m_i \), charge \( e \) and damping constant \( \gamma \). If the lossless case is considered, that is no damping, the permittivity is found to be

\[
\frac{\varepsilon(\omega)}{\varepsilon_0} = (n^*)^2 = 1 + \sum_i \frac{N_i e_i^2}{\varepsilon_0 m_i (\omega_{0i}^2 - \omega^2)} = 1 + \sum_i \frac{\omega_{pi}^2}{\omega_{0i}^2 - \omega^2}
\]

(41)

where \( \omega_{pi} \) is the plasma frequency given by \( \omega_{pi}^2 = N_i e_i^2 / m_i \varepsilon_0 \).

For a real dielectric, there is always a polarization effect from the surrounding medium. At a particular point, the so-called Lorentz contribution to the polarization must be taken into account. This results in a shift of the resonance frequencies to new values represented by \( \bar{\omega}_{0i} \).

Let us consider a system having only two resonance frequencies \( \bar{\omega}_{01} \) and \( \bar{\omega}_{02} \). Take \( \bar{\omega}_{01} \) in the infrared region and \( \bar{\omega}_{02} \) at a much higher frequency. We then have

\[
\frac{\varepsilon(\omega)}{\varepsilon_0} = 1 + \frac{\omega_{p1}^2}{\omega_{01}^2 - \omega^2} + \frac{\omega_{p2}^2}{\omega_{02}^2 - \omega^2}
\]

(42)
The last term in the above equation represents the high frequency electronic polarization. Its contribution to $\varepsilon$ in the infrared is constant. If we define $\varepsilon(\infty) = \varepsilon_\infty$ we can write

$$\frac{\varepsilon(\infty)}{\varepsilon_0} = \frac{\varepsilon_\infty}{\varepsilon_0} = 1 + \frac{\omega p_l^2}{\omega_0^2 - \omega^2}$$

then Eqn.(42) becomes

$$\frac{\varepsilon(\omega)}{\varepsilon_0} = \frac{\varepsilon_\infty}{\varepsilon_0} + \frac{\omega p_l^2}{\omega_0^2 - \omega^2}$$

We can also introduce the static permittivity $\varepsilon(\infty) = \varepsilon_0$ and get

$$\frac{\varepsilon(\omega) - \varepsilon(\infty)}{\varepsilon_0} = \frac{\omega p_l^2}{\omega_0^2}$$

Substituting $\omega p_l^2$ from this expression into Eqn.(44) gives

$$\varepsilon(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \frac{\omega_0^2}{\omega_0^2 - \omega^2}$$

From this expression we see that if we go from the infrared resonant frequency to lower frequencies, the permittivity approaches the static value. If we go to higher frequencies the permittivity approaches the electronic value. The refractive index and permittivity are connected by $n^2 = \varepsilon$. Therefore, the physical origin of $n$ at frequencies above and below the infrared region can be attributed to these two factors.

Figure 2. Permittivity and Resonance Frequency Relationships
6. STRONGLY ABSORBING DIELECTRIC MEDIA

We now want to consider strongly absorbing media, which are of prime interest. We begin with Maxwell's equations for the general case of dielectric and conductive medium.

\[ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (47) \]
\[ \nabla \times \vec{B} = \varepsilon_0 \mu_0 \frac{\partial \vec{E}}{\partial t} + \mu_0 \frac{\partial \vec{P}}{\partial t} + \mu_0 \vec{J} \quad (48) \]
\[ \nabla \cdot \vec{B} = \rho \quad (49) \]
\[ \nabla \cdot \vec{D} = 0 \quad (50) \]

In addition to the previously defined quantities, we now have the polarization vector \( \vec{P} = \chi^* \varepsilon_0 \vec{E} \), where \( \chi^* \) is the complex electric susceptibility, and the current density vector \( \vec{J} = \sigma \vec{E} \), where \( \sigma \) is the conductivity. A manipulation of Maxwell's equations, very similar to that done for the lossless dielectric case, results in the following wave equation

\[ \nabla^2 \vec{E} = \mu_0 \varepsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} + \mu_0 \frac{\partial^2 \vec{P}}{\partial t^2} + \mu_0 \frac{\partial \vec{J}}{\partial t} \quad (51) \]

If the dielectric properties of the material are represented by one-dimensional oscillator model with losses, we can write \( \vec{P} = \varepsilon_0 \chi^* \varepsilon_0 \vec{E} = \varepsilon_0 \frac{\partial^2 \vec{E}}{(\omega_0^2 - \omega^2 - i\gamma \omega)}. \) If the conductive properties of the medium are represented by an oscillator model without restoring forces, we can write

\[ \vec{J} = \frac{\sigma}{1 - i\omega T} \varepsilon_0 \vec{E} = \sigma \vec{E} \quad (52) \]

