Far Ultraviolet Absorption Spectrum of Magnesium*

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The transmissivity of magnesium has been measured over the spectral range from 220 Å to 750 Å. The linear absorption coefficient is nearly free from structure and is of the order of magnitude of 10^4 to 10^5 cm^{-1} over this spectral region. The dominant absorption mechanism is interband excitation. Treating the valence electrons of magnesium by a nearly free-electron approximation yields semiquantitative agreement with the observed absorption spectra.

I. INTRODUCTION

THE experimental spectral range corresponds to photon energies from about 16 to 55 eV. For photons whose energies are insufficient to cause L-shell ionization (the $L_{2,3}$ edge of magnesium occurs at 50.2 eV), the most important absorption mechanism is presumably interband excitation of valence electrons. While this process is not expected to introduce much structure into the absorption curves,[1] a detailed understanding of this mechanism is necessary in order to study those optical properties of metals which are associated with the plasma behavior of valence electrons. For example, far ultraviolet spectroscopy has been used to measure the plasma frequencies of certain metals by observation of the "onset of transmission" expected to occur at the plasma frequency.[2–4] Recently Tzoar and Klein have predicted that photon absorption by plasmon creation can occur in metals.[5] The proper identification of both of these phenomena requires that their effect on absorption curves be distinguishable from structure whose origin is interband excitation of valence electrons. Magnesium was chosen to be studied because of its relatively simple electronic structure and because its plasma frequency does not occur within the experimental spectral range.

The present optical experiment also has some utility in identifying the origin of characteristic electron energy losses.[6–9] According to Nozières and Pines,[10] electron energy losses which have no counterpart in photon absorption experiments are those whose origin is due to excitation of plasma oscillations in the solid.

II. EXPERIMENTAL

The main features of the monochromator were described by Baker, Bedo, and Tomboulian.[11] It is emphasized here that the photon beam was essentially incident normally on the samples. This experimental arrangement precludes significant coupling to the radiative surface plasma oscillations described by Ferrell[12] and Stern.[13]

The absorbers were thin layers of magnesium deposited on a supporting substrate by vacuum evaporation. Two methods were used for the production of these samples. In the first method a glass slide, previously coated with a wetting agent (Victawet), was dipped in a Zapon (cellulose acetate) solution so as to form the supporting film. The metal was evaporated onto the slide and the Zapon substrate with its metallic coating was subsequently floated off the slide on a distilled water surface. The water made no contact with the metal in this process. The absorber was then lifted off the water surface and mounted. In the second method, the substrate was peeled off the glass slide and mounted prior to the evaporation. In some cases the substrate was backed by a fine mesh (100 meshes per inch) in order to provide additional support. The absorption spectra did not depend upon the method used to prepare the samples. During the initial heating of the filament the substrate was shielded to prevent volatile material on the filament from condensing on the Zapon. Initially the pressure in the evaporation chamber was less than 10^{-6} mm Hg. During the evaporation the pressure rose to about 10^{-5} mm Hg. In both methods the samples were exposed to the atmosphere during transfer to the spectrometer. It was found that magnesium would consistently condense on a Zapon surface and form a layer of high luster only if either the Zapon was backed by a glass slide or if the metallic support on which the Zapon was mounted was placed in good thermal contact with a liquid-nitrogen reservoir.

After the transmission measurement was completed, the samples were removed from their supports and weighed on a microbalance. Their weight was used to

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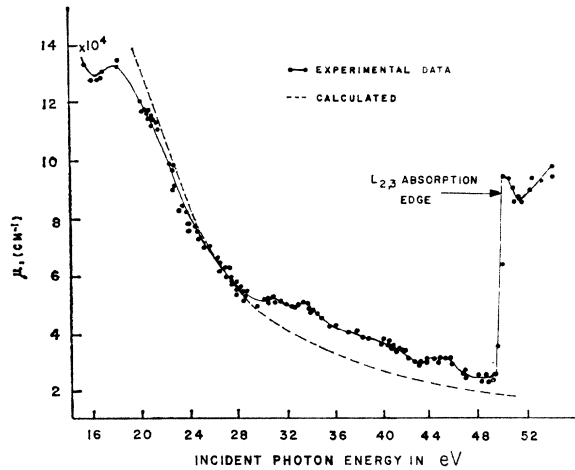[13] E. A. Stern, Phys. Rev. Letters 8, 7 (1962).

