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Optical conductivity of bcc transition metals: V, Nb, Ta, Cr, Mo, W

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The optical constants n and k were determined for the bcc transition metals of the V and Cr groups from reflection and transmission measurements in the spectral range 0.5–6.5 eV. The optical measurements were made at room temperature on polycrystalline thin films, vacuum evaporated rapidly onto high-temperature (700–1000°C) fused-quartz substrates. The films were found to be well crystallized, and the reflectance of opaque films agreed with previous bulk values. For the thin-film results to be representative of bulk crystals, high substrate temperature was essential for the Cr group, and rapid evaporation rate for the V group. The values for Cr are a significant improvement over earlier results of Johnson and Christy, but those for V are only a slight improvement. Some recent calculations of the interband optical conductivity agree reasonably well with our results for V, Cr, Nb, and Mo. Direct transitions between d bands seem to account for the optical structure.

I. INTRODUCTION

There is considerable interest in understanding the electronic energy-band structure of the transition metals. Extensive and increasingly realistic theoretical band calculations of both the *ab initio* and pseudopotential types have led to detailed predictions of many physical properties of these metals. Results of optical studies have been particularly important since the interaction with photons is directly linked to the intraband and interband transitions between electronic states predicted by the theoretical models. There is general agreement among different investigators as to the large-scale structure of the experimentally determined optical conductivity of the transition metals, but frequently there is disagreement in the detailed structure, magnitudes occasionally disagreeing by as much as a factor of 2. Recent quantitative calculations of the interband optical constants have taken into account joint density of states and sometimes transition-probability matrix elements throughout the Brillouin zone, and, as a consequence, it has become important to reduce the scatter in accepted experimental results. In this study we report on the experimental optical properties of the body-centered-cubic (bcc) transition metals V, Nb, Ta, Cr, Mo, and W, over the photon-energy range 0.5 to 6.5 eV. These are absolute results, not dependent on a Kramers-Kronig analysis.

Our thin-film technique, for determining the optical constants and film thickness self-consistently, utilizes the measured normal-incidence transmittance and reflectance and p-polarized transmittance at 60° incidence angle.[1,2] The method does not rely on extrapolations of data outside the measured photon-energy range, and was found to be relatively insensitive to oxide layers. It is assumed that the sample is smooth, homogeneous, and with a large grain size sufficient to give the bulk optical properties. Vapor-quenched thin films of high-melting-point materials (such as the metals studied here), however, may be highly disordered (microcrystalline)[3–5] so that special precautions are required to produce well-crystallized films with bulk optical properties—in particular, we find that the substrate must be heated to high temperatures and the evaporation rate must be fast. In this paper we report optical conductivities that we believe to be characteristic of the bulk material, and compare the results with recent band-structure calculations.

II. EXPERIMENTAL RESULTS

Our general procedure has been described previously.[2] The films were produced in an oil-pumped, liquid-nitrogen-trapped bell-jar vacuum system with a base pressure of 2×10^{-7} Torr (3×10^{-5} Pa). The evaporation of these refractory metals was by means of an Airco-Temescal 6-kW electron-beam evaporator, from material supplied by the Materials Research Corp., MARZ grade. The substrates were polished fused-silica blanks, $\frac{1}{16}$ in. (0.158 cm) thick; they were cleaned in chromic-sulfuric acid solution, followed by two distilled water rinses and a methanol rinse in an ultrasonic sink. Prior to evaporation, the substrates were heated to above 500 °C in the vacuum system by a 0.0005-in.-thick tantalum-foil heater backing the substrate.[6] The substrate temperature (Table I) necessary during evaporation to produce well-crystallized films varied for the different metals. The substrates were protected by a shutter that opened and closed in the same direction, giving uniform film thickness even for fast evaporation rates. Film thickness was controlled by a

TABLE I. Evaporation conditions and film thicknesses.

Element	Substrate temperature (°C)	Deposition rate (Å/sec)	Average pressure (Torr)	Film thickness (Å)
V	550	20	5×10^{-7}	219
	750	215	2×10^{-7}	430
	750	317	2×10^{-7}	2000
Nb	750	40	5×10^{-7}	288
	800	18	7×10^{-7}	246
	750	55	5×10^{-7}	1740
Ta	1000	52	5×10^{-7}	234
	1000	60	2×10^{-6}	1770
Cr	700	100	5×10^{-7}	319
	700	150	3×10^{-7}	269
	700	350	5×10^{-7}	2000
	700	500	5×10^{-7}	2000
Mo	1000	90	7×10^{-7}	201
	1000	110	7×10^{-7}	273
	1000	100	8×10^{-7}	1700
W	1000	30	3×10^{-6}	264
	1000	30	3×10^{-6}	242
	1000	40	5×10^{-6}	1700