The wave equation may then be written as

\[ \frac{\partial^2 \vec{E}}{\partial x^2} = \mu_0 \varepsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} + \mu_0 \varepsilon_0 \chi^* \frac{\partial^2 \vec{E}}{\partial t^2} + \mu_0 \sigma \frac{\partial \vec{E}}{\partial t} \quad (53) \]
Introduction of a trial solution $E = E_0 e^{i(Kx - \omega t)}$ into Eqn. (53) gives

$$K^2 = \mu_0 \varepsilon_0 \omega^2 + \mu_0 \varepsilon_0 \chi^* \omega^2 - i\omega\mu_0\sigma^*$$
or

$$\frac{K^2}{\omega^2} = \mu_0 \varepsilon_0 + \mu_0 \varepsilon_0 \chi^* - i\mu_0\sigma^*/\omega = \mu_0 \varepsilon^*$$  \hspace{1cm} (54)

Comparing Eqn. (54) with its lossless analogue, Eqn. (12), we see that for this case, we have an effective complex permittivity $\varepsilon^*$ instead of the real permittivity $\varepsilon$. In Eqn. (12), for the lossless case we saw that the refractive index and permittivity are related by $n = \sqrt{\varepsilon/\varepsilon_0}$. A complex $\varepsilon$ implies a complex $n$, thus $n^* = \sqrt{\varepsilon^*/\varepsilon_0}$ now describes the optical properties of the material. If we represent the complex refractive index by $n^* = n + ik$, we see that the losses are associated with the imaginary part $k$, called the extinction coefficient.

The formal substitution of $\varepsilon^*$ for $\varepsilon$ and $n^*$ for $n$ does not change the formal derivation of the law of refraction and Fresnel's formulae, the law of refraction becomes

$$\sin \theta = n^* \sin \theta''$$  \hspace{1cm} (55)

and the reflection coefficients, obtained from Fresnel's formulae are, for $n_1 = 1$,

$$R_{E\perp} = \frac{\cos \theta - n_2^* \cos \theta''}{\cos \theta + n_2^* \cos \theta''}$$  \hspace{1cm} (56)$$

and

$$R_{E\parallel} = \frac{\cos \theta'' - n_2^* \cos \theta}{\cos \theta'' + n_2^* \cos \theta}$$ \hspace{1cm} (57)

There are three points to be mentioned here:

1) Both $R_{E\perp}$ and $R_{E\parallel}$ are complex and can be written as a product of an amplitude factor and a phase factor as
The angle $\alpha$ is the phase shift introduced after reflection.

2) There is no Brewster angle for $r_{E_{||}}$. We can see this by introducing $n^*_2 = n_2 + ik_2$ into the Brewster angle relation $\tan \theta_B = n^*_2$. Then $\tan \theta_B = n_2 + ik_2$. Since $\theta_B$ is real, no solution exists.

3) There is an attenuated wave in the absorbing medium. Considering only normal incidence, we have

$$E = E_0 e^{i(K^*x - \omega t)} = E_0 e^{i(\omega/c)(n+ik)x - \omega t)}$$

$$E = (e^{-\omega kx}) E_0 e^{i(\omega/c)n x - \omega t})$$

where the first factor on the right side is the attenuation factor and the second represents a travelling wave. The amplitude of the wave is attenuated to a value of $1/e$ after travelling a distance

$$d' = \frac{1}{\omega K} = \frac{c}{\omega K} = \frac{c}{2\pi c K / \lambda} = \frac{\lambda}{2\pi K}$$

into the medium. Since the intensity is proportional to $|E|^2$, the power flux decreases to $1/e$ of its value at the surface in a distance $d = \lambda/4\pi k$. We see that the optical constant $k$ can be determined through attenuation measurements.

6.1 Evaluation of Optical Constants of Highly Absorbing Materials. Graphical Methods

The reflection coefficients, as given in Eqns.(56) and (57), can be expressed as functions of the complex refractive index $n^*$ and the angle of incidence $\theta$ if Snell's law Eqn.
(55), is used to eliminate \( \theta \). If we calculate the square of the absolute value of the reflection coefficients, we get

\[
|r_{E\perp}|^2 = I_{E\perp} = \frac{(a - \cos b)^2 + b^2}{(a + \cos b)^2 + b^2} \tag{58}
\]

and

\[
|r_{E\parallel}|^2 = I_{E\parallel} = \frac{(a - \sin \theta \tan \theta)^2 + b^2}{(a + \sin \theta \tan \theta)^2 + b^2} \tag{59}
\]

where

\[
a^2 = \frac{1}{2} \left\{ \left( (n^2 - k^2 - \sin^2 \theta) + 4n^2k^2 \right)^{\frac{3}{2}} + (n^2 - k^2 - \sin^2 \theta) \right\}
\]

\[
b^2 = \frac{1}{2} \left\{ \left( (n^2 - k^2 - \sin^2 \theta) + 4n^2k^2 \right)^{\frac{3}{2}} - (n^2 - k^2 - \sin^2 \theta) \right\}
\]

