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Optical constants of transition metals: Ti, V, Cr, Mn, Fe, Co, Ni, and Pd

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The optical constants n and k were determined for some transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Pd) from reflection and transmission measurements on vacuum-evaporated polycrystalline thin films at room temperature, in the spectral range 0.5–6.5 eV. Three optical measurements were inverted to determine the film thickness d as well as n and k. The estimated error in d was ± 2 Å and that in n, k was less than $\pm 2\%$ over most of the spectral range. Transmission measurements were made on films in the thickness range 200–500 Å. Many transition metals oxidize rapidly in the air and so measurements on those samples were performed in a nitrogen atmosphere. A detailed analysis of the effect of oxidation on the measured quantities indicates that it is small. The effects on the optical constants of the film thickness and the evaporation rate are discussed. Some recent theoretical calculations of the interband optical conductivity are compared with the results for V, Cr, and Ni. In addition, some other recent experiments are compared with our results.

I. INTRODUCTION

The optical constants of only a few transition metals have been accurately determined throughout a continuous spectral range from the near infrared to the near ultraviolet. However, band-structure calculations for some of the transition metals have been or are now being performed, and in a few recent cases the calculated band structures have been used to obtain theoretical values for the interband optical absorption.[1,2] In order to allow comparison of calculations with accurate values of the dielectric constants, we have determined values for the $3d$ transition metals (except scandium) plus palladium over a spectral range which coincides with recent calculations. This work on transition metals represents a continuation of our previous study of the noble metals.[3]

Most earlier determinations of the dielectric constants disagree as to their actual magnitudes, although in almost all cases the energies at which structure is observed are in good agreement. The disagreement in the magnitudes of the dielectric constants is due to problems of sample preparation, accuracy of the optical measurements, and the method by which the experimental data are analyzed. These difficulties were reviewed in detail for the noble metals.[3] Briefly problems of sample preparation arise for mechanically or electrolytically polished bulk samples or slowly evaporated thin films. These techniques may leave the sample surface in a rough condition, which will decrease its measured reflectance. An oxide layer also decreases the reflectance, and in addition affects the measured phase change on reflection. Since Drude's ellipsometric method depends on measurement of the phase change, it is very sensitive to the condition of the surface. On the other hand, in the Kramers-Kronig analysis of reflectance, additional errors in the magnitude of the dielectric constants result from the extrapolation of the measured reflectance to frequencies outside the range of measurement, and some smoothing of structure usually occurs.

Some additional problems which are encountered with transition metals (but not with the noble metals) are: alloying with the tungsten filament during evaporation, noncubic crystal structure (Ti, Co), ferromagnetism (Fe, Co, Ni) or antiferromagnetism (Cr) and rapid oxidation (Ti, V, Cr, Mn, Fe, Co).

We used a technique of inverting reflection and transmission measurements on thin rapidly evaporated films in order to determine values for the optical constants. The optical constants of those transition elements which can be evaporated from tungsten filaments, namely, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and palladium, were determined from 0.5–6.5 eV. We will discuss various aspects of sample preparation such as the effects of the evaporation rate on the optical properties of the films and problems of the source materials' alloying with and sputtering from the filament. In addition, we will comment on the effects of annealing our films and on the influence which oxide layers have on our measurements. Comparisons will be made with theoretical calculations of the optical conductivity for V, Cr, and Ni. Our results disagree with some other recent experiments, and we will discuss why we believe our measurements to be more accurate. We will also comment on some of the structure in the optical conductivity about which there is disagreement in the literature.

II. DETERMINATION OF THE OPTICAL CONSTANTS

We have previously discussed the details of our method for determining the optical constants of thin metal films,[3] and so we will now only briefly outline our procedure. The optical constants n and k as well as the thickness d of a thin metal film are determined by inverting normal-incidence reflection and transmission functions, R_0 and T_0, simultaneously with the transmission function for p-polarized light incident at 60°, T_{60}^{p}. Using this method, a three-parameter fit, in a spectral region where the reflection and transmission values lie on contours which intersect steeply enough in n-k-d space, we can usually determine the film thickness at eight different wavelengths to within a scatter of about ±4 Å. Using the average of these eight measurements for the film thickness, we use the normal-incidence reflection and transmission functions to determine n and k values throughout the entire spectral range of measurement.

For all of the metals in this study except nickel and palladium, we slightly modified the procedure previously used for the noble metals. Instead of using the normal-incidence reflectance of the thin semitransparent film in the inversion calculations, we used the normal-incidence reflectance of a separate opaque film (setting the exponentials equal to zero in the reflection function). This modified technique of using $R(\infty)$, the reflectance from opaque films, in conjunction with thin-film transmission measurements has several advantages over using $R(d)$, the reflectance of the thin film itself. The most important advantage for this study is that oxide layers, which form readily on some of the metals, have less effect on the reflectance from the thicker opaque films than on that from the thinner semitransparent films. (The effect of oxide on transmittance is not so significant.) A second, general, advantage is that the total time required to run several experiments on different films of the same material is greatly reduced. Once $R(\infty)$, the reflectance from opaque samples is known, one needs to measure only the transmittance from the thin films in order to determine the optical constants. A third advantage is that the inversion calculations may be more accurate. When $n<2$, the contours of $R_0(\infty)$ have larger slopes in the n-k plane than those of $R_0(d)$; thus they give better intersections with the T contours. The only disadvantage we see is that, for some materials, it is experimentally somewhat difficult to evaporate sufficiently opaque films.

Reflection and transmission measurements on the films were made at room temperature with a spectrophotometer in the spectral range 0.5–6.5 eV, exactly as previously described.[3] The accuracy of the spectrophotometer in R and T is about ±0.005 for measurements above 0.2, ±0.001 for measurements between 0.1 and 0.2, and ±0.0005 for measurements less than 0.1.

Because our theoretical reflection and transmission functions[4] refer to a semi-infinite substrate medium, the data must be corrected for reflection at the back surface of the actual substrate. In the R_0 measurement on semitransparent films the portion of this reflection which entered the detector was small enough to be neglected. Reflection measurements on opaque films cause no problem. The correction in the T measurements[5] is approximately

$$T \simeq (T_F \cos\theta_1 / T_B \cos\theta_3)(1 - R_S - R_S R_F T_B^2),$$

where the subscript F refers to measurements on the film-coated substrate, B on the blank substrate, and R_S is the reflectance at a single surface of the blank substrate; R_S and θ_3 were calculated from the refractive index of the substrate.[6] For T_{60}^{p}, $R_S \simeq 0$; for T_0 the correction is still only a few percent.

III. SAMPLE PREPARATION AND RESULTS

All of our samples were deposited onto fused-quartz substrates at room temperature by vacuum evaporation of the metals from resistance-heated sources. The purity of each metal is quoted in Table I from the supplier's specification of total metallic impurity. The evaporations were performed at pressures below 3×10^{-6} Torr in an oil-pumped bell-jar system. Before evaporation the substrates were cleaned ultrasonically in Lakeseal Laboratory Glass Cleaner and then ultrasonically rinsed in distilled water. The substrates were dried with a hot-air gun and placed immediately in the vacuum system. In all cases the substrates were masked until the source was at evaporation temperature, and the evaporation rate was made as high as possible. A fast rate of evaporation is necessary to insure the surface smoothness of the films.[7] The actual details of the type of source and the evaporation rate are given for each material in Table I.

Several of the materials we evaporated (Ti, V, Cr) acted as getters and so the pressure in the bell-jar system decreased during evaporation to pressures lower than 8×10^{-7} Torr. This gettering action was used to advantage, however, in order to lower the pressure in the system before the shutter was opened for the sample deposition.[8,9] Nevertheless a small amount of gettering was probably still taking place during deposition.

Several of the metals (Ti, V, Mn, Co, Fe) oxidized rapidly in the air. To minimize this effect,

TABLE I. Sample material and evaporation conditions.

