Optical constants of chromium
by Lawrence Chung-kuen Chor

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ABSTRACT

The frequency-dependent optical constants are derived in the range 0 - 25 eV for Chromium film by reducing the normal incidence reflectance data with the Kramers-Kronig relation. The film is prepared in a high vacuum reflectometer having a base pressure of about 5×10^{-5} torr. The film is irradiated with a H_2 discharge light source between 850 Å and 3100 Å, and with a He source below 850° dispersed by a vacuum ultraviolet monochromator. Because of the high energy measurements, the reflectometer is connected directly to the monochromator without a window in between.

The plasma energy of Chromium, found at 22.8 eV, agrees reasonably well with the published results obtained from characteristic energy loss experiments.

I. INTRODUCTION

Within the last decade, the optical properties of semi-
conductors and metals, particularly the alkali and noble
metals,[1] have been investigated rather thoroughly with reflec-
tance measurements. Little information is available, however,
on the optical behavior of the transition metals in the
spectral range above 5 eV. Cr is selected for this study
because it is typical of this group. The object of the study
of the optical properties of these metals is to gain an
understanding of the electronic structure in the solid form.

The optical properties of a solid in the ultraviolet
region are determined principally by the interaction of
electromagnetic radiation with the electrons in the solid.
Classically, the interactions are described in terms of the
optical constants defined by Maxwell's equations. Since
the definitions of the constants are not unique, many different
constants are found in the literature. To characterize a
response of a solid to radiation in a limited frequency range,
two frequency-dependent constants are needed, one for the in-
phase, (energy absorbing), and one for the out-of-phase, (non-
energy absorbing), response of the electron. The pair of
constants can be written as a complex number. If one optical

constant is known, however, for all frequencies, any pair of constants can be calculated with the Kramers-Kronig dispersion relations.

This paper is concerned with the determination of the optical constants of Cr obtained from normal incidence reflectance data. Data are obtained in the spectral range from 4 eV to 25 eV. The data of Lenham and Treherne are used to extend the measurements below 4 eV.[2] The real and imaginary parts of both the index of refraction and the dielectric constants, the optical conductivity, and the energy loss function are deduced from the reflectance data by the application of the Kramers-Kronig relation. The computer program for the evaluation of the Kramers-Kronig integral is taken from the work of E. L. Kreiger, D. J. Olechna, and D. S. Story.[3]

In Section II, different definitions of the optical constants with their interrelations are outlined and physical interpretations given. The computer programming techniques are also outlined in Section II. The equipment designed and constructed for this experiment is described in Section III. In Section IV, the experimental results are presented and discussed with emphasis on the plasma energy.

II. THEORY

A. Definition of Optical Constants

In a medium, Maxwell's electromagnetic wave equations are[4]

$$\nabla^2 \vec{E} = \frac{\varepsilon_1 \mu}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} + \frac{4\pi\sigma\mu}{c^2} \frac{\partial \vec{E}}{\partial t} \tag{1}$$

and

$$\nabla^2 \vec{H} = \frac{\varepsilon_1 \mu}{c^2} \frac{\partial^2 \vec{H}}{\partial t^2} + \frac{4\pi\sigma\mu}{c^2} \frac{\partial \vec{H}}{\partial t} \quad , \tag{2}$$

in which ε_1 is the real part of the dielectric constant, σ is the conductivity of the medium, and μ is the permeability. The constants are frequency dependent and characterize the medium through which the wave is propagating. For non-magnetic materials, such as Cr, $\mu = 1$.

The solutions of Eqs. (1) and (2) can be written as

$$\vec{E} = \vec{E}_{ox} \exp[i\omega(t - \frac{N}{c}z)] \tag{3}$$

and

$$\vec{H} = \vec{H}_{oy} \exp[i\omega(t - \frac{N}{c}z)] \quad , \tag{4}$$

where N is the complex index of refraction and z is taken as the direction of propagation.