These complicated formulae relate the intensity ratios of reflected light, for parallel and perpendicular components, to the angle of incidence \( \theta \) and the optical constants. To determine the optical constants, one needs the inverse relationship, that is, \( n \) and \( k \) as a function of the ratios of the reflected light and the angle of incidence. Unfortunately, the above equations can not be inverted analytically. However, J. Vasecek has calculated "Tables of Determination of Optical Constants from the Intensities of Reflected Light", (Czechoslovakian Academy of Science, Prague, 1963). In these tables, the following measurable quantities are tabulated as a function of \( \theta \), \( n \) and \( k \):

\[
I_{E\perp}, I_{E\parallel}, I = \frac{I_{E\perp} + I_{E\parallel}}{2}, \text{ and } I_\rho = \frac{I_{E\parallel}}{I_{E\perp}}.
\]

Numerical values are given for \( 0 \leq \theta \leq 80^\circ \), in increments of 5°. Values of \( n \) and \( k \) are given in increments of 0.2 for \( 0.2 \leq n \leq 7.0 \) and \( 0.0 \leq k \leq 6.0 \). A graphical analysis of the reflection data using Vasecek's tables can be used to
give values of $n$ and $k$ as follows: For a given angle of incidence one plots on an $n$-$k$ curve, the locus of all points having the same measured reflected intensity $I_{E_\perp}$, $I_{E_{||}}$, $I$ or $I_\rho$. This procedure is repeated for a second, and preferably a third, angle of incidence. The intersection of the three isoreflectance curves gives the optical constants of the material, see Fig. 3. Normally the curves do not intersect at a single point, but define a triangularly shaped region which, in effect, is an indication of the inherent error in the method. For such cases, the 'center of gravity' of the triangle is used to extract the values of $n$ and $k$ for the sample.

The behavior of the reflected intensities, as a function of angle of incidence, can be seen by plotting curves of $I_{E_\perp}$ and $I_{E_{||}}$ as functions of $\theta$. The parameters affecting the shapes of the curves are $n$ and $k$. W. R. Hunter has generated such plots for $0.2 \leq k \leq 3.3$ in increments of 0.1 and $0.3 \leq n \leq 2.3$ in increments of 0.5. A typical plot for $n = 1.3$ and $k = 2.3$ is shown in Fig. 4.

The difference between Fig. 4 and the corresponding plot for a lossless ($k = 0$) dielectric is that for the lossless case, $I_{E_{||}} = 0$ at the Brewster angle. When $k > 0$, $I_{E_{||}}$ never goes to zero.

---

In Fig. 4, we see that $I_{E\parallel}$ and $I_{E\perp}$ differ most for large values of $\theta$. Thus, experimentally, it is desirable to choose appropriately large values of $\theta$ to obtain the most accurate values of $n$ and $k$.

6.2 **Ellipsometry**

The reflection measurements considered so far have required the use of absolute values of two reflected intensities or the ratio of two measured reflection values. If light is scattered out of the light path and thus not accounted in the determination of the reflected intensities, errors in the values of $n$ and $k$ will result. Since the powder particles have a random orientation with respect to the plane of incidence, one may assume, in the first approximation, that the lost scattered light is the same for both components of the reflected light. If one derives formulae from the original Fresnel's equations, which make use of the difference between the intensities of the polarized components, the error cancels out. If a ratio of intensities is used, the error is reduced.

Ellipsometry, which has been used extensively in the visible region to determine optical constants of metals, uses only one ratio of reflection measurements. The second required piece of information follows from the fact the phase shift differences between $r_{E\perp}$ and $r_{E\parallel}$, at the principal angle, is $90^\circ$. That is, the light is circularly polarized. If one determines the principal angle $\theta_p$ and
then measures the ratio \( |r_{E\perp}/r_{E\parallel} | \) at \( \theta_p \), one will have the necessary experimental information to calculate \( n \) and \( k \).

The principal angle is determined using a compensator. Using the phase difference property of \( r_{E\perp} \) and \( r_{E\parallel} \), Eqns. (56) and (57) can be divided to yield

\[
\left( \frac{r_{E\perp}}{r_{E\parallel}} \right)_{\theta=\theta_p} = \frac{\cos \theta - n_2^* \sqrt{1 - (\sin \theta/n_2^*)^2}}{\sqrt{1 - (\sin \theta/n_2^*)^2} - n_2^* \cos \theta}
\]

(60)

If we calculate the square of the absolute value of Eqn. (60), we can, after lengthy calculations, obtain the following useful relations between the optical constants \( n \) and \( k \) and the experimental quantities \( \theta \) and \( \psi = |(r_{E\perp}/r_{E\parallel})_{\theta_p}|^2 \)

\[
n^2 + k^2 = \sin^2 \theta + \cos^2 \psi \tan^2 \theta \sin^2 \theta
\]

\[
2nk = \sin^2 \psi \tan^2 \theta \sin^2 \theta
\]

(61)

Using a CO\(_2\) laser operating at 10.6\( \mu \)m, ellipsometry has been used to evaluate infrared optical constants. The unavailability of suitably transparent compensator materials over a broad frequency band causes some experimental difficulties. For example, sapphire can only be used in the 2-3\( \mu \)m region. Another consideration in the infrared is the determination of the principal angle. Using a laser, with its narrow beam, no problem exists. But for a non-laser source, to get sufficient energy, the beam diameter must be enlarged. The result is a loss of accuracy in the principal angle measurement. This, in turn, affects the accuracy of the value of \( \psi \).

