

apparently exists and is mobile, it would seem that it is the proper exciton. Conversely, the energy absorbed in the peaks of the alkali halide absorption spectra is apparently not mobile. Perhaps these should be called excitation peaks rather than exciton peaks.

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Optical Measurement of the Plasma Frequency and $M_{2,3}$ Band of Chromium

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The transmission of thin chromium films has been measured in the extreme vacuum ultraviolet. The onset of transmission at 500 angstroms or 24.8 electron volts agrees well with the theoretical prediction by Pines of 25 electron volts; it also agrees well with the experimental electron eigenlosses measured by Watanabe, and Marton and Leder, of 26 electron volts and 22 electron volts, respectively. The $M_{2,3}$ band was also measured.

I. INTRODUCTION

THE free-electron theory¹⁻³ has proven successful in the understanding of many of the important properties of metals. On this model, the electrons in a metal may be considered to be free, and to move in a smoothed out potential of the ion cores and the other free electrons. On this model, the electrons move independently of one another; this will be called the independent-particle free-electron model. It is to be noted that if the Pauli Exclusion Principle is taken into account, the particles do not move completely independently of one another; electrons with the same spin tend to keep away from one another.

However, the independent-particle free-electron picture can be used successfully to calculate some of the optical properties of a metal.³ In particular, a calculation using classical electromagnetic theory, and the assumption of a free electron with damping acted upon by a periodic electric field, will yield values for a complex dielectric constant which are consistent with experiment. For a system with no damping, the dielectric constant should be imaginary at wavelengths greater than the critical wavelength, and real for wavelengths shorter than the critical wavelength. By use of the Fresnel equations, and the fact that the imaginary part

of the dielectric constant is proportional to the linear absorption coefficient, it can be seen that this is equivalent to stating that as the energy increases, the metal goes from a reflecting to a transmitting region. Hence, a measurement of the transmission should yield the critical wavelength; this depends upon the electron density and the effective mass. Friedel⁴ has mentioned that the real electron mass should be used at the high frequencies which correspond to the ultraviolet. Kittel⁵ has compared the results of optical measurements on the alkali metals, and it appears that use of the real mass yields better results than use of an effective mass.

An alternative explanation of this phenomenon can be made on the basis of the collective-interaction free-electron model.^{6,7} In this model, the long-range Coulomb interaction among all of the electrons is taken into account. Hence, instead of each electron being unaware of the individual presence of every other electron, the motion of one electron affects the motion of every other electron in the system. This results in a collective mode of behavior of the system in which the correlated motion corresponds to collective oscillations of the system as a whole, which resemble the plasma oscillations in gaseous discharge. This occurs for distances large compared to the interatomic spacing. An interesting point is that this more complete treatment also shows that the in-

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¹ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. IV, XVII.

² N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Dover Publications, New York, 1958).

³ M. Parker Givens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6, p. 313.

⁴ J. Friedel, Notes for École d'Été sur l'Etat Solide, Paris, 1958 (unpublished), p. 29.

⁵ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1953), 2nd. ed., p. 266.

⁶ S. Raimes, in *Reports on Progress in Physics* (The Physical Society, London, 1957), Vol. 20, p. 1.

⁷ D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 367.

dependent-particle model is usually adequate. The effective law of interaction between two electrons is the familiar screened Coulomb field. An important observation is that the collective motion can be approximated by a set of harmonic oscillators whose excitation energy is greater than the kinetic energy of an electron at the top of the Fermi distribution. Hence, the plasma oscillations do not interfere with the usual metallic properties.

The collective-interaction free-electron model predicts the change from a reflecting to a transmitting region, as did the independent-particle free-electron model.^{8,9} The frequency at which the transition occurs is predicted, on both models, to be

$$\omega_p^2 = 4\pi N e^2 / m^*,$$

where ω_p is the plasma frequency corresponding to the critical wavelength, N is the density of electrons, m^* is the effective electron mass, and e is the charge on the electron.

In addition, the collective-interaction free-electron model predicts the energies of some of the electron eigenlosses in thin films.¹⁰ These energies should correspond to the energies, $\hbar\omega_p$, at which the metals become transparent.^{11,12}

For an interpretation of the data at shorter wavelengths, the more extended discussions by Agarwal and Givens,¹³ and by Tombouliau, Bedo, and Neupert¹⁴ are recommended. Suffice it to say that the absorption coefficient, in the regions where the absorption is due to the internal photoelectric effect, is proportional to the density of states in the empty part of the conduction band. We have measured the $M_{2,3}$ band.