Fig. 1. Experimental and theoretical linear absorption coefficient for magnesium as a function of incident photon energy. Calculations are described in text.

estimate their thickness under the assumption that the density of the evaporated foils was the same as that of bulk magnesium.

III. RESULTS AND DISCUSSION

Over almost the entire experimental wavelength region, it was found that the transmitted intensity, I, was related to the incident intensity, I_0, by the simple relation

$$I = I_0 e^{-\mu x}, \tag{1}$$

where x is the thickness of the absorber. Over region of the validity of Eq. (1), μ was found to be independent of x, and the same μ was found (to within experimental uncertainties) regardless of whether I_0 represents the intensity transmitted by a Zapon substrate alone, or by a magnesium-coated substrate. This suggests that the reflectivity of the samples was quite low (no greater than about 5%) over the wavelength region for which (1) is applicable. However, Eq. (1) did not adequately describe the transmission of magnesium for wavelengths longer than about 650 Å, indicating that the reflectivity is somewhat higher and/or the surface has a more important effect upon the optical properties of magnesium for these longer wavelength radiations.

A typical absorption curve is shown in Fig. 1 (sample thickness ≈ 1000 Å). The experimental linear absorption coefficient at 20 eV is about 100 times greater than that predicted by the Drude theory of intraband excitations[14] with an assumed relaxation time of about 10^{-14} sec. It is therefore apparent that an interband mechanism is responsible for the large absorption coefficient.

The experimental data are in semiquantitative agreement with the following approximate calculation of the

interband absorption. In this calculation the Fermi surface is taken to be spherical in the extended zone scheme. Such an approximation for the electronic structure of polyvalent metals has been discussed by Harrison.[15]

The energy of the occupied states is assumed to be represented by the expression

$$E(k) = \hbar^2 k^2 / 2m^*. \tag{2}$$

The effective mass, m^*, is chosen to be $1.1m$ by requiring that $E_{Fermi} = \hbar^2 k^2 / 2m^* = 6.4$ eV. (6.4 eV is the energy width of the valence band of magnesium as measured by Cady and Tomboulian.[16]) The unfilled states were assumed to be described by exactly the free-electron expression, $E(k) = \hbar^2 k^2 / 2m$.

The value of the interband momentum matrix element which determines the transition probabilities is taken to be the expression given by the "nearly-free-electron approximation,"

$$\left(k + \frac{2\pi}{a}g \left| \frac{\partial}{\partial x} \right| k\right) = -[4\pi i m a g_x V_g / h^2 (\pi g^2 + a g \cdot k)]. \tag{3}$$

The matrix element was first evaluated by Sergeiev and Tchernikovsky[17] and used by Butcher[18] to discuss the absorption of the alkali metals and by Wilson[19] to discuss the absorption of silver. In the above expression, a is the lattice constant; g is a principal vector in the reciprocal lattice and V_g is a coefficient in the Fourier expansion of the periodic potential.

Only direct transitions are considered in this calculation. The momentum of the most energetic photons observed in this experiment is less than 2% of the Fermi momentum.

The values of the V_g which determine the strengths of the various absorption bands were taken to be proportional to the Fourier coefficients of the periodic potential of magnesium as calculated by Siota.[20] The choice of the V_g to be about three-fifths those calculated by Siota gave the best fit with experimental data.