We will not discuss further the possible application of ellipsometry to our problem. Instead we will concentrate on the applications using (1) reflection measurements at different angles, (2) reflection measurements with polarized light at a single angle or combination thereof.
7. EFFECT OF POLARIZATION PROPERTIES ON MEASURED REFLECTANCES

We assume that the experimental apparatus consists of a conventional double beam infrared spectrophotometer with an auxiliary reflection unit mounted in the sample beam light path. Of interest here is the influence of the polarization properties of the instrument and their affect on the resulting measurements. Initially, we will consider only the use of a single reflection attachment.

Since both reflection coefficients are functions of $\theta$, $n$, and $k$, in general, measurements at two angles of incidence will be required. That is, since $r_{E\perp} = f(\theta,n,k)$ and $r_{E\parallel} = g(\theta,n,k)$, then $f(\theta_1,n,k)$, $f(\theta_2,n,k)$, $g(\theta_1,n,k)$ and $g(\theta_2,n,k)$ are required to extract $n$ and $k$ values from the measured data.

A schematic diagram of the optical path of the instrument, set up for reflection measurements, is shown in Fig. 5.

7.1 Unpolarized Light. Two Angles of Incidence

Let us call the intensity of light emitted from the source, and polarized perpendicular and parallel to the plane of incidence, $A$ and $B$ respectively. Then $A + B$ represents the intensity of the sample beam. We call $A' + B'$ the corresponding light passing through the reference beam. From the sample emerges light attenuated by a factor of $R_A$ for the perpendicular component and $R_B$ for the parallel component. At the point of recombination of the two beams, the total intensity is $A R_A + B R_B$. This amount of light is compared with the light passing through the reference beam $A' + B'$ in such a way that a comb attenuates the reference beam until both beams are of equal intensity. That is, until we have

$$A R_A + B R_A = (A' + B') T_1$$  \hspace{1cm} (62)
Figure 5. Schematic Diagram of Optical Path of Spectrophotometer with Reflection Unit, Showing Polarization Components. Legend: L = source, S = sample/standard, H = half mirror, G = diffraction grating, D = detector. A and B represent components of polarization perpendicular to and parallel to plane of incidence respectively, for sample beam. Sample and reference beam are shown as displaced from H to D for purposes of clarity only.
where $T_1$ presents the deflection of the pen on the chart paper. In order to obtain the attenuation of the two polarized beams, that is $R_A$ and $R_B$, we make the same measurement with a standard replacing the sample. If it is assumed that the reflectivity of the standard is essentially unity, we obtain for that measurement

$$A + B = (A' + B') T_2$$  \hspace{1cm} (63)

where $T_2$ is the chart pen deflection when the standard is used. The desired result, that is the reflection properties of the sample are obtained from the ratio.

$$\frac{T_1}{T_2} = \frac{AR_A + BR_B}{A + B}$$  \hspace{1cm} (64)

The reflection coefficient, using unpolarized light can only be extracted if we assume that $A = B$. Then Eqn.(64) gives

$$\frac{T_1}{T_2} = R_A + R_B$$  \hspace{1cm} (65)

The assumption that $A = B$ may be made in most cases since the source emits unpolarized radiation and, to a first approximation, it may be assumed that mirrors do not polarize infrared light.

We now must account for the polarization properties of the instrument between the beam recombination point and the detector. We know, for example, that the diffraction grating polarizes the incident parallel and perpendicular beams differently. Light from the sample beam which reaches the detector may be represented by $(AR_A R_A + BR_B R_B)$ where $R_A$ and $R_B$ are the attenuation factors, due to the instrument polarization for the perpendicular and parallel components, respectively. For the reference beam, the corresponding term is $(A' R_A + B' R_B)$. For the measurement on the standard surface, we would get $(AR_A + BR_B)$ for the sample beam and
(A'R_A + B'R_B) for the reference beam. When the beams are combined, the equalization is given by

\[(A'R_A + B'R_B) = (A'R_A + B'R_B)T_1 \] (66)

and

\[(A'R_A + B'R_B) = A'R_A + B'R_B)T_2 \] (67)

Dividing Eqn.(66) by (67) gives

\[
\frac{T_1}{T_2} = \frac{AR_A + BR_B}{A'R_A + B'R_B} \] (68)

To get the desired result, \(T_1/T_2 = R_A + R_B\), we must not only assume that \(A = B\), as before, but also that \(R_A = R_B\). That is, the instrument polarization for each component must be assumed to be equal.