The complex index of refraction N is defined by

$$N = n - ik \tag{5}$$

where n is the usual index of refraction and k is the
extinction coefficient.[5]

The following relations between the electromagnetic and
optical constants are obtained by substitution of the plane
wave solution (3) into the wave equation (1) and making use
of the definition (5):

$$\varepsilon_1 = n^2 - k^2 \tag{6}$$

and

$$\frac{4\pi\sigma}{\omega} = 2 n k \quad . \tag{7}$$

Another useful way to describe the effects of the
electromagnetic wave on the solid is to define a complex
dielectric constant

$$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 \quad .$$

With this definition, the wave equation (2) may be written
as

$$\nabla^2 \vec{H} = \frac{\varepsilon}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} \quad .$$

On substituting the plane wave solutions, the following
relation is obtained:

$$N^2 = \varepsilon(\omega) \quad . \tag{8}$$

Thus

$$\varepsilon_2 = -2nk \quad . \tag{9}$$

Combining Eqs. (7) and (9), we have:

$$\sigma = - \frac{\omega \varepsilon_2}{4\pi} \tag{10}$$

The extinction coefficient, k, is a measure of the decrease in the amplitude of the electromagnetic wave. It is simply related to the absorption coefficient which is a measure of the electromagnetic energy absorbed per unit distance and is defined by:

$$\alpha = - \frac{1}{|\vec{s}|} \frac{d|\vec{s}|}{dz} \quad , \tag{11}$$

where $\vec{s}$ is the Poynting vector. By substituting Eqs. (3) and (4) into (11), one can express α in terms of k:

$$\alpha = \frac{4\pi k}{\lambda} \quad , \tag{12}$$

which is the rate of decay as the wave travels through the medium.

Of particular interest is the optical constant which is most naturally related to the number of photons absorbed per unit time. Using the correspondence principle, Spicer,[7] by

equating the classical and quantum mechanical expressions for
the energy density associated with an electromagnetic field,
has shown that

$$\sigma = \frac{1}{4\pi} \frac{1}{N'} \frac{dN'}{dt} \quad , \tag{14}$$

where N' is the density of photons. Therefore, σ is the
probability per unit time of a photon being absorbed by the
solid. Since ε_2 is simply related to σ, it also describes
the absorption behavior of a solid.

B. The Technique of Measurement

The measurement technique used in this study obtains
the optical constants from the normal incidence reflectance
data, $R(\omega)$. The reflectance is the ratio of the reflected
to incident power and is equal to the square of the ratio of
reflected to incident amplitude, r. The optical constants
are related to reflectance by the Fresnel equation for normal
incidence,[8]

$$r = R^{1/2} e^{i\theta} = \frac{n - ik - 1}{n - ik + 1} \tag{15}$$

if the interface is between vacuum and solid. If the reflec-
tance is known for all frequencies, the phase angle θ can be
calculated with the Kramers-Kronig relation:[9]

$$\theta(\omega_o) = -\frac{2\omega_o}{\pi} P \int_0^\infty \frac{\ell nR(\omega)}{\omega^2 - \omega_o^2} d\omega \tag{16}$$

where P stands for principal values. Since the spectral range of laboratory data is limited, an extrapolation procedure is required to evaluate the integral in (16). The extrapolation procedure is discussed in Section II, D. For computer integration, it is convenient to write (16) in the following way:[10]

$$\theta(\omega_o) = \frac{1}{2\pi} \int_0^\infty \frac{d\ell nR(\omega)}{d\omega} \ell n \left| \frac{\omega + \omega_o}{\omega - \omega_o} \right| d\omega \tag{17}$$

Using equations (15), (6), and (9), the complex index of refraction and complex dielectric constant are obtained in terms of R and θ:

$$n = \frac{1 - R}{1 + R - 2R^{1/2}\cos\theta} \; ; \tag{18}$$

$$k = \frac{-2R^{1/2}\sin\theta}{1 + R - 2R^{1/2}\cos\theta} \; ; \tag{19}$$

$$\epsilon_1 = \frac{(1-R)^2 - 4R\sin^2\theta}{(1+R - 2R^{1/2}\cos\theta)^2} \; ; \tag{20}$$

$$\epsilon_2 = \frac{4R^{1/2}(1-R)\sin\theta}{(1+R - 2R^{1/2}\cos\theta)^2} \; . \tag{21}$$

Thus measurements of the spectral reflectance over a large energy range are used to calculate the optical constants.