The imaginary part of the dielectric constant, ϵ_2, was calculated using the above approximations. The contribution to the real part of the dielectric constant, ϵ_1, from interband absorption was determined from ϵ_2, using the dispersion relation

$$(\epsilon_1 - 1)_{interband} = \frac{2}{\pi} \int_0^\infty \frac{(\epsilon_2)_{interband}(\nu')d\nu'}{\nu^2 - \nu'^2}, \tag{4}$$

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as done by Mott and Jones.[21] In using the dispersion relation, ϵ_2 was assumed to have various long-wavelength limits in the infrared. The value of $(\epsilon_1-1)_{\text{interband}}$ in the far ultraviolet is quite small and was not sensitive to the exact cutoff in the infrared. Over the present frequency range it was found that ϵ_1 differed almost negligibly from the interband expression, $1-\omega_p{}^2/\omega^2$. The greatest difference (several percent) occurs at low frequencies (less than 20 eV).

From these calculations for ϵ_1 and ϵ_2 and using the relationships,

$$\mu = 4\pi K/\lambda = 2\pi\epsilon_2/n\lambda, \tag{5}$$

$$K^2 = \tfrac{1}{2}[(\epsilon_1{}^2+\epsilon_2{}^2)^{1/2}-\epsilon_1], \tag{6}$$

$$n^2 = \tfrac{1}{2}[(\epsilon_1{}^2+\epsilon_2{}^2)^{1/2}+\epsilon_1], \tag{7}$$

the linear absorption coefficient, μ, was evaluated and is shown in Fig. 1. K and n are the extinction coefficient and index of refraction, respectively.

The failure of the above calculation to predict the fine structure in the absorption (near 16, 34, and 45 eV) is presumably due to the oversimplified model of the electronic structure used. It is known, for example, that the density of states, $N(E)$, differs considerably from the free-electron value near the top of the magnesium valence band. A consequence of this is the well-known kink in the soft x-ray emission band of magnesium. Trlifaj[22] has explained the kink in the density of states as being largely due to the considerable overlap of the Fermi surface across the $\{10\bar{1},0\}$ faces of the Brillouin zone and the discontinuity of $E(k)$ across these faces. The kink in $N(E)$ near the $\{10\bar{1},0\}$ faces should also be evident in interband transitions arising from states near this region of the Brillouin zone. Furthermore, the calculation described above shows that most of the absorption arises from transitions in which the change in wave vector, Δk, of the electronic state is equal to $(2\pi/a)\{10\bar{1},1\}$. Photons of energy approximately equal to 15–16 eV, 34–35 eV, and 44–45 eV are absorbed in $\Delta k = (2\pi/a)\{10\bar{1},1\}$ transitions if the initial state lies near one of the $\{10\bar{1},0\}$ zone faces. The prominent structure in the experimental absorption curves lies within or very near these regions.

Since the index of refraction, n, calculated from Eq. (7) does not have a marked dependence upon wavelength, one may consider the linear absorption coefficient as being approximately proportional to ϵ_2/λ. From the experimentally determined μ, it is clear that there are no marked peaks in ϵ_2 over the wavelength region considered. Nozières and Pines[10] have shown that characteristic electron energy loss experiments probe $\text{Im}(1/\epsilon)$ $=\epsilon_2/(\epsilon_1{}^2+\epsilon_2{}^2)$. Peaks in the energy loss spectrum due to maxima in ϵ_2 are caused by preferred single-particle excitations; peaks in the energy loss spectrum due to zeroes of ϵ_1 are caused by collective excitations. The present experiment therefore indicates that marked structure in characteristic energy loss spectra are not due to maxima in ϵ_2, since such behavior should also have been detected in the present experiment.

CONCLUSIONS

The measurements and calculations reported here show that for magnesium, the index of refraction is of the order of magnitude unity over the experimental spectral range which the extinction coefficient takes on values between 2×10^{-3} (at 250 Å) and 5×10^{-2} (at 650 Å). Interband excitations are responsible for the dispersion in the far ultraviolet. It is probable that this mechanism is also responsible for the slight structure in the absorption curves reported here.

The calculations described above should be regarded as useful rather than realistic. There is some indication that the expression for the matrix element used in the calculation has too strong a dependence upon the energy of the absorbed photon: the absorption of low-energy photons is predicted to be greater than that observed while the reverse is true at higher photon energies. A more accurate calculation of the interband absorption, based upon band calculations, is presently being undertaken and will be reported in the future.

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