



Optical constants of chromium
by Lawrence Chung-kuen Chor

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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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 H₂ 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 semiconductors and metals, particularly the alkali and noble metals,¹ have been investigated rather thoroughly with reflectance 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 are⁴

$$\nabla^2 \vec{E} = \frac{\epsilon_1 \mu}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} + \frac{4\pi\sigma\mu}{c^2} \frac{\partial \vec{E}}{\partial t} \quad (1)$$

and

$$\nabla^2 \vec{H} = \frac{\epsilon_1 \mu}{c^2} \frac{\partial^2 \vec{H}}{\partial t^2} + \frac{4\pi\sigma\mu}{c^2} \frac{\partial \vec{H}}{\partial t} \quad , \quad (2)$$

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

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

and

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

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

$$N = n - ik \quad (5)$$

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):

$$\epsilon_1 = n^2 - k^2 \quad (6)$$

and

$$\frac{4\pi\sigma}{\omega} = 2nk \quad (7)$$

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

$$\epsilon(\omega) = \epsilon_1 + i\epsilon_2$$

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

$$\nabla^2 \vec{H} = \frac{\epsilon}{c^2} \frac{\partial^2 \vec{H}}{\partial t^2}$$

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

$$N^2 = \epsilon(\omega) \quad (8)$$

Thus

$$\epsilon_2 = -2nk \quad (9)$$

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

$$\sigma = -\frac{\omega \epsilon_2}{4\pi} \quad (10)$$

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:

$$\alpha = -\frac{1}{|\vec{S}|} \frac{d|\vec{S}|}{dz}, \quad (11)$$

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

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

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

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

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

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

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

$$\theta(\omega_0) = -\frac{2\omega_0}{\pi} P \int_0^{\infty} \frac{\ln R(\omega)}{\omega^2 - \omega_0^2} d\omega \quad (16)$$

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

$$\theta(\omega_0) = \frac{1}{2\pi} \int_0^{\infty} \frac{d \ln R(\omega)}{d\omega} \ln \left| \frac{\omega + \omega_0}{\omega - \omega_0} \right| d\omega \quad (17)$$

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

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

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

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

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

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

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

It is known that when a beam of electrons of fixed energy is incident upon a thin film of material, some of the transmitted 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 lose 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

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

Thus the plasma energy given by the peak position in the energy loss measurements should correspond to the plasma energy obtained optically.¹⁴ Since $\text{Im} \epsilon^{-1}$ is equal to $-\epsilon_2/(\epsilon_1^2 + \epsilon_2^2)$, in order for $\text{Im} \epsilon^{-1}$ 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 $\epsilon = 0$.¹⁵

For the simple free electron model, which approximates

metals rather well, the plasma energy is given by

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

where ω_p is the plasma frequency, ρ the electron density, e the electronic charge, 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 , $\text{Im } \epsilon^{-1}$ 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:

$$\theta(\omega_0) = \sum_{1}^N K_N (X_{N-1} - X_N)$$

where the slope,

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

comes from the term $d \ln R(\omega)/d\omega$, and x_N is related to the term $\ln|(\omega + \omega_0)/(\omega - \omega_0)|d\omega$ 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 $N \times M/60$ 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 $\ln R^{1/2}$ vs $\ln E$.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.