C. The Energy Loss Function $\text{Im} \varepsilon^{-1}$

It is known that when a beam of electrons of fixed energy is incident upon a thin film of material, some of the trans-mitted electrons will lose energy by a discrete amount. The energy loss spectrum is characteristic of the target material.[11] The determination of the characteristic energy losses is usually achieved by measurements of scattering through thin-solids.[12] The same information can also be obtained through the knowledge of the optical constants. This is due to the fact that the energy loss probability function $P(E)$, the probability that an electron will loose an amount of energy between E and $E + dE$ in interacting with the medium, can be related to the complex dielectric constant in the following way:[13]

$$P(E) \propto \text{Im } \varepsilon^{-1} \quad . \tag{24}$$

Thus the plasma energy given by the peak position in the energy loss measurements should correspond to the plasma energy obtained optically.[14] Since $\text{Im } \varepsilon^{-1}$ is equal to $-\varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2)$, in order for $\text{Im } \varepsilon^{-1}$ to have a maximum, it is necessary that both ε_1 and ε_2 be small. In fact, the general condition for the existence of plasma frequency is that $\varepsilon = 0$.[15]

For the simple free electron model, which approximates

metals rather well, the plasma energy is given by

$$\Delta E = \hbar \, \omega_p = \hbar (\frac{4\pi\rho e^2}{m})^{1/2} \tag{25}$$

where ω_p is the plasma frequency, ρ the electron density, e the electronic change, and m the electronic mass.

D. The Computer Program for the Evaluation of the Kramers-
    Kronig Integral

The computer program used in this study to evaluate the phase angle θ with the Kramers-Kronig integral is taken from the work of Kreiger, Olechna, and Story.[3] After calculating θ, the program computes n, k, ε_1, ε_2, Im ε^{-1} and α. The rationale for the computer program is outlined in the following discussion.

The difficulty found in the evaluation of the integral in (17) is due to the fact that the experimental curve for the reflectance cannot be written in terms of elementary functions. Even though it is possible to fit a polynomial to the experimental reflectance curve, we may still have problems in integration. An alternative way is to do the integral graphically, which is very time-consuming and inaccurate. The best procedure seems to be a numerical integration with a digital computer. The integral in (17) can be approximated by a trapasoidal sum as the following:

$$\theta(\omega_o) = \sum_1^N K_N(X_{N-1} - X_N)$$

where the slope,

$$K_N = (\ln|R_N| - \ln|R_{N-1}|)/(\ln E_N - \ln E_{N-1}) \quad ,$$

comes from the term $d \ln R(\omega)/d\omega$, and x_N is related to the term $\ln|(\omega + \omega_o)/(\omega - \omega_o)| d\omega$ in (17).[3]

The input of the computer program is N pairs of E and R picked off at an interval of 0.2 eV from the $\ln|R|$ vs. E curve. The output is computed at 0.2 eV intervals. The first value of E, or E_1, must not be zero, but must be close to zero so that the slope k_1 is zero. The integral in (17) is evaluated for every desired output. After the first output is printed, the program computes the next required output until all the desired outputs are obtained. If N pairs of the energy and reflectance values are the input to the computer and results are wanted for M values of the energy, the approximate computer time can be estimated as N x M/60 minutes. In this study the computer time for a complete calculation is about one hour. For evaluation of the integral in (17), it is necessary that the reflectance be known over the entire energy range, i.e. from zero to infinity. In this work, the experimental values of reflectance are known up to only 25 eV, thus

an extrapolation for the high-energy values is necessary. The

reflectance is usually extrapolated linearly in a plot of

$\ell nR^{1/2}$ vs ℓnE.[16] Without an adequate extrapolation, the

values of the optical constants are inaccurate and may even

appear to be physically unreasonable. The extrapolation is

adjusted in such a way that the results of the computation

agree with the independently determined low-energy values of

the optical constants. In this work, the reflectance is

linearly extrapolated to 0.19% at 100 eV.

III. EXPERIMENTAL SET-UP AND APPARATUS

A. General Experimental Arrangement

The experimental determination of the optical constants from the reflectance data requires that the sample have the cleanest possible surface. The technique used in this study for obtaining a clean surface is to form the sample by evaporation in vacuum. This experiment is concerned primarily with the optical constants at high photon energies where no material exists which can be used for a window to separate the experimental vacuum chamber from the monochromator. Because of this windowless construction, the best vacuum in the reflectometer is limited by the vacuum in the monochromator which is about 5×10^{-5} torr. Therefore the sample is conceivably subject to some surface contamination. To minimize the contamination, the experiment is performed as soon as the film is made.

The light source used is a one-meter McPherson model 225 vacuum ultraviolet monochromator which is equipped with a Hinteregger type DC discharge lamp. In the spectral range 850 - 3100 Å, hydrogen is used; and for 450 - 900 Å, helium is used. A quartz filter is used to eliminate the second order effect in the hydrogen spectrum above 1600 Å. The experiment is terminated at 3100 Å (4 eV), where the quartz filter begins to transmit higher order reflections from the grating in the monochromator.