Notice that both Eqns. (65) and the result from (68), contain two unknown quantities \(R_A\) and \(R_B\). To extract either reflection component requires two measurements of \((T_1/T_2)\) at different angles of incidence.

### 7.2 One Component of Polarized Light. Two Angles of Incidence

If a properly oriented polarizer is inserted into the optical beam before the detector, only one component of the total recombined beam will be sensed. If we retrace the analysis of the previous section, it is clear that this case can be treated by setting either \(A = 0\) or \(B = 0\). For example, if \(B = 0\), Eqn.(69) gives

\[
\frac{T_1}{T_2} = \frac{AR_A R_B}{A'R_A} = R_A \] (69)

Thus, we get the attenuation of one component of the light irrespective of the polarization properties of the instrument. Because the ratio \(T_1/T_2\) is obtained by a manual division as opposed to the ratio recording done by the instrument, possible differences between \(A\) and \(A'\) are divided out.
and have no effect on the results. Such measurements at two angles of incidence will yield the information required to determine $n$ and $k$.

7.3 **Both Components of Polarized Light. One Angle of Incidence**

For each component of polarized light, the argument presented above in paragraph 7.2 is valid. Since two components are measured, only one angle of incidence is necessary.

7.4 **Ratio of Polarized Light Components. Two Angles of Incidence; No Standard**

If measurements of the attenuation of reflected light from the sample are made for both components of polarized radiation, and no standard is used for comparison, the equalization of the beam intensity is represented by

$$\frac{A'R_A}{A'T_A} = \frac{B'R_B}{B'T_B}$$

Here $T_A$ is the chart pen deflection for the sample with component $A$ of polarized light and $B$ that of component $B$. Note that these are two distinct measurements and that no standard is used for reference. The ratio $T_A/T_B$ is given by

$$\frac{T_A}{T_B} = \frac{AR_AB'}{BR_BA'}$$

and only for $A = A'$ and $B = B'$ is the desired result $T_A/T_B = R_A/R_B$, obtained. If this measurement is made at two angles of incidence, $n$ and $k$ can be extracted from the data.

Since we are considering the use of a double beam instrument in which the ratio recording method senses the difference between the sample beam and reference beam, it seems reasonable to consider using a reflection unit in each beam. In the following, we consider arguments similar to those presented above, but now for the case where the instrument is operated with two reflection units.
7.5 Sample in Sample Beam, Reference in Reference Beam. Unpolarized light

For this case, the equalization of the beam intensity at the comb is given by

\[ AR_A^R + BR_B^R = (A'R_A + B'R_B)T \]  

(73)

The attenuation due to the sample, i.e. \( T=RA+RB \), is given only if \( A=A'=B=B' \) and \( \hat{R}_A = \hat{R}_B \). In addition, it is assumed that the light paths through both reflection units are identical.

7.6 Sample in Sample Beam, Reference in Reference Beam. One Component of Polarized Light

With a polarizer mounted in the common beam before the detector, the attenuation of one component (e.g. \( B=0 \)) of reflected light is given by

\[ AR_A^R = A'R_A^T \]  

(74)

One only need require that \( A=A' \) to get \( T=RA \). Thus assuming equivalent optical paths for each beam, we can directly get the reflection properties. Such measurements at two angles of incidence will allow for the calculation of \( n \) and \( k \).

7.7 Samples in Both Beams. Polarizers in Both Beams

Consider the possibility of using identical reflection units, polarizers and samples in each beam. Then if the polarizers are crossed, i.e. oriented orthogonally, the condition for beam intensity equalization is given by

\[ AR_A^R = B'R_B^R \]  

(75)

That is, the polarizer orientations produce \( A'=B=0 \). The desired result, \( T=R_A/R_B \), is only obtained if \( A=B' \) and \( \hat{R}_A = \hat{R}_B \). These restrictions are more severe than those previously discussed. While appearing to be an efficient technique, this method actually is the most difficult to apply.
From the above discussions one can see that using polarized light for measuring the reflected intensities from both sample and standard require the minimum number of assumptions on the instrument properties. For these cases, it is not necessary to assume equality of intensity of source components or grating polarization.

From a practical point of view, the most convenient method for isotropic samples, for example pressed powder disks, is to measure the reflected intensity from both sample and standard at one angle of incidence and one direction of polarization. The measurements are then repeated for the other direction of polarization.