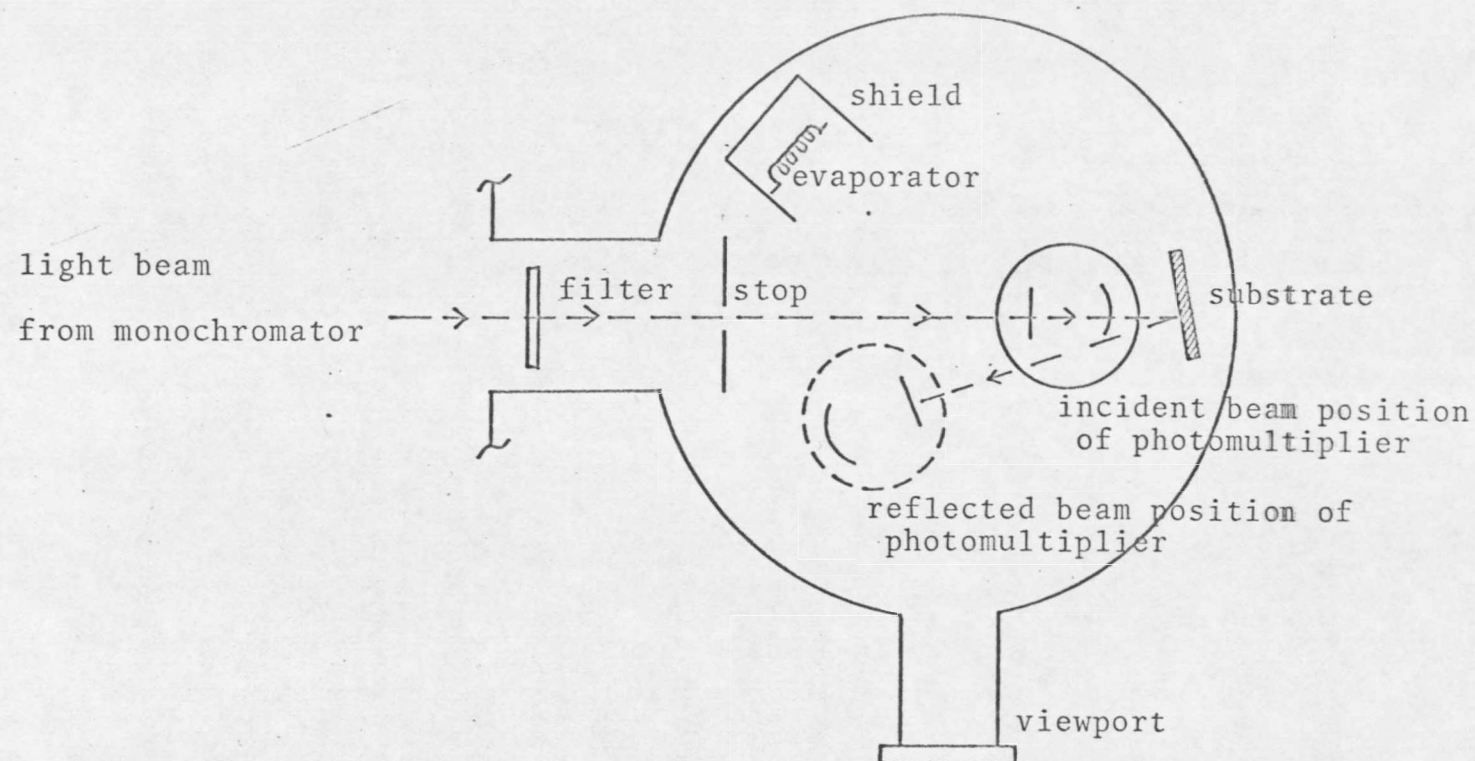
The light source used is a one-meter McPherson model 225 vacuum ultraviolet monochromator which is equipped with a Hinteregger type DC discharge lamp. In the spectral range 850 - 3100 Å, hydrogen is used; and for 450 - 900 Å, helium is used. A quartz filter is used to eliminate the second order effect 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



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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 K Ω 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 H₂ 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 wavelengths 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 scattered light must be accounted for. The light spectrum of He terminates at about $500 \text{ \AA}$, thus it is justifiable to assume that all the signals below $400 \text{ \AA}$ are due to the scattered light. It is observed that the scattered light level increases linearly with decreasing wavelength below $400 \text{ \AA}$. The scattered light correction, then, is made by linear extrapolation to long wavelengths. This extrapolation gives zero correction above $700 \text{ \AA}$. At $640 \text{ \AA}$ (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 , $\text{Im } \epsilon^{-1}$, 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