II. EXPERIMENTAL

The information was obtained by introducing two thin films of chromium of different thickness into a vacuum spectrograph,¹⁵ and measuring the relative intensities reaching the photographic plates as a function of the wavelength. The chromium samples were prepared by vacuum deposition of chromium onto thin films of Zapon at pressures of the order of 5×10^{-5} mm as read on a VGIA ionization gauge. The filament was flashed, to clean it, prior to evaporation. The temperature during the evaporation was high enough to sublime the chromium readily and cause small, luminous par-

ticles to fly off. The gauge reading rose during evaporation to higher than 10^{-4} mm, but this was partly due to the heating of the gases that were already present, as well as hot gases emitted from the chromium. The tungsten filament had been preflashed by evaporating chromium from the tungsten wires in the vacuum chamber, before the experimental samples were prepared.

In order to be able to make the Zapon films thin enough to transmit radiation, and yet still be self-supporting, the Zapon was lifted from water onto screens with a mesh of 750 and a transmission of 60-70%.

The thickness of the films was measured by means of fringes of equal chromatic order in reflection. These thicknesses were correlated with density measurements on an Ansco-Sweet densitometer. The Ansco-Sweet was then used as a secondary standard.

In order to separate orders, gaseous and metallic filters were used. A gaseous filter was obtained by introducing argon or helium into the spectrograph to a pressure of a few mm Hg.

III. DISCUSSION OF RESULTS

The results of the measurements are shown in Fig. 1, where μ , the linear absorption coefficient, is shown as a function of the wavelength of the incident light. The curve is a composite of four runs on three sets of samples. From 225 Å to 390 Å the measurements were taken in second order on two different sets of samples. The thinner film of each set was approximately 200 Å thick, and the thickness difference was 250 Å and 255 Å, respectively, in the two cases. For these runs argon was used in the source.

A 65-Å film was used to obtain data from 340 Å to 800 Å in first order. One run covered the region from 507 Å to 800 Å using helium in the spectrograph to filter out the shorter wavelengths. A second run on the same sample covered the region from 325 Å to 535 Å; here helium was used in the source but not in the spectrograph. In the region of overlap, 507 Å to 535 Å, the absorption coefficients from these two runs were in agreement within 5%. The data from the two runs at the shorter wavelengths were "normalized" before plotting to agree with the longer wavelength data in the region overlap. The normalizing factors were 3.5 and 5.6. We believe this gives some indication that the samples are not reproducible, perhaps in porosity, since (1) measurements on the same sample reproduce to about 5%, (2) the techniques for thickness measurement give results reproducible to about 10%, and (3) the shape of the curves appears to be reproducible from sample to sample.

The long-wavelength data (crosses and dots) presented in Fig. 1 were obtained by comparing the average of four exposures through a bare Zapon film with the average of three exposures through the Zapon film coated with 65 Å of chromium. The shorter-wavelength data (circles and triangles) were obtained in the same

⁸ See reference 7, p. 437.

⁹ P. Nozières and D. Pines, Phys. Rev. **113**, 1245 (1959).

¹⁰ D. Pines, Revs. Modern Phys. **28**, 184 (1956).

¹¹ H. Fröhlich and H. Pelzer, Proc. Phys. Soc. (London) **A68**, 525 (1955).

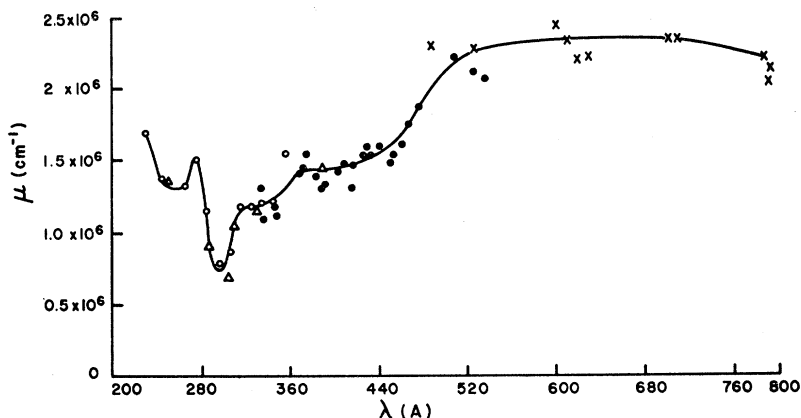
¹² W. C. Walker, O. P. Rustgi, and G. L. Weissler, J. Opt. Soc. Am. **49**, 471 (1959).