8. ANISOTROPIC CRYSTALS

So far we have been concerned with the characteristics of isotropic materials. For anisotropic crystals, additional considerations are introduced. Recall that Fresnel's formulae are usually derived for isotropic materials where the optical properties are the same in all directions. For uniaxial crystals, the index of refraction has a different value along the optical axis than it has for the two directions perpendicular to the optic axis. To understand this, we might visualize a crystal with a structure having planar symmetry. That is, the crystal's molecular layers are shaped such that there is no asymmetry for the two perpendicular directions in the plane of the molecules (x,y planes). If the molecular layers are now stacked up, as for example with pancakes, the molecular structure in the direction perpendicular to the planes (z axis) is different from that in the planes. If an electromagnetic wave propagates along the z axis, both electromagnetic field components oscillate in the plane of the molecule, and, since there is molecular symmetry, they "feel" the same polarization. Their propagation velocity is the same and so also
is their dielectric constant or index of refraction. For a wave traveling along the x or y axis, the situation is different. The electric field component parallel to the Z axis will "feel" a different polarization of the molecules than the component in the plane of the molecules. Consequently, the velocity of propagation will be different and the index of refraction will be different.

8.1 Measurements on Anisotropic Crystals

Uniaxial crystals are examined experimentally as follows. One prepares a sample having its optic axis in the plane of the sample. For the reflection measurements, one orients the sample in such a way that the optic axis is oriented perpendicular to the plane of incidence. In order to measure the optical constants parallel to the crystal axis, one polarizes the incident light perpendicular to the plane of incidence. Then the sample is rotated by 90 degrees and the measurements are repeated. For this second case, the incident light is polarized perpendicular to the optic axis. By using polarized light on an oriented crystal, one can study separately the optical properties of the crystal in directions parallel and perpendicular to the optic axis.

9. APPLICATIONS TO POWDER SPECTROSCOPY

From the above considerations, it is clear that measurement of the optical constants of anisotropic crystals must be made with care. The relationship between the optic axis and direction of incident light is critical. Consequently, the sample must be prepared appropriately if accurate material parameters are to be obtained. A similar situation is found for powders. The determination of the optical constants of powders requires careful sample preparation and controlled measurements. We first discuss powders made from isotropic materials. It is necessary to
consider refraction and scattering effects. If transmission measurements are to be made, the initial problem in preparing a sample is to eliminate the voids between the powder particles. Such voids will cause the incident radiation to interact differently at particle-air interfaces. These different interactions will result in an optical characterization which can be significantly different from that of the bulk material. One can try to form a pressed disk sample by subjecting the powder to a high pressure, say in a die. If the technique is successful and the sample's mechanical properties are accommodating, pressed disks having a density approaching that of the bulk can be prepared. In such cases, the measured optical properties should be quite close to the values determined from a solid.

An example of such an isotropic material is KBr. Pressed KBr pellets having the visual transparency of a polished crystal can be prepared, although probably not by everyone and not consistently.

Another isotropic material of interest is ZnS. Eastman Kodak manufactures optical quality disks obtained by pressing ZnS under high pressure and elevated temperatures. Irtran 2, as the product is known commercially, is transparent to about 14.5μm. Its refractive index at 1.5μm compares very well to that obtained from amorphous films and the bulk as the following table shows.

32
Index of Refraction of ZnS at 1.5 μm

<table>
<thead>
<tr>
<th>Material</th>
<th>n</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irtran 2</td>
<td>2.27</td>
<td>Kodak Publication U-72</td>
</tr>
<tr>
<td>amorphous ZnS film</td>
<td>2.26</td>
<td>J.F.Hall &amp; W.F.C.Fergerson</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Am. 41,416(1951)</td>
</tr>
</tbody>
</table>

Well characterized materials such as ZnS, which are available in various forms, are of use in studying the optical properties of powders. Principally, they serve as "optical standards" by which the accuracy and sensitivity of a given experimental method can be checked.

9.1 Highly Absorbing Materials

For highly absorbing materials, of prime interest in this work, transmission measurements may not be feasible. The low concentrations and/or thin sample paths required for adequate energy throughput may introduce errors due to unabsorbed source radiation reaching the detector. In such cases, reflection measurements on solid samples must be considered. Here again, surface conditions are important. For sensitive specular reflection measurements, the reflecting surface should not introduce significant scattering effects. We have found that, for example, carbon and graphite powders can both be cold pressed at room temperature in a polished stainless steel die to yield acceptable reflecting surfaces. The graphite disks are quite stable mechanically while the carbon disks are fragile and must be handled with care. Providing the mechanical stability of these pressed disks can be adequately preserved, reflection measurements from good quality surfaces should be realized and the optical constants calculated from procedures discussed above.
10. EXPERIMENTAL RESULTS

During the period covered by this report, experimental work was focused mainly on the following areas.

10.1 Quantitative Absorption Measurements on Tri-n-Butyl Phosphate.

Measurements begun in the previous contract period were completed. Initial measurements were repeated and some additional absorption bands were investigated. The completed work was submitted for printing in the original report (Survey of Infrared Absorption Phenomena and Experimental Methods for Liquids and Solid Films. DAAK 10-77-C-0121, Oct. 1977). No data will be reported here.