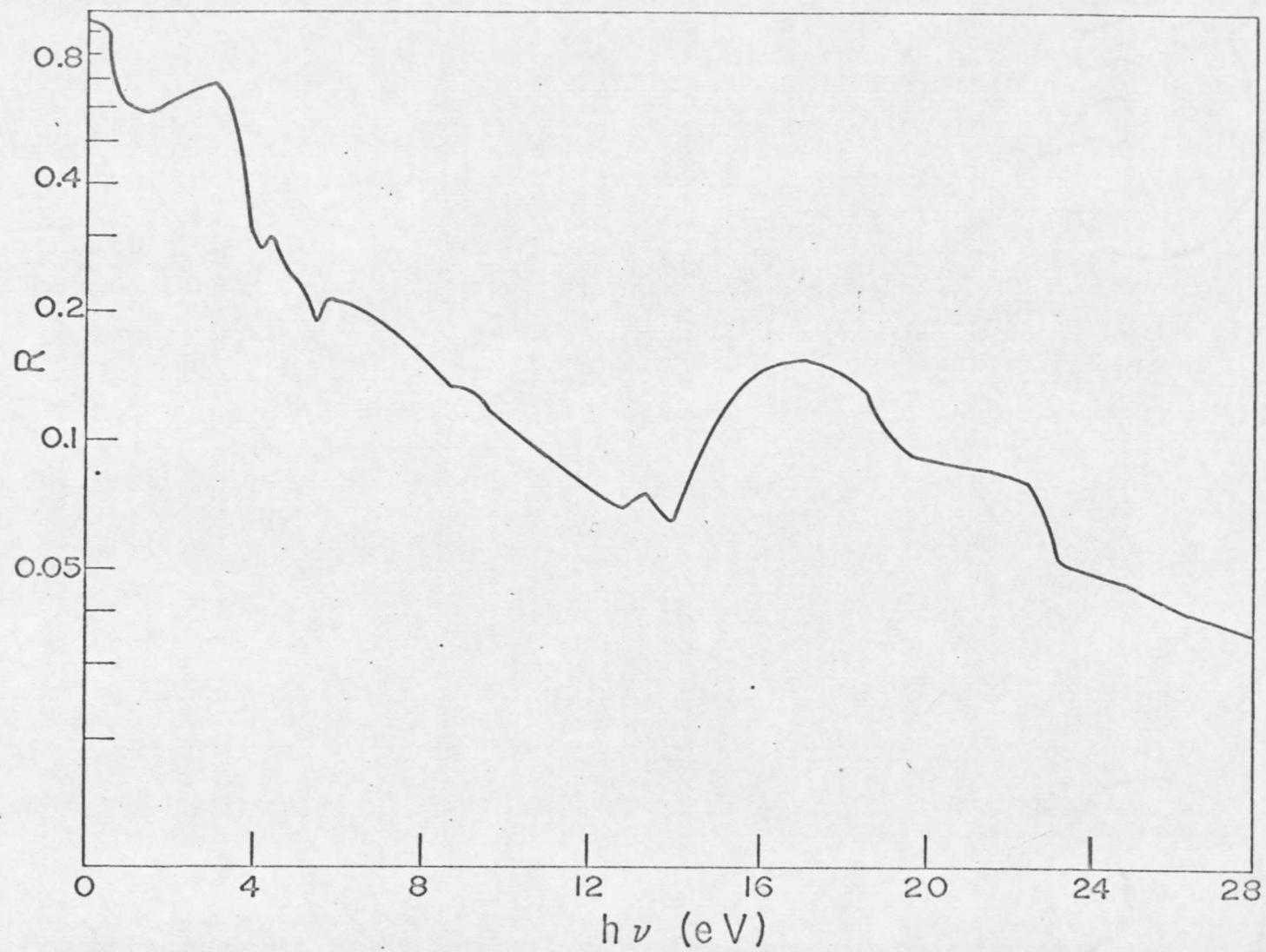


Fig. 2 Reflectance Data of Cr

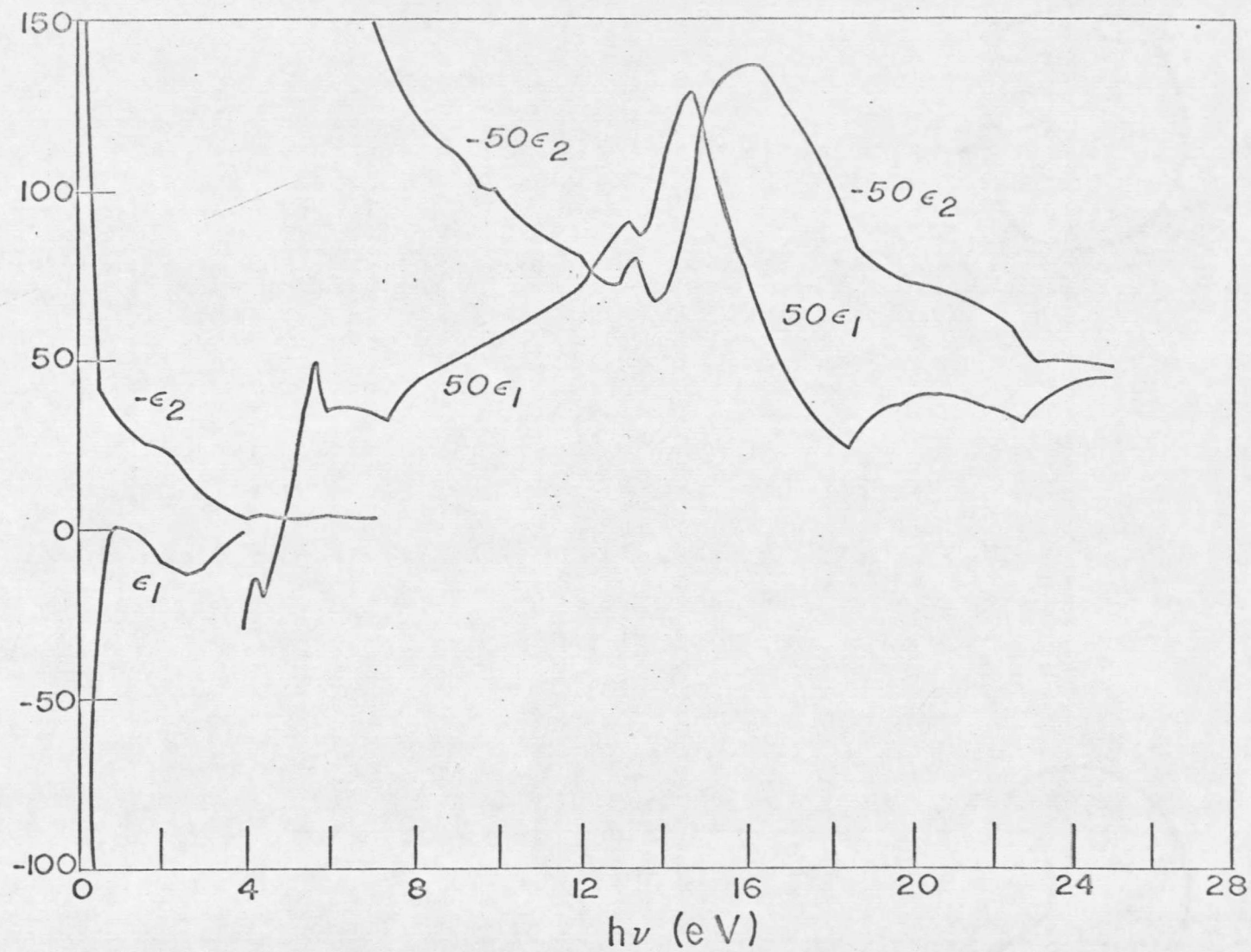


Fig. 3 The Spectral Dependence of the Complex Dielectric Constant

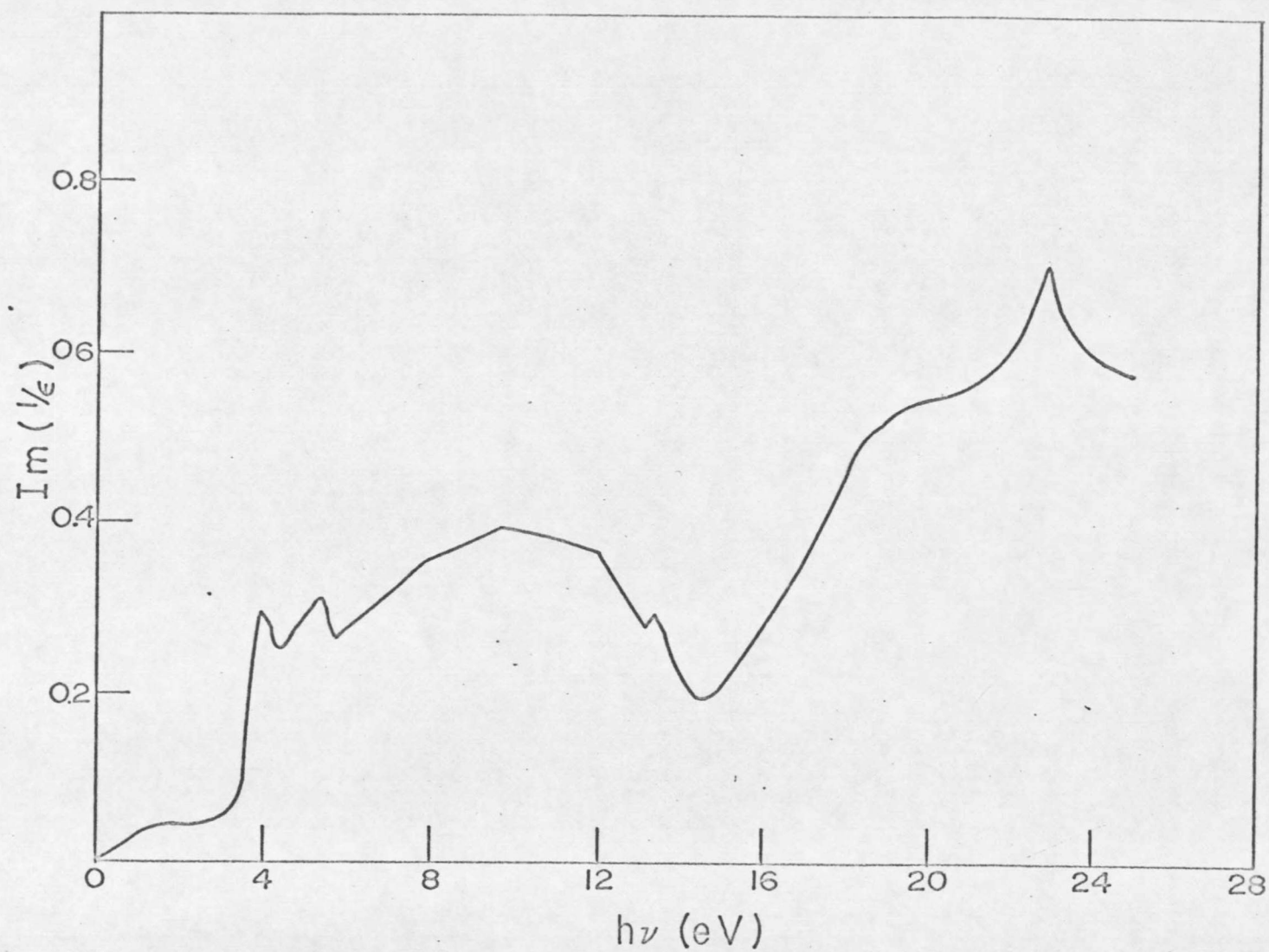


Fig. 4 The Spectral Dependence of the Energy Loss Function

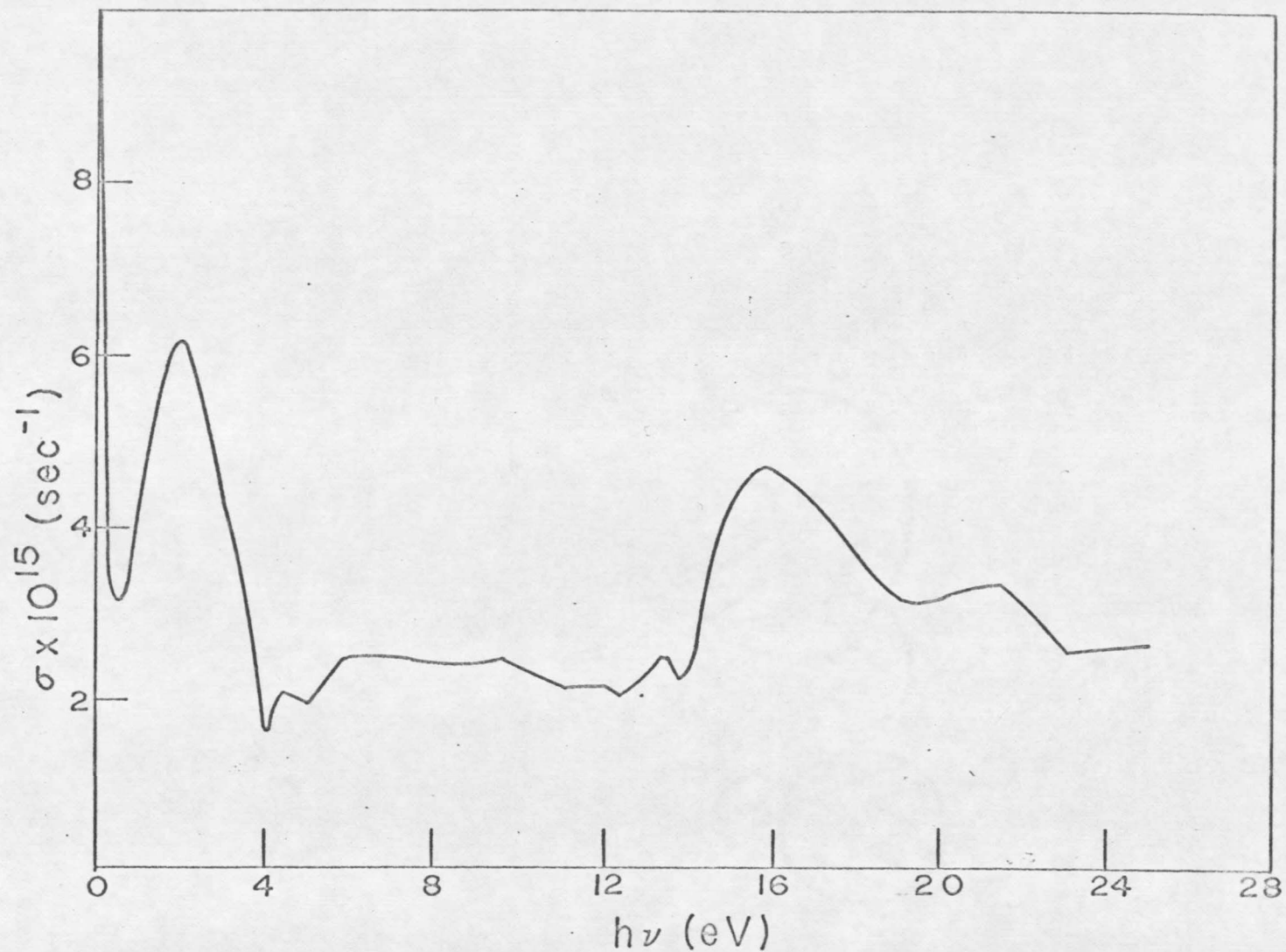


Fig. 4. The Spectral Dependence of the Optical Conductivity

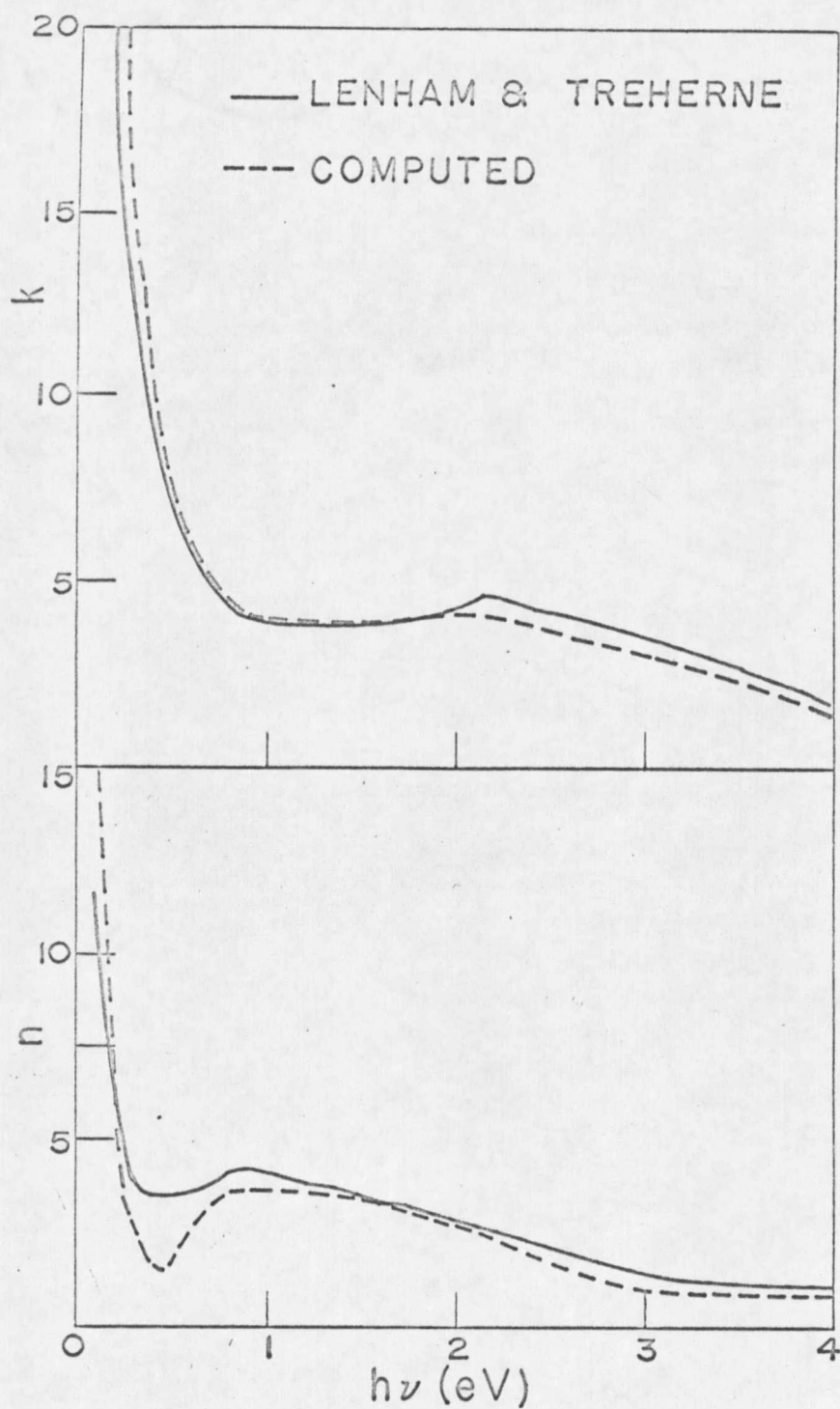


Fig. 6 Comparison of the Computer Output with the Data of Lenham and Treherne

the reflectance at 4.4 eV and 13.2 eV are reproducible, it is not certain, on the basis of this study, that they are real. There is little doubt, however, about the main features