The detector used inside the reflectometer is a sodium-salicylate-coated photomultiplier tube. The current output of the detector is measured with a Cary model 401 vibrating reed electrometer.

B. Reflectometer

The reflectometer, which is connected to the monochromator, is shown in Fig. 1. It is evacuated through the slit assembly with the monochromator vacuum system. The best pressure in the monochromator is about 5×10^{-5} torr. After the light source is turned on, the vacuum in the reflectometer decreases to 10^{-4} torr.

The reflectometer is designed in such a way that the same photomultiplier can be positioned to read either the reflected or the incident light intensity. This is achieved by supporting the photomultiplier on a rotary feedthrough mounted on the top flange of the reflectometer. It can be rotated to the incidence beam position or to the reflected beam position. The substrate is fixed at the proper angle on the optical axis. The evaporator is positioned inside a stainless-steel shield so the deposition is directed toward the substrate. During evaporation the photomultiplier is rotated behind the evaporator shield. The electrical feedthrough for the photomultiplier and for the evaporator are brazed into the top
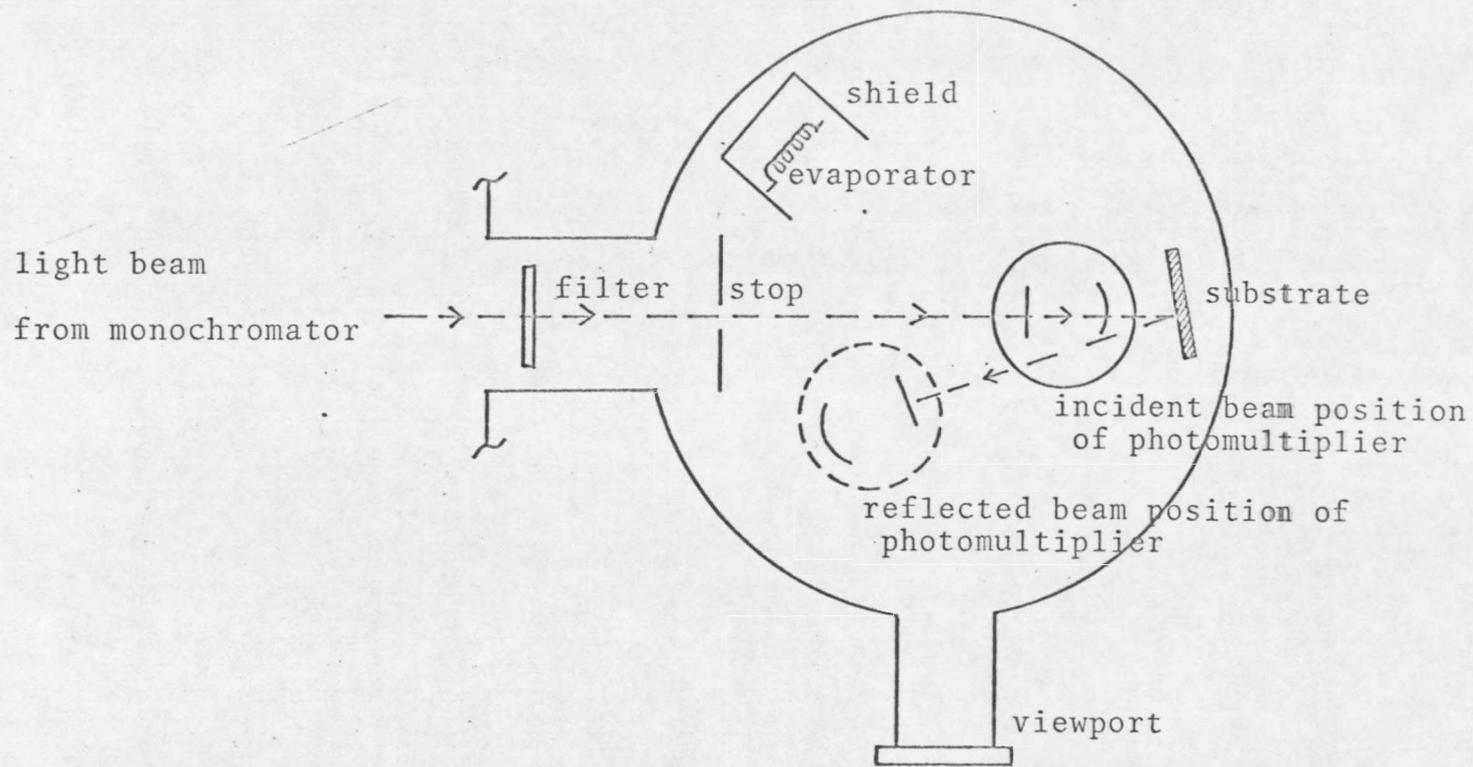
Fig. 1   Plan View of the Reflectometer

flange of the reflectometer. A viewport is mounted on the end of a side arm on the reflectometer for observation.