10.2 Infrared Reflection Methods for Powders

Developmental work was continued on methods of determining the optical constants using reflection methods. Variable angle reflection accessories, obtained for this study, were mounted in the spectrophotometer for test measurements. Special sample holders were constructed. Optical alignment of reflection accessories was achieved. It was found that a more precise angle of incidence determination, than was available from the stock unit, was necessary. A He-Ne laser was purchased and used for the angle of incidence measurements. Calibration curves, resulting from these measurements, were obtained. As discussed above in paragraph 9.1, preliminary work showed that, for example, carbon and graphite powder samples could be cold pressed, using a die and hydraulic press, to yield reasonably good solid disks. The surface smoothness of the pressed disks were not significantly different from that of polished solid specimens, where available. Refinements in the sample holder design were found to be necessary, especially for the carbon disks which tend to crumble quite easily. Test procedures were begun using powders and solid samples of known optical constants.
A computer interfaced data processing system was also introduced during this time. The system is shown schematically in the block diagram below:

![Block Diagram](image)

Radiation intensity vs. wavenumber data from the infrared spectrophotometer is digitized by a digital display accessory. An interface unit encodes the data and directs the Teletype to punch the coded data onto paper tape while printing out the intensity values to four significant figures on chart paper. The paper tape is then transported to the computer center where processing and/or calculations are performed. After considerable initial difficulty with the analog to BCD processing components, the system has been rendered functional. A primary application of the system is to extract, by computer calculation, the values of n and k from the input values of the reflected intensities and angle of incidence. The inability to invert, say I, θ data to n, k data, was discussed in paragraph 6.1. See, for example, Eqns. (58) and (59).
<table>
<thead>
<tr>
<th>Names</th>
<th>Copies</th>
<th>Names</th>
<th>Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DEPARTMENT OF THE ARMY</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commander</td>
<td>US Army Research Office – Durham</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Box CM, Duke Station</td>
<td></td>
<td>Durham, NC 27706</td>
</tr>
<tr>
<td></td>
<td>HQDA (DAMO-SSC)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HQDA (DAMA-ARZ, Dr. Verderame)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HQDA (DAMA-CSM-CM)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HQDA (DAMI-FIT)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>WASH DC 20310</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>US ARMY MATERIEL DEVELOPMENT AND READINESS COMMAND</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commander</td>
<td>US Army Materiel Development and Readiness Command</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRCDE-DM</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRCLDC</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRCMT</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRCSF-S</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRCDL (Mr. N. Klein)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRCBS (COL Gearin)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRCDMD-ST (Mr. T. Shirata)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5001 Eisenhower Ave.</td>
<td></td>
<td>Alexandria, VA 22333</td>
</tr>
<tr>
<td></td>
<td><strong>US ARMY ARMS AND ARMAMENT COMMAND</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commander</td>
<td>US Army Missile Command</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Redstone Scientific Information Center</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: Chief, Documents</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRDM-CGA (Dr. B. Fowler)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRDM-TE (Mr. H. Anderson)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRDM-KL (Dr. W. Wharton)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Redstone Arsenal, AL 35809</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commander</td>
<td>US Army Armament Research and Development Command</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRDAR-TSS</td>
<td>5</td>
<td>Dover, NJ 07801</td>
</tr>
<tr>
<td></td>
<td><strong>US ARMY ARMAMENT MATERIEL READINESS COMMAND</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commander</td>
<td>US Army Armament Materiel Readiness Command</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRSAR-ASN</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Attn: DRSAR-PE</td>
<td>1</td>
<td>Rock Island, IL 61299</td>
</tr>
</tbody>
</table>

37
### DISTRIBUTION LIST FOR ARCSL-CR-80024 (Contd)