Element	Supplier	Purity	Form	Source	Deposition rate	Film thicknesses [a]
Ti	Materials Research Corp.	99.97%	0.020-in. wire	6-strand twisted W filament	>100 Å/sec	298 Å 350 Å ∞
V	Materials Research Corp.	99.99%	0.020-in. wire	4-strand twisted W filament	100 Å/sec	167 Å 252 Å 324 Å 412 Å ∞
Cr	Materials Research Corp.	99.99%	Small crystallites	Conical basket of twisted W wire	50 Å/sec [b]	403 Å 509 Å ∞
Mn	Alfa inorganics	99.97%	Chips [c]	Conical basket of twisted W wire	100 Å/sec	203 Å 290 Å 318 Å 430 Å ∞
Fe	Materials Research Corp.	99.99%	0.020-in. wire	6-strand [d] twisted W filament	150 Å/sec	294 Å 380 Å ∞
Co	Materials Research Corp.	99.9+%	0.010-in. foil	6-strand [d] twisted W filament	50 Å/sec	272 Å 369 Å ∞
Ni	A. D. Mackay Inc.	99.97%	0.020-in. wire	W filament	70 Å/sec	282 Å 314 Å 316 Å 402 Å
Pd	Materials Research Corp.	99.97%	0.020-in. wire	4-strand twisted W filament	50 Å/sec	277 Å 375 Å

[a] The symbol ∞ indicates that the reflection measurements were made on separate sets of opaque films.

[b] Since the chromium could not be melted in the tungsten basket without burning out the filament, the films were formed from chromium sublimed from the crystallites without melting them.

[c] Before the material was evaporated, the oxide was removed from the metal with hydrochloric acid.

[d] In all cases the weight of the evaporant was less than about 30% of the weight of the tungsten filament. This precaution was taken to prevent the rapid disintegration of the tungsten filament which would otherwise occur (Ref. 7).

the bell jar was back filled with prepurified nitrogen in these cases. In addition, nitrogen could be constantly flowed through the sample compartment of the spectrophotometer while the optical measurements were being made. With use of this technique the samples were exposed to the air for at most 2 min, while they were being transferred from the vacuum evaporator to the sample compartment of the spectrophotometer. When this procedure was followed transmission values did not change for any of the metal films over at least a 2-h period. Reflectance changed more quickly than transmittance, and for opaque films was found initially to decrease linearly with time in the nitrogen atmosphere above 3.5 eV (with no change below 3.5 eV during the first 2 h). Since the measurements above 3.5 eV were all made within 10 min of the time of formation of the films, any correction at our observed linear rate, even in the worst cases, would have been well within our error of measurement.

Some of our chromium and nickel samples which did not oxidize rapidly in the air, were annealed in a nitrogen atmosphere at 170 °C for 12 h. However when these films were annealed the reflectance measurably decreased by as much as 25% of the preannealed values. The reflectance decreased most notably in the ultraviolet, but a measurable decrease occurred at all photon energies. The most probable explanation for this decrease is that the films were oxidized by the residual oxygen in the nitrogen filled dessicator used for the anneal.

Finally we checked to see if the ferromagnetic metal films (Fe, Co, Ni) demonstrated any anisotropy in their transmission of polarized light when the films were rotated about their normal axis. No effect was seen even after the films were placed in a magnetic field. In the case of cobalt we were able to compare our absorption results to others[10] for single-crystal cobalt with the electric field of the light wave parallel and perpendicular to the optic axis. The structure in our isotropic curve is qualitatively an average of that in the single-crystal curves for the two orientations (although the magnitudes disagree), again indicating that our films are fine grained and nonoriented.

Our final results for the optical constants *n* and *k* are listed in Tables II and III as a function of photon energy. These values are averaged for several film thicknesses as listed in Table I (or extrapolated in the case of vanadium as explained below). All of the results on films of the different tabulated thicknesses agreed within the estimated error. The estimated error in *k* is less than ±1.5% and that in *n* is less than ±4%; both errors grow smaller toward the uv beyond 2.5 eV, and they are smaller over the whole range for titanium, manganese, and cobalt.[5] Theoretical calculations are usually expressed in terms of the complex dielectric constant $\epsilon_1 + i\epsilon_2$, where $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$. For graphical presentation of the results on the transition metals, the conductivity $\sigma_1 + i\sigma_2$ is more convenient than the dielectric constant; they are related by $\sigma_1 = \epsilon_2\omega/4\pi$, $-\sigma_2 = (\epsilon_1 - 1)\omega/4\pi$. The conductivities calculated from the optical constants in Tables II and III are graphed in Fig. 1. The widths of the curves represent the estimated errors due to instrumental precision.

Vanadium, chromium, and palladium exhibit other interesting features which deserve comment. Each showed a characteristic thickness dependence and palladium demonstrated the effect of too slow a deposition rate.

Using the normal-incidence reflection measurements for opaque vanadium samples along with the normal-incidence transmission measurements for four vanadium films of thicknesses 167, 252, 324, and 412 Å, the resulting conductivities of the four films above 2 eV demonstrated a systematic thickness dependence. The values of the conductivities increased with film thickness, although, in the case of the three thickest films, the successive differences were not more than the assumed experimental error.

The apparent thickness dependence of the derived conductivities is probably due to an oxide layer on the films, and the effect of this layer should be smallest in the thickest films. Some confirmation of this assertion is given by the observed change in transmittance due to oxidation. When vanadium

TABLE II. Optical constants for titanium, vanadium, chromium, and manganese.

	Titanium		Vanadium		Chromium		Manganese	
eV	*n*	*k*	*n*	*k*	*n*	*k*	*n*	*k*
0.64	3.51	5.19	2.79	7.90	3.71	5.04	3.89	5.95
0.77	3.69	4.70	2.77	6.34	3.66	4.31	3.78	5.41
0.89	3.67	4.37	2.64	5.18	3.69	3.84	3.65	5.02
1.02	3.62	4.15	2.70	4.33	3.67	3.60	3.48	4.74
1.14	3.50	4.02	2.87	3.78	3.58	3.58	3.30	4.53
1.26	3.35	3.97	2.94	3.50	3.41	3.57	3.10	4.35
1.39	3.29	3.96	3.12	3.34	3.30	3.52	2.97	4.18
1.51	3.21	4.01	3.16	3.25	3.20	3.48	2.83	4.03
1.64	3.00	4.01	3.20	3.20	3.08	3.42	2.70	3.91
1.76	2.86	3.96	3.18	3.15	3.05	3.39	2.62	3.78
1.88	2.76	3.84	3.25	3.09	3.09	3.34	2.56	3.65
2.01	2.67	3.72	3.54	3.02	3.17	3.30	2.51	3.54
2.13	2.60	3.58	3.83	3.00	3.22	3.30	2.47	3.43
2.26	2.54	3.43	4.00	3.04	3.18	3.33	2.39	3.33
2.38	2.44	3.30	3.86	3.18	2.94	3.33	2.32	3.23
2.50	2.36	3.19	3.92	3.26	2.75	3.30	2.25	3.14
2.63	2.32	3.10	3.81	3.38	2.51	3.24	2.19	3.06
2.75	2.27	3.04	3.59	3.46	2.33	3.14	2.11	2.98
2.88	2.21	3.01	3.52	3.49	2.19	3.04	2.06	2.90
3.00	2.14	2.98	3.31	3.49	2.08	2.93	2.00	2.82
3.12	2.08	2.95	3.07	3.48	2.00	2.83	1.96	2.74
3.25	1.99	2.93	2.87	3.45	1.92	2.74	1.92	2.67
3.37	1.90	2.90	2.68	3.40	1.87	2.69	1.89	2.59
3.50	1.82	2.87	2.51	3.34	1.84	2.64	1.89	2.51
3.62	1.72	2.82	2.42	3.29	1.76	2.58	1.87	2.45
3.74	1.61	2.74	2.37	3.22	1.69	2.53	1.86	2.38
3.87	1.55	2.66	2.28	3.15	1.65	2.47	1.86	2.32
3.99	1.50	2.57	2.17	3.06	1.58	2.40	1.86	2.25
4.12	1.45	2.46	2.07	2.95	1.53	2.34	1.86	2.19
4.24	1.40	2.36	1.93	2.84	1.48	2.28	1.85	2.14
4.36	1.35	2.26	1.87	2.73	1.45	2.21	1.85	2.08
4.49	1.30	2.17	1.81	2.63	1.43	2.15	1.86	2.03
4.61	1.27	2.07	1.77	2.55	1.39	2.08	1.85	1.99
4.74	1.27	1.99	1.70	2.45	1.38	2.03	1.84	1.94
4.86	1.26	1.91	1.64	2.37	1.37	1.97	1.83	1.91
4.98	1.27	1.83	1.60	2.29	1.36	1.91	1.82	1.86
5.11	1.28	1.77	1.57	2.20	1.36	1.85	1.82	1.82
5.23	1.30	1.72	1.58	2.14	1.38	1.80	1.81	1.79
5.36	1.31	1.68	1.59	2.07	1.40	1.77	1.78	1.76
5.48	1.32	1.66	1.62	2.01	1.43	1.74	1.74	1.73
5.60	1.32	1.66	1.63	1.98	1.45	1.73	1.73	1.70
5.73	1.32	1.67	1.65	1.95	1.47	1.72	1.72	1.67
5.85	1.31	1.68	1.66	1.94	1.46	1.72	1.70	1.64
5.98	1.31	1.69	1.68	1.94	1.46	1.71	1.67	1.61
6.10	1.27	1.69	1.65	1.94	1.43	1.70	1.63	1.58
6.22	1.25	1.68	1.62	1.94	1.39	1.70	1.62	1.55
6.35	1.22	1.66	1.58	1.93	1.35	1.68	1.59	1.52
6.47	1.16	1.64	1.54	1.92	1.31	1.65	1.55	1.50
6.60	1.10	1.62	1.47	1.90	1.28	1.64	1.48	1.47