Sloan deposit thickness monitor. System pressure was typically in the range $2-50\times10^{-7}$ Torr ($3-70\times10^{-5}$ Pa) during evaporation, the lower pressure for materials that acted as getters (V, Cr). Evaporation rates for opaque films were the highest rates that could be achieved with the electron-beam apparatus; for thin films the rate was limited to less than 100 Å/sec to maintain control of thickness. Reflection and transmission measurements on the films were made at room temperature with a Unicam SP 700 double-beam recording spectrophotometer equipped with a Harrick V-W absolute reflectance attachment. The accuracy of reflectance measurements was about ± 0.005. It was found that all the metals except for vanadium were resistant to oxidation: UV reflectance measurements did not change at least for several hours, and in the case of Cr, Mo, and W, for months.

The optical constants n and k as well as film thickness d were determined by inverting the normal incidence reflectance and transmittance along with the p-polarized transmittance at 60° angle of incidence, with the reflectance measured from opaque films (about 2000 Å thick). This allowed us to compare our reflectance directly with published bulk results, and provided a more accurate inversion[2] for n, k, and d. The frequency-dependent dielectric function and conductivity were found from $\hat{n}=n+ik$ by the relations $\hat{\epsilon}=\hat{n}^2$ and $\hat{\sigma}=-i(\hat{\epsilon}-1)\omega/4\pi$. The values were averaged from reflectance measurements on opaque films and transmission measurements on semitransparent films with thickness shown in Table I, which also gives the deposition conditions. It was found from ancillary measurements that films with thickness greater than about 200 Å gave consistent results within the instrumental error (about ± 2% in n and k). These results, in terms of the optical conductivity $\hat{\sigma}(\omega)=\sigma_1(\omega)+i\sigma_2(\omega)$, are presented graphically in Figs. 1–6. The width of the curves represents the effect of instrument uncertainties on the values for $\hat{\sigma}(\omega)$. (The numerical results for the optical constants n and k are available on request from the authors.)

X-ray-diffraction experiments[3] were performed on the films to determine grain size, lattice constant (a possible indicator of film stresses), and crystal structure. Films were considered to be well crystallized and smooth when (1) x-ray-diffraction patterns showed sharp lines of the correct crystal structure, with no indication of oxides, nitrides, or silicides (a product of film-substrate reactions), and (2) the reflectance of opaque films agreed with published bulk values. X-ray-diffraction studies of opaque films revealed a grain size of 150 Å for V and 200 Å for Nb, as determined by the Scherrer equation.[7] Films evaporated onto substrates hotter than 750 °C (V) or 800 °C (Nb) reacted with the substrate, as evidenced by the presence of silicide lines in the diffraction pattern. Both V and Nb films were highly textured, with (110) planes parallel to the substrate. The lattice constant determined from the (110) reflection was about 1% smaller than bulk American Society for Testing and Materials (ASTM) values: 2.988 Å for V and 3.270 Å for Nb, probably be-

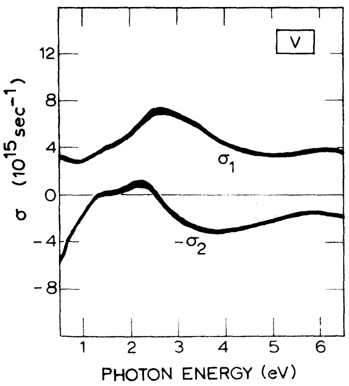

FIG. 1. Experimental optical conductivity of V. The width of the curves is representative of experimental error.

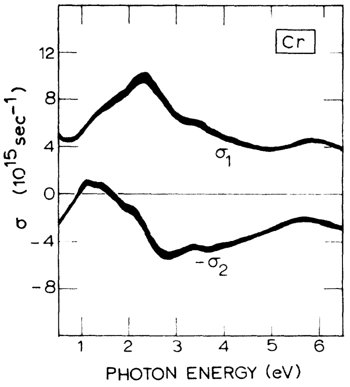

FIG. 4. Same as Fig. 1 for Cr.

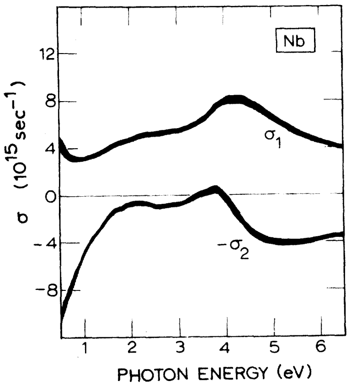

FIG. 2. Same as Fig. 1 for Nb.