<table>
<thead>
<tr>
<th>Names</th>
<th>Copies</th>
<th>Names</th>
<th>Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commander</td>
<td>US Army Test &amp; Evaluation Command</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Harry Diamond Laboratories</td>
<td>Attn: DRXDO-RDC (Mr. D. Giglio)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2800 Powder Mill Road</td>
<td>Aberdeen Proving Ground, MD 21005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adelphi, MD 20783</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chief, Office of Missile Electronic Warfare</td>
<td>Dugway Proving Ground</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>US Army Electronic Warfare Laboratory</td>
<td>Attn: STEDP-FO</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRSEL-WLM-SE (Mr. K. Larson)</td>
<td>Attn: Technical Library, Docu Sec</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>White Sands Missile Range, NM 88002</td>
<td>Attn: STEDP-MT-DA-E</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Project Manager for Smoke/Obscurants</td>
<td>Attn: STEDP-MT (Dr. L. Salamon)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRCP-SMK</td>
<td>Dugway, UT 84022</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aberdeen Proving Ground, MD 21005</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commander</td>
<td>US Army Training &amp; Doctrine Command</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Atmospheric Sciences Laboratory</td>
<td>Commandant</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRSEL-BR-AS-P</td>
<td>US Army Infantry School</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRSEL-BR-MS-A (Dr. R. Gomez)</td>
<td>Combat Support &amp; Maintenance Dept</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRSEL-BL-AS-OP (Mr. J. Lindberg)</td>
<td>Attn: NBC Division</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRSEL-BL-SY (Mr. F. Horning)</td>
<td>Fort Benning, GA 31905</td>
<td></td>
<td></td>
</tr>
<tr>
<td>White Sands Missile Range, NM 88002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Director</td>
<td>DEPARTMENT OF THE NAVY</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>US Army Materiel Systems Analysis Activity</td>
<td>Commander</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRXSY-D (Dr. Fallin)</td>
<td>Naval Surface Weapons Center</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRXSY-MP</td>
<td>Attn: Tech Lib &amp; Info Svcs Br</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Aberdeen Proving Ground, MD 21005</td>
<td>White Oak Laboratory</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Fort Belvoir, VA 23651</td>
<td>Silver Spring, MD 20910</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Director</td>
<td>Commander</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>US Army Mobility Equipment Research and Development Center</td>
<td>Naval Intelligence Support Center</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: Code/DROME-RT (Mr. O. F. Kezer)</td>
<td>4502 Sultland Road</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Fort Belvoir, VA 22060</td>
<td>Washington, DC 20390</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commander</td>
<td>Commander</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>US Army Electronics Command</td>
<td>Naval Surface Weapons Center</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRSEL-CT-LG (Dr. R. G. Rohde)</td>
<td>Attn: DX-21</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRSEL-CT-I (Dr. R. G. Buser)</td>
<td>Dahlgren Laboratory</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRSEL-WL-S (Mr. J. Charlton)</td>
<td>Aberdeen Proving Ground, MD 21005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fort Monroe, VA 23651</td>
<td>Savannah, GA 31401</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commanding Officer</td>
<td>Commander</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>US Army Ballistic Research Laboratories</td>
<td>Naval Surface Weapons Center</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRXBR-DL (Mr. T. Finnerty)</td>
<td>Dahlgren Laboratory</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRXBR-P (Mr. N. Gerri)</td>
<td>Attn: DX-21</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Attn: DRDAR-DBL (Mr. R. Reits)</td>
<td>Dahlgren, VA 22448</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Attn: DRDAR-DBL (Mr. A. LaGrange)</td>
<td>Aberdeen Proving Ground, MD 21005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aberdeen Proving Ground, MD 21005</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### DISTRIBUTION LIST FOR ARCSL-CR-80024 (Contd)

<table>
<thead>
<tr>
<th>Names</th>
<th>Copies</th>
<th>Names</th>
<th>Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commander</td>
<td>1</td>
<td>Department of the Air Force</td>
<td>1</td>
</tr>
<tr>
<td>Naval Weapons Center</td>
<td></td>
<td>HQ, Foreign Technology Division (AFSC)</td>
<td></td>
</tr>
<tr>
<td>Attn: Code 3311 (Dr. R. Bird)</td>
<td></td>
<td>Attn: PDRR</td>
<td></td>
</tr>
<tr>
<td>Attn: Code 382 (Dr. P. St. Amand)</td>
<td></td>
<td>Wright-Patterson AFB, OH 45433</td>
<td></td>
</tr>
<tr>
<td>China Lake, CA 93555</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commanding Officer</td>
<td>1</td>
<td>Armament Development &amp; Test Center</td>
<td>1</td>
</tr>
<tr>
<td>Naval Weapons Support Center</td>
<td></td>
<td>Attn: DLOS (Technical Library)</td>
<td></td>
</tr>
<tr>
<td>Attn: Code 5041 (Mr. D. Johnson)</td>
<td></td>
<td>Eglin AFB, FL 32542</td>
<td></td>
</tr>
<tr>
<td>Attn: Code 5042 (Mr. C. Dingman)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crane, IN 47522</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commander</td>
<td>1</td>
<td>USEUCOM</td>
<td>1</td>
</tr>
<tr>
<td>Naval Research Laboratory</td>
<td></td>
<td>Attn: ECJ5-O/LTC James H Alley</td>
<td></td>
</tr>
<tr>
<td>Attn: Code 5709 (Mr. W. E. Howell)</td>
<td></td>
<td>APO, NY 09128</td>
<td></td>
</tr>
<tr>
<td>4555 Overlook Avenue, SW</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Washington, DC 20375</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>USA Biomedical Laboratory</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Attn: SGRD-UV-ZA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>US Army Training &amp; Doctrine Command Liaison Officer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>German NBC School</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C/o 7261 MUNSS, Box 24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APO New York 09035</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>