TABLE III. Optical constants for iron, cobalt, nickel, and palladium.

	Iron		Cobalt		Nickel		Palladium	
eV	*n*	*k*	*n*	*k*	*n*	*k*	*n*	*k*
0.64	3.17	6.12	3.87	7.79	3.47	9.09	3.34	9.89
0.77	3.11	5.39	3.61	7.26	3.14	7.96	3.01	8.59
0.89	3.09	4.83	3.42	6.77	2.96	7.08	2.80	7.65
1.02	3.03	4.39	3.17	6.31	2.79	6.43	2.66	6.90
1.14	2.97	4.06	2.94	5.88	2.65	5.93	2.52	6.33
1.26	2.92	3.79	2.78	5.50	2.48	5.55	2.34	5.89
1.39	2.96	3.56	2.65	5.16	2.40	5.23	2.23	5.50
1.51	2.94	3.39	2.53	4.88	2.26	4.97	2.06	5.19
1.64	2.87	3.28	2.40	4.64	2.13	4.73	1.95	4.89
1.76	2.86	3.19	2.31	4.45	2.06	4.50	1.86	4.65
1.88	2.92	3.10	2.25	4.27	1.99	4.26	1.80	4.42
2.01	2.88	3.05	2.19	4.11	1.99	4.02	1.75	4.21
2.13	2.94	2.99	2.13	3.96	1.96	3.80	1.68	4.02
2.26	2.95	2.93	2.05	3.82	1.92	3.61	1.64	3.84
2.38	2.86	2.91	1.97	3.68	1.85	3.42	1.57	3.68
2.50	2.74	2.88	1.88	3.55	1.82	3.25	1.52	3.54
2.63	2.67	2.82	1.81	3.41	1.78	3.09	1.46	3.39
2.75	2.59	2.77	1.74	3.28	1.73	2.95	1.41	3.26
2.88	2.48	2.71	1.67	3.17	1.71	2.82	1.37	3.14
3.00	2.35	2.65	1.61	3.05	1.70	2.69	1.33	3.03
3.12	2.24	2.58	1.57	2.93	1.72	2.57	1.30	2.93
3.25	2.12	2.50	1.53	2.82	1.72	2.48	1.26	2.83
3.37	2.02	2.43	1.50	2.71	1.70	2.40	1.24	2.74
3.50	1.93	2.35	1.49	2.61	1.74	2.32	1.23	2.65
3.62	1.85	2.27	1.48	2.52	1.78	2.26	1.22	2.57
3.74	1.78	2.19	1.46	2.44	1.84	2.22	1.20	2.50
3.87	1.74	2.12	1.45	2.37	1.93	2.19	1.21	2.42
3.99	1.69	2.06	1.44	2.31	2.01	2.18	1.21	2.35
4.12	1.67	2.00	1.44	2.25	2.02	2.18	1.20	2.29
4.24	1.65	1.94	1.44	2.19	2.03	2.20	1.18	2.23
4.36	1.64	1.88	1.44	2.14	2.03	2.23	1.18	2.18
4.49	1.62	1.84	1.44	2.09	2.01	2.26	1.19	2.13
4.61	1.59	1.79	1.44	2.04	1.96	2.29	1.16	2.10
4.74	1.56	1.75	1.44	2.01	1.89	2.30	1.13	2.07
4.86	1.53	1.70	1.45	1.97	1.82	2.32	1.11	2.03
4.98	1.51	1.66	1.45	1.93	1.73	2.31	1.08	1.99
5.11	1.50	1.61	1.46	1.91	1.65	2.29	1.04	1.95
5.23	1.48	1.57	1.47	1.89	1.57	2.25	1.00	1.91
5.36	1.48	1.53	1.47	1.87	1.49	2.20	0.97	1.86
5.48	1.47	1.49	1.45	1.86	1.43	2.15	0.94	1.81
5.60	1.47	1.47	1.43	1.85	1.38	2.09	0.92	1.76
5.73	1.47	1.44	1.41	1.84	1.34	2.02	0.91	1.70
5.85	1.47	1.43	1.38	1.82	1.32	1.96	0.89	1.65
5.98	1.49	1.41	1.36	1.78	1.29	1.89	0.87	1.60
6.10	1.47	1.40	1.32	1.75	1.28	1.82	0.86	1.55
6.22	1.45	1.40	1.29	1.71	1.28	1.75	0.85	1.50
6.35	1.42	1.39	1.26	1.67	1.29	1.69	0.85	1.46
6.47	1.35	1.37	1.21	1.63	1.29	1.64	0.85	1.42
6.60	1.29	1.35	1.16	1.59	1.26	1.60	0.84	1.38

films were aged for several days in the air, the transmission increased above 2-eV photon energy. The increase in the transmission will decrease the derived optical constants. Thus the smaller the oxide thickness the higher the optical constants (above 2 eV). Therefore, the thickest film, with the relatively thinnest oxide and the highest optical constants, is the most nearly characteristic of bulk vanadium.

Even better values, however, can be obtained by extrapolating our measured values to infinite thickness. To seek the asymptotic values we plotted our measured values of *n* and *k* at each measured photon energy versus the reciprocal of the film thickness. The values are found to lie very close to straight lines, much closer than the experimental error. Therefore, at each measured photon energy we fit our *n* and *k* values versus reciprocal thickness to straight lines using the least-squares formula. We then took the intercepts, which correspond to infinite thickness, as the best values of *n* and *k*. These extrapolated *n* and *k* values are listed in Table II as our preferred values, and the corresponding conductivities are shown in Fig. 1(b). The error estimates represent the assumed instrumental precision of a measurement; statistically the extrapolation should increase the uncertainty by about 50%.

The reflectance from two separate sets of opaque chromium films agreed well with one another. Normal-incidence transmission measurements were made on four films of thicknesses 260, 363, 403, and 509 Å. The values of the optical constants determined from the two thickest films (403 and 509 Å) agreed with one another well within our estimated error. However, the real part *n* of the optical constants determined from the two thinnest films did not agree so well. The values determined from the 363-Å film were larger below 4 eV by about the estimated error and the values of the 260-Å film were larger by about three times the estimated error. The values of the imaginary part *k* of the optical constants all agreed well; however, this agreement is not surprising since these *k* values are mainly dependent on the reflectance, which was taken from measurements on the same opaque films for use in conjunction with each of the thin-film transmittances.