of the reflectance spectra. To resolve this problem, a more detailed study is required. A suggested improvement would be the use of a different type of lamp below 1000 Å, for example, a pulse lamp.

C. Discussion

The optical constants ϵ_2 , α , and σ , which are simply related through Eqs. (10), (11), and (14), all describe the absorption behavior in the metal. Thus it is sufficient to discuss only one of them. In this discussion, σ is chosen. To examine the plasma oscillations at higher energies, however, the energy loss function $\text{Im } \epsilon^{-1}$ is the important constant to be investigated. Since an optical measurement of the plasma energy is the principal motivation for this study, this point is discussed in some detail.

The spectral dependence of the optical conductivity σ is shown in Fig. 5. Its features are discussed in terms of the different physical phenomena which contribute to the energy loss in different energy regions. There are three types of energy loss mechanisms: free-electron excitation, interband excitation, and plasma excitation.

The free-electron effects dominate at the low photon energies, from zero to about 1 eV, and cause σ to be large. According to the Drude free-electron theory of metals, σ should fall off linearly as a function of wavelength in the free-electron region. However, Lenham has shown that σ falls off as $\lambda^{0.74}$ for Cr, where λ is the wavelength.²⁰ The threshold for interband transitions is very close to zero photon energy since the Fermi level is in the d-band. However, the interband contribution is small in the free-electron region. This fact enables one to distinguish rather unambiguously the contributions from free-electrons and interband transitions. Interband transitions dominate in the range between one and 8 eV. The electrons excited in interband transition are frequently called bound electrons. For Cr, the interband absorption is due mainly to transitions between the occupied d-bands below the Fermi energy and the empty d-bands above the Fermi energy. From the photoemission study, it is found that the interband transitions in Cr are predominately nondirect, that is, the conservation of the Bloch state wavevectors is not an important selection rule.²¹ Finally, the region where plasma oscillations occur is characterized by large values of $\text{Im } \epsilon^{-1}$ and small values of ϵ_1 and ϵ_2 . This region occurs at the high photon energies. The separation of the plasma and interband transition regions is

not well defined. Generally, the onset of the plasma oscillation is where σ starts to rise sharply, which is at about 13 eV for Cr. The method of determination of the plasma energy is discussed in the next several paragraphs.