¹³ B. K. Agarwal and M. P. Givens, Phys. Rev. **107**, 62 (1957).

¹⁴ D. H. Tombouliau, D. E. Bedo, and W. M. Neupert, J. Phys. Chem. Solids **3**, 282 (1957).

¹⁵ For a description of the instrument and details of absorption measurements, see C. J. Koester and M. P. Givens, Phys. Rev. **106**, 241 (1957), and R. W. Woodruff and M. P. Givens, Phys. Rev. **97**, 52 (1955).

FIG. 1. The soft x-ray absorption of chromium: ● and ×, measurements from 65-A chromium film; ○, normalized measurements from chromium films having a thickness difference of 250 Å; Δ, normalized measurements from chromium films having a thickness difference of 255 Å.



manner except that each run employed two different thicknesses of chromium on Zapon and five determinations were averaged to obtain each point.

It is interesting to compare the absolute magnitude of the absorption coefficient at 340 Å as obtained in these data, in the data of Tomboulian, Bedo, and Neupert,¹⁴ and in the data of Agarwal and Givens.¹³ Using the bulk value for chromium to convert the data of Tomboulian *et al.* from inverse surface density to inverse centimeters, the absorption coefficient was $6 \times 10^5 \text{ cm}^{-1}$. Extrapolating the data of Agarwal and Givens by 30 Å, the absorption coefficient was approximately $5 \times 10^5 \text{ cm}^{-1}$. The best data, that is, the data with the least scattered light and the least scatter of points, were from the measurements on the 65 Å film; it yielded a coefficient of approximately $1.4 \times 10^6 \text{ cm}^{-1}$. The second-order data gave an absorption coefficient of $2 \times 10^5 \text{ cm}^{-1}$ and $4 \times 10^5 \text{ cm}^{-1}$. The data of Agarwal and Givens and of Tomboulian *et al.* do not extend to wavelengths longer than 345 Å. The shapes of the curves of the three experimental groups are in general agreement.

One might well question the effect of reflectivity on the data taken through the 65-Å film. We point out that our films were exposed to air between preparation and measurement. It is to be noted that Sabine¹⁶ measured the reflectivity of chromium on glass at an angle of 18° . The reflectivity is of the order of 7% at 800 Å and decreases uniformly to about 3–4% at approximately

¹⁶ G. B. Sabine, *Phys. Rev.* **55**, 1064 (1939).

450 Å. The samples in the measurements discussed in this paper were mounted at nearly normal incidence, so that one might suppose that the reflectivity did not much disturb the measurements, particularly since the reflectivity is higher at 18° than it is at normal incidence. It might well be supposed that the chromium had an oxide layer, but it would be supposed that this oxide layer existed in both Sabine's¹⁶ measurements and ours. Also, one might suppose that since a chromium oxide layer closes the surface, we also had some chromium left.¹⁷

IV. CONCLUSION

The experimental results for the onset of the transmitting region, and consequently for the plasma frequency, give good agreement with the theoretical predictions of Pines,¹⁸ and good agreement with the electron characteristic losses as measured by Watanabe¹⁹ and Marton and Leder.^{20,21} Pines predicted 25 electron volts. Watanabe measured 26 electron volts, while Marton and Leder measured 22. Our measurement gives 24.8 electron volts, corresponding to 500 Å.

¹⁷ L. Holland, *Vacuum Deposition of Thin Films* (John Wiley & Sons, Inc., New York, 1958), p. 453.

¹⁸ D. Pines, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 435.

¹⁹ H. Watanabe, *J. Phys. Soc. (Japan)* **9**, 920–928 (1954).

²⁰ L. Marton, L. B. Leder, and H. Mendlowitz, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, New York, 1955), Vol. 7, p. 211.

²¹ L. Marton and L. B. Leder, *Phys. Rev.* **94**, 203–204 (1954).