Apparently chromium films exhibit a thickness dependence below 4 eV for film thicknesses less than about 400 Å. The values of *n* decrease with increasing film thickness. Such a decrease in *n* is characteristic of films which are too thin to yield bulk values of the optical constants. We have observed such decreases in gold[3] and palladium (see below). In both of these cases, however, the thick-film limit was observed in films as thin as 250 Å, whereas in chromium a deviation already occurred for 350-Å thickness. For all of these materials the large values for *n* are qualitatively predicted by Maxwell-Garnett theory.[11] (This type of thickness dependence is in sharp contrast to that described above for vanadium.) Our values for the conductivity of chromium are the average

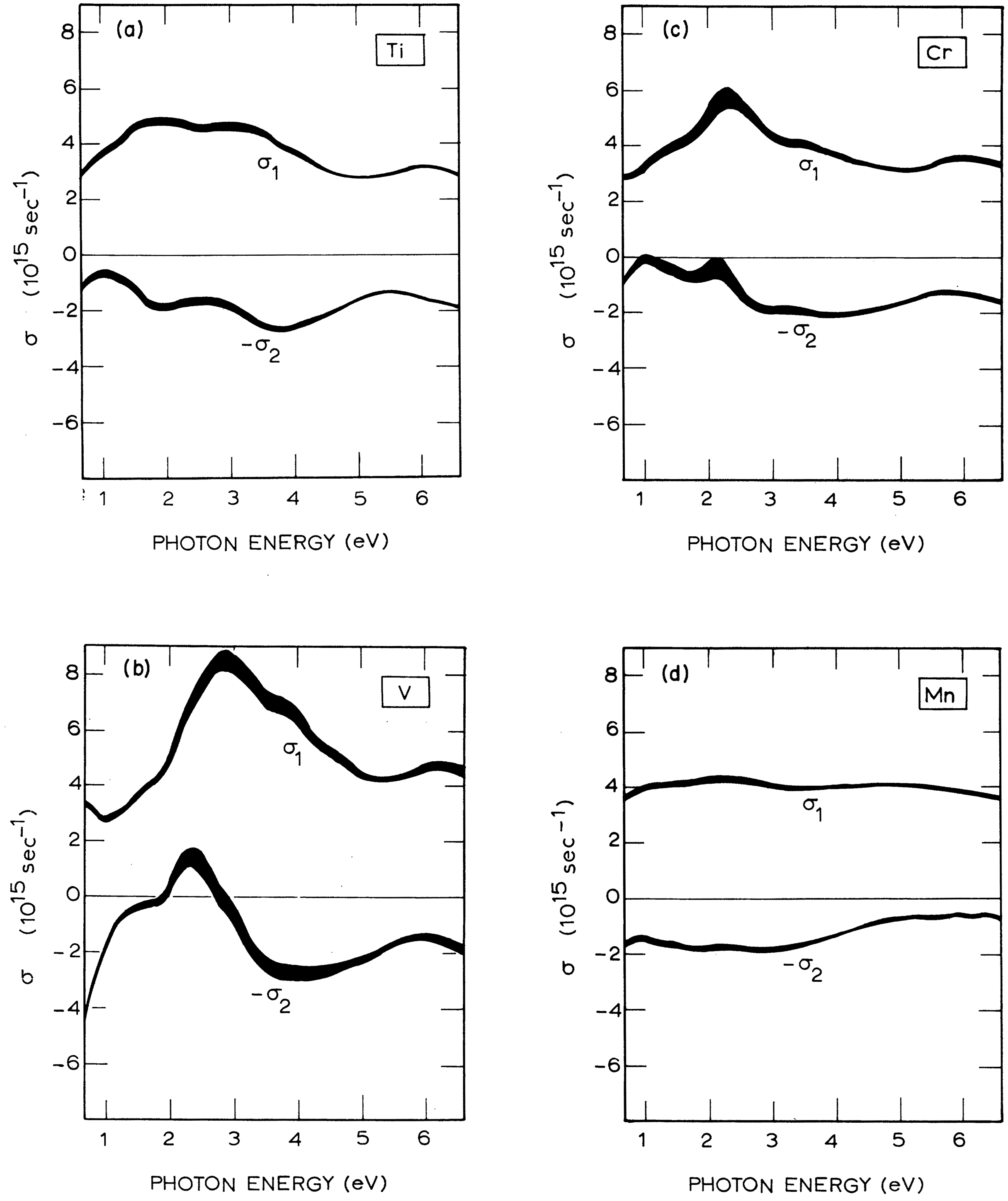

FIG. 1. Optical conductivity in 10^{15} sec^{-1} as a function of photon energy in eV, for (a) titanium, (b) vanadium, (c) chromium, (d) manganese, (e) iron, (f) cobalt, (g) nickel, and (h) palladium. The width of the curves is representative of the instrumental error.

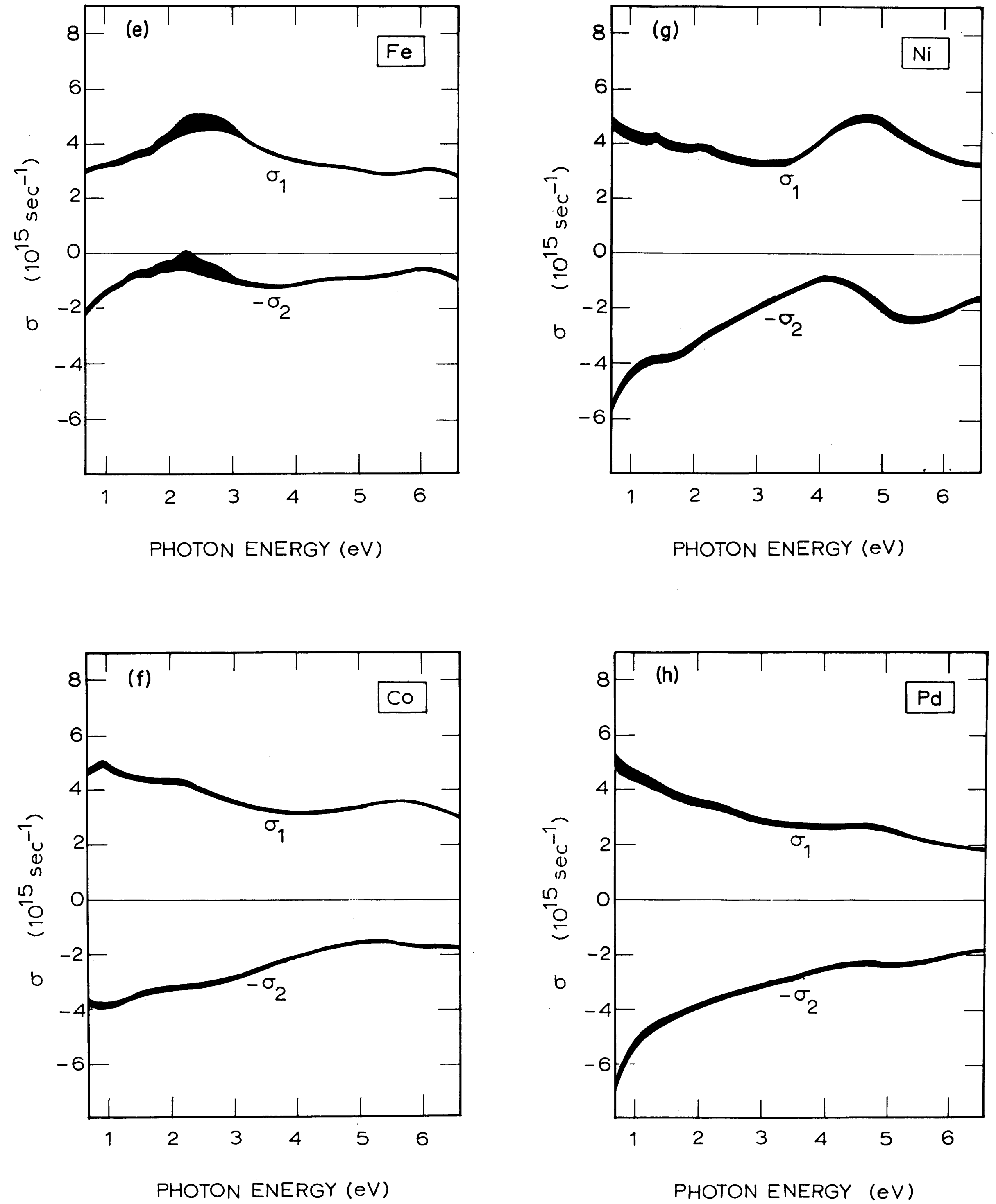

FIG. 1. *(Continued)*

of the experiments on the 403- and 509-Å films.