The location of the plasma energies is obtained from the peaks of the energy loss function $\text{Im } \epsilon^{-1}$. The plasma resonance can be distinguished from the interband transition by the fact that both ϵ_1 and ϵ_2 are small in the vicinity of the maximum in $\text{Im } \epsilon^{-1}$.²² In Fig. 4, it is observed that the maximum peak of $\text{Im } \epsilon^{-1}$ occurs at 22.8 eV. The narrowness of the peak may be due to instrumental problems, as discussed in Section IV B. This peak is generally accepted as due to the so-called classical "volume" plasmons which can be explained in terms of the simple free-electron model.²³ The measurement of the plasma energy of Cr has been made by several investigators by means of the characteristic energy loss experiments. Their results are given in Table I. It is seen from Table I that the agreement between the present optical measurement and the energy loss measurements is good.

The electronic configuration of Cr is $(\text{Ar})3d^54s^1$ which has the characteristic unfilled d-shell of the transition metals as well as an unfilled s-shell. Thus the Fermi energy level is located simultaneously within both the d- and s-bands, a fact that greatly complicates the interpretation of the

Table I. Comparison of the plasma energy values obtained from the optical measurement and the energy loss measurements.

Date	Investigator	Plasma energy
1954	Marton and Leder ²⁴	21.8 eV
1954	Watanabe ²⁵	26.0 eV
1958	Fert and Pradal ²⁶	28.0 eV
1960	Robins and Swan ²⁷	24.3 eV
1968	Present work	22.8 eV

plasma oscillations in Cr. Pines has suggested a two-plasma model of coupled d and s electrons in which the low energy plasma is associated with an in-phase motion of s vs. d electrons; the high energy plasma is associated with an out-of-phase motion.²⁸ In the energy loss function, an additional peak is observed at about 10 eV. The two peaks in the loss function observed at 10 eV and 22.8 eV are consistent with the two-plasma model. The value of the plasma energy of Cr, calculated by assuming all the 3d and 4s electrons to be free, is 26.1 eV. The difference between the experimental and the calculated free-electron-model values is possibly due to the effects of core polarization and the interband transitions associated with the d-band electrons.²⁹

Ritchie has shown that there is a plasma loss at energy $(1/\sqrt{2}) \hbar\omega_p$ due to the "surface" plasmons.³⁰ However, in Fig. 4, no peak is observed at around 16 eV, but there is some weak structure at 13.4 eV which is about $1/\sqrt{3}$ times 22.8 eV. It is uncertain whether this is real or just due to instrumental difficulties. If it is real, it can be explained by Ritchie's interpretation that "the resonance frequency of plasma contained in a small sphere is less than the value appropriate to an infinite plasma by a factor of $1/\sqrt{3}$ and that this shift is due to the depolarizing effect of surface charge on the sphere."³¹ Because of the fact that thin metallic films may have a strongly granular structure.³² one would expect the surface loss in an actual thin film to lie closer to the value $(1/\sqrt{3}) \hbar\omega_p$, appropriate to a spherical grain, than to the value $(1/\sqrt{2}) \hbar\omega_p$. The relative weakness of the structure at 13.4 eV may be due to the oxidation of the surface which reduced the intensity of the surface loss.³³

V. SUMMARY

In this study, a reflectometer is designed and constructed. It is designed in such a way that the same photomultiplier detector can be positioned to read either the reflected or the incident light intensity. This design eliminates the possibility of error due to the different spectral dependences of detectors when two or more detectors are used.

The optical constants are calculated in the photon energy range 0 - 25 eV for thin Cr film by reducing the normal incidence reflectance data. The plasma energy is found at 22.8 eV where the energy loss function $\text{Im } \epsilon^{-1}$ has its maximum peak. The result of this optical experiment compares favorably with the published results of the characteristic energy loss experiments. In addition, the free-electron effect and interband transitions have been discussed.

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