The photomultiplier used is a RCA 1P28 tube. The window of the photomultiplier is coated with sodium salicylate by an atomizer. The coating is thick enough to make the window become opaque to the eye. The photomultiplier bias voltage is 850 v., so that each stage has about 100 v. across it. A series of 87 KΩ resistors are used in a voltage divider to achieve this dynode bias.

The reflectometer and its components are cleaned and assembled with conventional vacuum technology.[17] The substrate is made of copper and requires special handling. It is polished with aluminum oxide to obtain a smooth surface. It is then cleaned by dipping into concentrated nitric acid and rinsed with deionized water.

The measuring procedures start immediately after evaporation of the Cr film is completed. The photomultiplier is rotated into the path of normal incidence and the intensity of the He light source is measured from 450 - 900 Å. Then the tube is rotated into the path of the reflected beam from the sample and its spectral intensity is likewise measured. The H_2 gas then replaces He gas for longer wavelength measurements. The spectral dependences of the lamp and the detector cancel because the dependences are the same in both the measurements

of incident and reflected spectral intensities.

C. Evaporator

The Cr film is formed by condensation from the vapor phase. The evaporator is made by electroplating Cr,[18] onto a 0.009" diameter tungsten wire. The tungsten wire is cleaned by electropolishing in NaOH solution, and then placed in the chromic acid solution for electroplating. The tungsten wire is connected as the cathode and a platinum screen basket is used for the anode. A plate current of 600 ma is used and the solution is kept at a temperature of about 53°C by a controlled heater. The temperature and the current must be carefully controlled for good results. After electroplating for three to four hours, a mass of about 100 mg of Cr is plated on the tungsten wire. The evaporator is then ready for use after it is rinsed with deionized water and degreased in acetone.

The procedure for forming the film is to outgas the evaporator first by slowly increasing the current. Then the evaporator is evaporated for about ten seconds to obtain a smooth and bright Cr film on the substrate. A current of about 4 amperes is required to give a sufficient rate of evaporation.

IV. RESULTS

A. Data Reduction

The reflectance at a certain energy is obtained by
measuring the relative intensities of reflected and incident
light at that energy. The ratio of these intensities is the
reflectance. Since the spectral dependence of the lamp is a
strong function of the wavelength, matching the wavelengths
of the two spectral curves is very important. The wave-
lengths of the spectra are correlated by matching peaks and
valleys.

In the data reduction the scattered light in the output
of the monochromator must be taken into consideration. When
the H_2 lamp is used, the scattered light is negligible in
comparison with the monochromatic light. For the data taken
at short wavelengths, where He is used in the lamp, the scat-
tered light must be accounted for. The light spectrum of
He terminates at about 500 Å, thus it is justifiable to assume
that all the signals below 400 Å are due to the scattered
light. It is observed that the scattered light level increases
linearly with decreasing wavelength below 400 Å. The scat-
tered light correction, then, is made by linear extrapolation
to long wavelengths. This extrapolation gives zero correction
above 700 Å. At 640 Å (19.4 eV), the correction is 11.6%
of the recorder level for the incident intensity, and 30%

for the reflected intensity.

After the data are obtained in the above manner, the computer is used to analyze the data to obtain the optical constants.

B. Experimental Results

The reflectance data obtained in this study from 4 - 25 eV are shown in Fig. 2. The reflectance is measured with two samples and the results are essentially the same. The reflectance data between 0.1 and 4.2 eV are obtained from the work of Lenham and Treherne.[2] The optical constants ε, Im ε^{-1}, and σ determined from the reflectance data are shown in Figs. 3, 4, and 5, respectively. As discussed in Section II D, the reflectance curve is extrapolated above 25 eV in such a way that the computed values of n and k agree with the work of Lenham and Treherne. The comparison is shown in Fig. 6. The general agreement is good. The minor inconsistencies are explained by the fact that at low photon energies, both n and k are very sensitive to the reflectance. For example, a difference of less than 1.0% in reflectance can change n and k by a factor of three or four.[19]

Because of the strong line structure in the He spectrum between 20 and 24 eV, the determination of the reflectance at these energies is very difficult. Although the structures in