The optical constants of palladium exhibited a thickness dependence when the films were excessively thin. For a 92-Å film the values of *k* were too small and the values of *n* were too large as compared with results on films thicker than 250 Å. This behavior is analogous with our results for gold[3] and chromium and is qualitatively predicted by Maxwell-Garnett theory.[11] Our final results on palladium are the average of experiments on 277- and 375-Å films. Both of these sets of films were evaporated at a rate of about 50 Å per second, and both films yielded results which agree within the estimated error.

Finally in the case of palladium several additional films were formed by sublimation of the palladium at a rate of 0.3 Å per second. One film was sublimed from palladium on a single-strand tungsten filament and another directly from a palladium wire itself used as a filament. Both of these methods agreed well with one another, thereby indicating that although palladium alloys with tungsten (even when it is sublimed), no tungsten was being deposited in our palladium films. Nevertheless, the optical constants determined from the sublimed films differed from the preferred values obtained from the quickly evaporated films. The difference is due to the fact that the reflectance was much lower for the sublimed films.

Annealing of the films in a nitrogen atmosphere indicated that the quickly evaporated films were smooth and homogeneous since, like the noble metals,[3] they did not change after annealing. When the sublimed films were annealed, however, the transmission increased in the ultraviolet and decreased in the infrared, while the reflection did just the opposite. (The crossover point was near 4 eV.) Since the sublimed films changed during the anneal, it seems likely that these films were inhomogeneous to begin with. Therefore, the quickly evaporated films give values of the optical constants more representative of bulk palladium.

IV. DISCUSSION

A. Comparison with theory

One would like to discuss separately free-electron and interband contributions to the optical conductivity. In the noble metals, free-electron effects are dominant for photon energies as large as 2 eV.[3] The intraband contribution to the dielectric constants can, therefore, be separated from the interband contribution by determining values for the free-electron optical mass and relaxation time at long wavelengths. The optical mass is determined from the long-wavelength slope of a plot of $-\epsilon_1$ vs λ^2 and then the relaxation time from the slope of a plot of ϵ_2/λ vs λ^2. Such a technique fails for the transition metals discussed here, since the plots are not linear as required by free-electron theory. Thus it seems that interband transitions contribute significantly throughout our entire spectral range.

Several attempts have been made previously to determine the free-electron contribution by extending reflection measurements further into the infrared. Lenham and Treherne[12] made measurements out to 15 μm for most of the metals we are discussing. At these long wavelengths, they determined values for the optical mass and the relaxation time τ, but even their plots clearly showed contributions of interband transitions. We note[3] furthermore that the straight line plot of ϵ_2/λ vs λ^2 is only expected in the approximation that $\omega \gg 1/\tau$. For the relaxation time calculated from a typical dc conductivity of transition metals, $1/\tau$ corresponds to a wavelength of about 15 μm. Since this wavelength is near the end of Lenham and Treherne's measured range, the approximation may not be valid in the interpretation of their data. Lenham[10] later attempted to fit their data in the far infrared to a relation λ^α by plotting ϵ_2/λ versus wavelength on a log-log scale to get a linear plot with slope α. Although this is purely an empirical procedure, Lenham found reasonably straight lines, but α was closer to 1 than to 2. A value of $\alpha \approx 1$ is not surprising, however, since as we noted $\alpha = 2$ results only when $\omega \gg 1/\tau$. When $\omega \ll 1/\tau$, $\alpha = 0$. Therefore, when $\omega \approx 1/\tau$ an intermediate value of α seems reasonable. Recently Jones, Palmer and Tien[13] made absorptivity measurements on chromium, iron, and nickel to wavelengths as long as 50 μm. They found that the anomalous-skin-effect theory fairly well represented their measured absorptivity for wavelengths longer than 15 μm. In addition Barker and Ditzenberger[14] used a free-electron-gas model to estimate the size of the anomalous skin effect and to calculate the corresponding absorptivity of chromium. Finally Sasovskaya and Noskov[15] did a free-electron analysis of nickel in the spectral range 0.3–18 μm and calculated the free-electron contribution. We have used the free-electron parameters of all these authors to calculate the intraband contribution to our values of the conductivity. The results of these calculations contribute a negligible part of our total values. Therefore, our measurements (which are all below 2 μm) are presumed on all the evidence to be entirely within the interband portion of the spectrum.

In this interband region of the spectrum, we will compare our results with two recent calculations of optical conductivity. Moruzzi, Williams, and Janak[1] have calculated the interband contribution to ϵ_2 for vanadium, chromium, and nickel. These self-consistent effective one-electron calculations use the approximate treatment of exchange and correlation due to Kohn and Sham[16,17] and the "muffin-tin" approximation to both the charge density and the potential. These approximations permitted the evaluation of the excitation energies and probabilities (momentum matrix elements) throughout the Brillouin zone. The results are compared with our experimental values of σ_1 in Figs. 2, 3, 4, respectively. The agreement is encouraging, although not quite so good as in the case of copper,[3] for which Williams *et al.* previously carried out a similar calculation (Fig. 5). The experimental peaks can all be correlated with theoretical ones, but they are generally broader and lower than the theoretical ones, however, and most are shifted about $\frac{1}{2}$ eV down in energy. These differences may be partly because the measurements were made at room temperature, but it seems unlikely that the temperature dependence can be strong enough to account for the entire discrepancies.

Wang and Callaway[2] have calculated σ_1 for ferromagnetic nickel, and their results are also shown in Fig. 4. Their calculation of energies started from a self-consistent potential using the tight-binding method. The spin-orbit interaction and the exchange coupling of spins were included. The

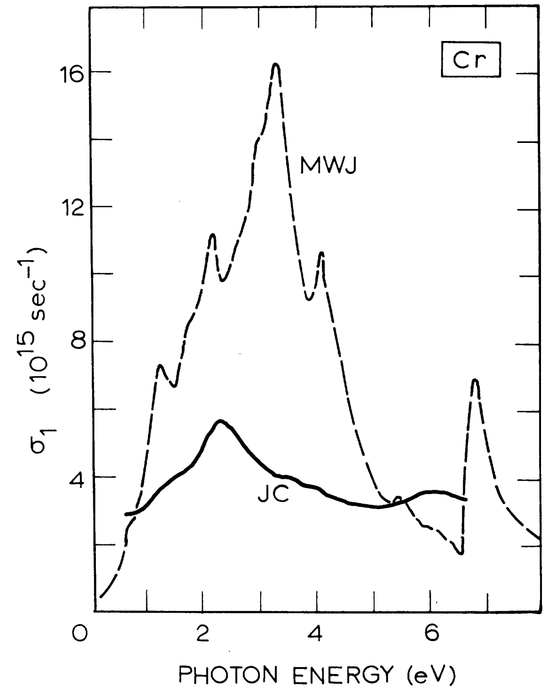

FIG. 3. Our experimental optical conductivity of chromium (JC) compared with the theoretical curve of Moruzzi, Williams, and Janak (MWJ).

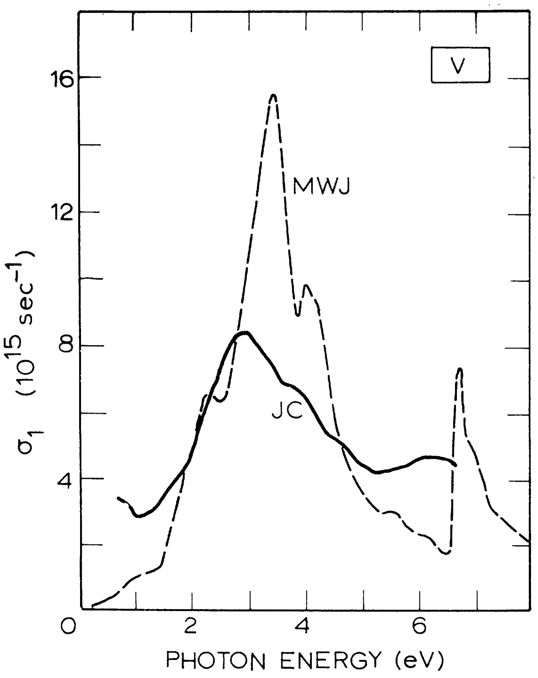

FIG. 2. Our experimental optical conductivity of vanadium (JC) compared with the theoretical curve of Moruzzi, Williams, and Janak (MWJ).

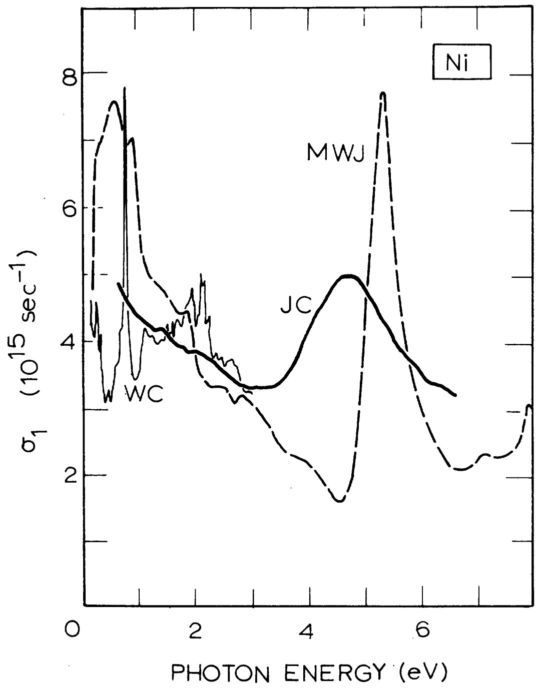

FIG. 4. Our experimental optical conductivity of nickel (JC) compared with the theoretical curves of Moruzzi *et al.* (MWJ) and of Wang and Callaway (WC).

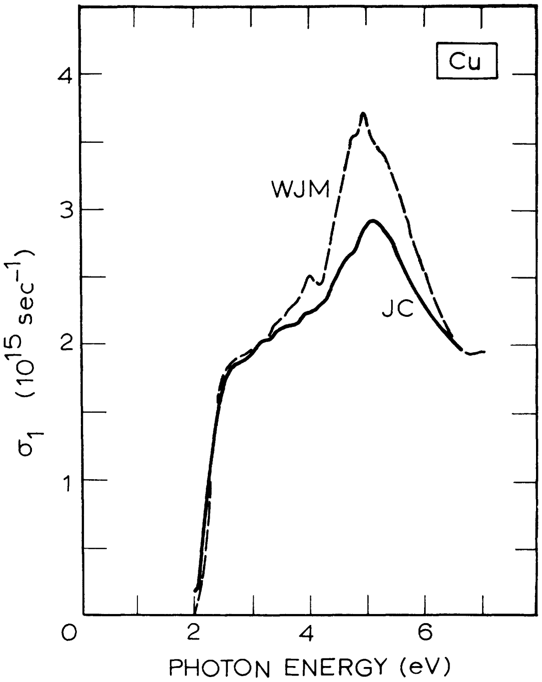

FIG. 5. Our experimental interband optical conductivity of copper (JC) compared with the theoretical curve of Williams, Janak, and Moruzzi (WJM), from Ref. 3.

calculated anisotropy is negligible over the range shown in Fig. 4, and the general magnitude of σ_1 is again in good agreement with experiment in this range. Again, some thermal smoothing of the experimental results could be expected, but we do not see the sharp fine structure of the theoretical calculation. (Our instrumental energy resolution is considerably better than would be required to see it.)

In the past, especially for nickel, considerable effort has been made to identify experimental conductivity peaks with energy gaps at symmetry points in calculated band structures. (See Ref. 2 for a representative band diagram of Ni.) This has led to controversy, partly because the possibility of a shift in the calculated energies is admitted and also because even the ordering of the bands is uncertain at some points in k space. In nickel, for example, the energy of the $L_{2'}$ point may be higher[2,18] or lower[2,19-21] than that of L_{32}, for either or both spin systems, with consequent uncertainty in the detailed identification of peaks. Recently it has been more generally appreciated that in metals (in contrast to semiconductors) the structure may arise from transitions in large volumes of k space at general points in the Brillouin zone.[22] In terms of the band structure and transition probabilities calculated by Moruzzi *et al.*[1] all over k space, we can try to identify structures in their calculated conductivity curves (recognizing that the experimental curves are all offset to lower energies).

All three theoretical curves for V, Cr, and Ni have a high-energy peak (Ni near 5.3 eV, V and Cr near 6.7 eV). In the case of Ni this peak appears to be due to transitions between bands 1→6 (where the bands are numbered in order of increasing energy at each k), with large contributions along all three of the Λ, Δ, and Σ directions in the Brillouin zone. (The possibility of contributions along Σ was suggested early on.[18]) The 1→6 transition in these regions is from the lowest d band to a free-electron-like band. For V and Cr the high-energy peak also appears to be due to a 1→6 transition; contributions are coming from transitions over a large volume of k space along the three major directions (Λ, Δ, and Σ). In these cases of the 1→6 transition, both bands appear to be more free electronlike.

The 1.8-eV structure in the theoretical Ni curve as well as the main peaks in σ_1 for V and Cr near 3.4 eV are primarily due to transitions between bands 3→5 around the Λ direction, with some additional contribution to the Ni curve from a 3→5 transition near Z.

The band structures calculated for V and Cr are almost identical. The Fermi level of vanadium is about 1.3 eV lower; nevertheless, many of the transitions causing structure in the conductivity curves are the same (e.g., 1→6 and 3→5, as mentioned above), even in energy. In addition for Cr and V the peaks near 4 eV correspond to 1→4 transitions and the peaks just above 2 eV correspond to 3→4 transitions. The strongest contribution to the 1→4 transitions seems to be near the P symmetry point with additional 1→4 contributions resulting from transitions along Δ and near G. The 3→4 transitions corresponding to the 2-eV peak probably occur away from a symmetry point along Λ or near G.

B. Comparison with other experiments

We next compare our results for each metal with other recent experiments and discuss possible reasons for differences. All experiments are in reasonably good agreement about the location of structure in the conductivity curves. We will comment only on structures about whose existence there has been some controversy in the literature, and on differences between the general magnitude of our conductivity and others'.

1. *Titanium*

The reflectance of freshly deposited opaque titanium films was measured from 0.1 to 6.2 eV by

Hass and Bradford.[8] Their films were evaporated at a pressure less than 5×10^{-6} Torr at a deposition rate greater than 40 Å per second. Although the structure in their reflectance curve agrees well with ours, their values for the reflectance are everywhere lower than the reflectance from our opaque films. Their lower values for the reflectance may result from the longer exposure of their films to the air. Our films were measured in a nitrogen atmosphere.

In addition to measuring the reflectance from titanium films, Hass and Bradford also measured the optical constants of titanium with an ellipsometric method at four different wavelengths. Their values of the optical constants are in reasonably good agreement with ours. Their values of n are slightly smaller at higher energies and bigger at lower energies while their values of k are slightly smaller than ours at all of their measured energies.

2. *Vanadium*

The reflectance of vanadium has recently been obtained by Weaver.[23] He made absorptivity measurements[24] ($A=1-R$) on bulk vanadium samples at liquid-helium temperature in the spectral range 0.15–4.88 eV. The gross magnitude of our reflectance (measured on opaque films at room temperature) in general agrees with Weaver's; however, his curve has more structure. It seems likely that our curve is thermally broadened.

Weaver used a Kramers-Kronig analysis of his absorptivity data to determine the dielectric constants of vanadium. Our values of ϵ_1 agree rather well, but our values of ϵ_2 are noticeably higher. This difference is probably due to a combination of thermal effects and Weaver's high- and low-energy extrapolations necessary to evaluate the Kramers-Kronig integrals.

3. *Chromium*

Bos and Lynch investigated the absorptivity of bulk chromium at 4.2 K from 0.1 to 5 eV using a calorimetric technique.[24] Their corresponding reflectivity ($R=1-A$) is about 7–15% greater than ours throughout the measured range. This discrepancy is puzzling since it seems very unlikely that it could be entirely due to the temperature dependence or to oxidation.[5] The agreement with Barker and Ditzenberger[14] below 1.5 eV is even worse.

Graves and Lenham[25] have also investigated chromium. They determined the dielectric constants from 2 to 5.6 eV at room temperature, using three reflectance measurements at various angles from a mechanically polished bulk sample. Their values of $-\epsilon_1$ and ϵ_2 are larger than ours. This discrepancy may be due to the fact that reflectance measurements at large angles of incidence are very dependent on the sample's surface preparation.

4. *Manganese*

We could find no recent measurements on manganese except those of Lenham and Treherne[12] previously referred to.

5. *Iron*

The reflectance from an etched slab of high-purity iron was measured by Blodgett and Spicer.[26] Their measured reflectance is in reasonably good agreement with our measured reflectance from vacuum-evaporated opaque films.

The optical constants of iron in the visible region of the spectrum have been determined by Yolken and Kruger[27] using an ellipsometric technique. Their values of the optical constants are everywhere higher than ours. When their optical constants are used to calculate the reflectance from opaque samples, one finds that the predicted reflectance is about 10% greater than the above measured values over most of their wavelength range. Their high values for the optical constants probably result from the surface preparation for their samples, on which the ellipsometric technique is highly dependent. A similar and more conclusive case will be discussed below for nickel.

6. *Cobalt*

The reflectance of cobalt has been measured by Yu, Donovan, and Spicer.[28] The normal-incidence reflectance from opaque cobalt films evaporated in ultrahigh vacuum (2×10^{-9} Torr) was measured *in situ* from 3.5 to 11.8 eV. In the region of overlap from 3.5 to 6.5 eV, our reflectance values were about 1% higher than theirs. The fact that our film's reflectance was even higher than their ultrahigh vacuum measurements is probably because their films were deposited at a slow evaporation rate (about 5 min total). We observed that slow evaporation rates decrease the reflectance in palladium (see below).

They also measured the reflectance of their samples from 0.05 to 5.1 eV after a short exposure to air. In the region of overlap with their own high-vacuum measurements, a decrease in the reflectance was observed. They accounted for this decrease by assuming that a 25-Å film of CoO was formed on the cobalt film's surface after the brief exposure to air. Our technique of backfilling the bell-jar system with nitrogen instead of air seems to greatly reduce the oxidation rate of the films.

Finally, Yu, Donovan, and Spicer use their reflectance measurements to determine the dielectric constants of cobalt by means of a Kramers-Kronig analysis. However, they point out that the magnitudes of their dielectric constants depend on the extrapolations chosen for the Kramers-Kronig integrals.

7. *Nickel*

Nickel has been the most extensively investigated of the metals under consideration. Vehse and Arakawa[29] measured in a vacuum of 10^{-8} Torr the reflectance of opaque evaporated nickel films deposited at a rate of 150 Å per second. Their measured reflectance agrees well with the reflectance of opaque samples which we calculated using our n and k values from measurements on thin semitransparent films. Our calculated reflectance also agrees well with the reflection measurements of Ehrenreich, Philipp, and Olechna[18] on electrolytically etched and those of Seib and Spicer[30] on mechanically polished bulk samples.

Ehrenreich, Philipp, and Olechna used a Kramers-Kronig analysis of their reflectance data to obtain the dielectric constants. Although the gross structure of their dielectric constants agrees with ours, the magnitudes of the curves differ. The discrepancy is probably due to their choice of extrapolation to frequencies outside the range of measurement.

Shiga and Pells[20] made ellipsometric measurements on mechanically polished bulk nickel samples. As was also the case in copper and gold,[3] their values of ϵ_2 are considerably larger than ours. When one uses their values of n and k for nickel to calculate the reflectance from opaque samples, the calculated reflectance near 6 eV is as much as 10% greater than the four experimental values referred to above. This discrepancy may be due to the surface preparation of their samples, since ellipsometric measurements are highly dependent on surface condition.

Finally the optical properties of single-crystal nickel at 4 K were investigated by Lynch, Rosei, and Weaver.[22] They used a calorimetric technique[24] to measure the absorptivity from 0.08 to 3 eV. Their corresponding values for the reflectivity of nickel are everywhere slightly lower than ours, although this difference may be due to the different temperatures for the measurements.

The structure in the absorption (ϵ_2 or σ_1) of nickel has been discussed.[18,20-22,31,32] There is general agreement that a small peak in σ_1 exists near 1.4 eV and a large principal absorption peak exists near 4.7 eV. These two peaks appear in our data but we also see an additional small shoulder just above 2 eV. This shoulder is smaller than our estimated error, but we think it is real since it appeared in all four of our thin nickel films. The existence of structure in this region of the spectrum was previously suggested[21,31] from ellipsometric measurements, but no evidence for it could be found in careful reflectance measurements.[22,32] This difference is understandable, since in our measurements the structure shows itself mainly in the transmittance, not the reflectance. (Also, application of the Kramers-Kronig analysis tends to smooth out structure.[5])

8. *Palladium*

The optical constants of palladium have been the subject of several recent investigations. The most recent is that of Vehse, Arakawa, and Williams,[33] which gives references to previous work. Their palladium films were deposited in a vacuum of 10^{-8} Torr at a high rate of 150 Å per second. The reflectance of their films was then immediately measured *in situ*. Using our values of n and k determined from measurements on thin semitransparent films, we calculated the reflectance from an opaque sample. These calculated reflectances agree well with their experimental values from opaque samples. Their values of the optical constants do not agree so well with ours, probably due to the form of their Kramers-Kronig extrapolations to frequencies outside their measured range.

Another recent study of palladium was made by Yu and Spicer,[34] who measured the reflectance of opaque palladium films from 2.2 to 11.6 eV. Their films were vacuum evaporated at a pressure of about 5×10^{-9} Torr. However, their evaporation rate was very much slower than ours or that of Vehse *et al.* As a result, their reflectance was measurably lower than ours, especially at higher photon energies. Their slowly evaporated films were probably similar in structure to our slowly sublimed palladium films, since these sublimed films showed a decreased reflectance similar to that of Yu and Spicer's. Their low reflectance values probably account for most of the differences between their values of the dielectric constants and ours, although their Kramers-Kronig analysis could have introduced additional error.

C. Effects of oxidation

Since so many of the materials we have discussed oxidize rapidly in the air, it is appropriate to investigate in some detail the error introduced by the oxide layers. The effect of a thin oxide layer on a thick metal layer can be calculated by applying the reflectance formula.[35] The normal-incidence reflectance of an opaque metal coated with a transparent oxide is

$$R=\frac{r_{12}^2+r_{23}^2-2r_{12}r_{23}\cos(\delta+\phi)}{1+r_{12}^2r_{23}^2-2r_{12}r_{23}\cos(\delta+\phi)},$$

where $\tilde{r}_{12}\equiv -r_{12}$ and $\tilde{r}_{23}\equiv r_{23}e^{i\phi}$ are the Fresnel coefficients for the air-oxide and the oxide-metal boundaries, respectively, $\delta\equiv 4\pi n_0 t/\lambda$, n_0 and t are the refractive index and thickness of the oxide layer, and λ is the vacuum wavelength of the light. The effect of a very thin transparent oxide is given by

$$\left.\frac{dR}{dt}\right|_{t=0}=-\left(\frac{8\pi n_0}{\lambda}\right)\frac{\mathrm{Re}\tilde{r}_{12}\mathrm{Im}\tilde{r}_{23}(1-r_{12}^2)(1-r_{23}^2)}{(1+r_{12}^2r_{23}^2+2\,\mathrm{Re}\tilde{r}_{12}\tilde{r}_{23})^2}.$$

Since $\mathrm{Re}\tilde{r}_{12}<0$ and $\mathrm{Im}\,\tilde{r}_{23}<0$, the effect of a thin transparent oxide is always to *reduce* the reflectance of the bare metal. If the oxide layer is absorbing, with optical constant n_0+ik_0, the expression[5] for $dR/dt|_0$ is much more complicated, but the leading term is still the same (with the properly modified Fresnel coefficients $\tilde{r}_{12}$ and $\tilde{r}_{23}$). Still the effect of the oxide is to reduce the reflectance when $k>k_0n/n_0$, as is always the case for these metals below 7 eV. For $n_0=2.5$ (typical of a transition-metal oxide), $-dR/dt|_0<10/\lambda$ in our wavelength range. Figure 6 shows the exact values of $-dR/dt|_0$ for transparent ($k_0=0$) and absorbing ($k_0=1$) cases. (For the absorbing case, the above expression gives values about 25% too small over most of the range.)

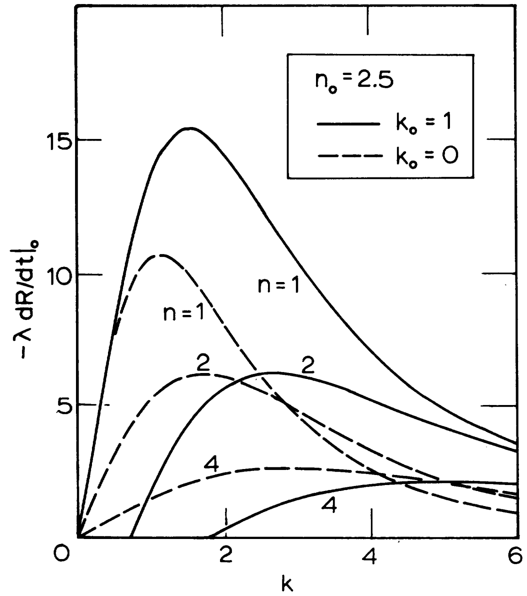

FIG. 6. Rate of decrease of reflectance R with oxide thickness t (X wavelength of light λ), for a very thin transparent ($k_0=0$) or absorbing ($k_0>0$) oxide of refractive index $n_0=2.5$, covering a very thick metal (optical constants n,k).

The largest errors in R occur at the shortest wavelengths. Our largest errors in the optical constants (particularly in n) result, however, near the tangency of the contours for $n\approx k+1$, and here $-dR/dt|_0<5/\lambda$. Since this case is approached in the visible region for some of the transition metals, here $dR/dt|_0\approx -0.1\%/\mathrm{\AA}$ of oxide. Thus a 5-Å oxide layer could reduce R by our nominal error of measurement, and so the effect of oxidation is serious. We may note, however, that an additional 10 Å of oxide would have spoiled the convergence of the inversion calculation in these cases; since the calculations always converged, the actual oxide layers must have been very thin. In the uv region, an oxide layer would reduce R by five times as much as in the visible, but on the other hand the effect of an error in R is more than five times smaller than in the visible, and so the net effect on the absorption is about the same throughout our range of measurement. Furthermore, in those cases where the measured rate of change of reflection in the uv due to oxidation was extrapolated to the moment of film formation, we found that any change which occurred was within our estimated error.

The effect of a very thin transparent oxide layer on the normal-incidence transmittance is similarly calculated to be[5]

$$\left.\frac{dT}{dt}\right|_{t=0}=\frac{T(8\pi n_0/\lambda)\,\mathrm{Re}\tilde{r}_{12}\,\mathrm{Im}\tilde{r}_{23}}{(1+r_{12}^2r_{23}^2+2\,\mathrm{Re}\tilde{r}_{12}\tilde{r}_{23})},$$

for a thick metal film in which multiple reflections are negligible. The effect of a thin transparent oxide is always to *increase* the transmittance. To a very rough approximation,

$$\left.\frac{dT}{dt}\right|_0\simeq -T\left.\frac{dR}{dt}\right|_0,$$

and so for thick films (small T) the change in T due to the oxide layer is small compared to the change in R. Additionally, since here the oxidation reaction actually consumes some of the metal, the transmittance is further increased because of the thinning of the metal layer. If β is the thickness ratio of metal consumed to oxide formed, the additional contribution to $dT/dt|_0$ is $T(4\pi/\lambda)\beta k$. This contribution to the increase is much greater than that of the oxide layer itself when $\beta\cong 0.8$, typical for a transition metal oxide. If the oxide is absorbing, the main result[5] is to replace βk by $\beta k-k_0$, as thinning of the metal is compensated by absorption in the growing oxide. Thus the transmittance is increased for $k>k_0/\beta$, as is generally true in our cases. Fortunately, with the

$R-T$ method, the increase in T partially compensates the effect of the decrease in R on the optical absorption. The over-all effect of an oxide layer could be to make our absorption values somewhat too large.

V. SUMMARY AND CONCLUSIONS

We have used the technique of measuring three reflections and transmissions from evaporated films in order to determine accurate values for optical constants in the spectral range from 0.5 to 6.5 eV. Our technique was essentially the same as that used for the noble metals[3]; however, in most cases (Ti, V, Cr, Mn, Fe, Co) we substituted the reflectance from opaque films for the reflectance from semitransparent films in our inversion method. Our estimates of error in the optical constants, based on the instrumental accuracy of the spectrophotometer, are less than ±1% in k and less than ±2% in n for most of the values. The results determined by our thin-film measurements are believed to be representative of the bulk material. In all cases (except as noted for vanadium) for sufficiently thick films the results from films of different thicknesses agreed well. The thick film limit was observed in films as thin as 250 Å, except in the case of chromium where this limit was not attained until about 400 Å.

The surfaces of all of the materials except Pd were subject to oxidation. (The rate of oxidation was greatly accelerated by raising the temperature to 150 °C.) Therefore, the measurements on films which oxidize rapidly were made in a nitrogen atmosphere, which in all cases slowed the rate of oxidation enough so that the observed decrease of reflectance was within our estimated instrumental error. Nevertheless, the samples were presumably covered by a few atomic layers of oxide. Estimates based on theory indicate that a 5-Å layer would measurably affect the results, but the evidence suggests that the oxide was not any thicker than that. In any case, the increase in T partially compensates the effect of the decrease in R on the optical absorption.

No anisotropy was observed for the noncubic (Ti, Co) or the magnetic (Cr, Fe, Co, Ni) materials. We therefore conclude that our values represent averages over all crystal directions.

In comparison with other recently published experiments, our measured or calculated values for the reflectance from opaque films were at least as large as other room-temperature values (with the possible exception of chromium), including some measurements made in ultrahigh vacuum. The gross structure in our conductivity curves agrees well with other experiments. In the case of nickel we definitely saw a small shoulder above 2 eV. The presence of structure here has previously been controversial.

The free-electron contribution to the optical conductivity is negligible over our whole spectral range. The interband conductivities calculated by Moruzzi, Williams, and Janak agree reasonably well with our results for vanadium, chromium, and nickel, and also for copper. They reproduce the structure as a function of photon energy. The calculation for nickel by Wang and Callaway also agrees reasonably well.

We are especially indebted to Dr. A. R. Williams and V. L. Moruzzi for helpful discussions. We also thank them, as well as Dr. C. S. Wang and Prof. J. H. Weaver, for sending us unpublished results.

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