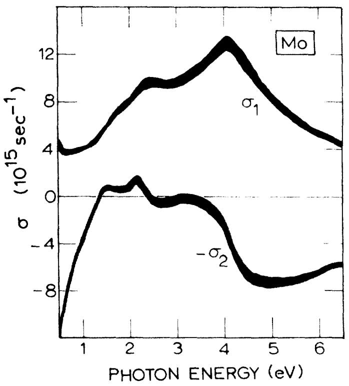

FIG. 5. Same as Fig. 1 for Mo.

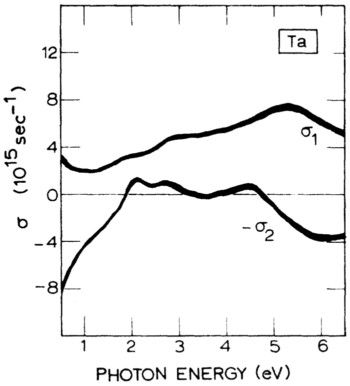

FIG. 3. Same as Fig. 1 for Ta.

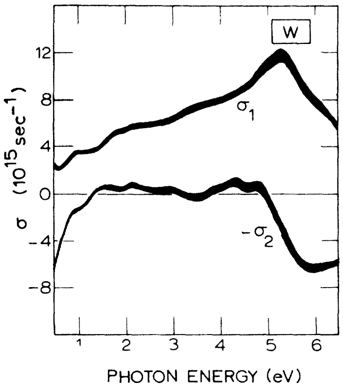

FIG. 6. Same as Fig. 1 for W.

cause of residual tensile stresses in the plane of the film leading to compressive strains in the [110] direction normal to the film (due to Poisson's ratio). X-ray diffraction showed the opaque Ta film to be well crystallized (> 400-Å grain-size) bcc material with a lattice constant the same as bulk material: 3.306 Å. The measured grain size of the semitransparent bcc Ta film used for optical properties was about 200 Å, film-thickness limited. (Some other thin films showed traces of a second phase, of β-Ta, even after several minutes annealing in vacuum at 1000 °C; the transmittance of these did not give convergence of the optical inversion routine.) All bcc Ta films were strongly textured with (110) bcc planes parallel to the substrate. The Cr, Mo, and W films showed well-crystallized bcc structure in all cases. Opaque films showed sharp x-ray diffraction lines limited by diffractometer slit resolution, indicating a crystallite diameter greater than 400 Å. Thin films showed broader lines, indicating a grain size of about 250 Å, essentially film-thickness limited. The lattice constant measured from the (110) x-ray line was found to be 0.5% smaller than the ASTM value for all three metals: 2.872 Å for Cr, 3.134 Å for Mo, and 3.139 Å for W. More accurate, higher-order x-ray lines were available for W, and the lattice constant was still found to be 0.3% smaller than bulk: 3.155 Å based on (200) and (211) reflections.

The reflectance of opaque V and Nb films showed a strong evaporation-rate dependence, with high rates producing the most highly reflecting films. The reflectance increased most in the ultraviolet energy range: 6% at 6-eV photon energy for V when the evaporation rate was increased from 21 to 317 Å/sec; 12% for Nb at the same energy for an evaporation rate increase from 20 to 55 Å/sec. This behavior suggests that the slowly evaporated films were rough, as was confirmed[4] by studying the detailed behavior of the reflectance difference between shiny and dull films as a function of wavelength, according to the model for scattering from rough surfaces in the Bennett-Porteus theory.[8] The reflectance of the rapidly evaporated opaque films was compared with bulk-sample results[9-11] measured at 4 K. Below 5 eV the agreement is quite good, with some fine structure seen in the bulk data that is probably washed out due to thermal broadening in ours, measured at 300 K. Above 5 eV our reflectance is much higher for V (Ref. 9) and slightly higher for Nb.[10,11] The discrepancies in the UV region are probably due to surface roughness of the bulk samples, resulting from etching by their perchloric-acid electropolish.[12] The reflectance of the opaque Ta film was in very good agreement with bulk-sample results,[9] except for some slight thermal broadening in our film compared to the 4-K bulk results. For the Cr group, the reflectance of opaque films was compared to recent results from bulk samples for Cr,[13] for Mo,[9,14] and for W.[15] In all cases the agreement was excellent. Thus we conclude that our films deposited on heated substrates at fast evaporation rates were smooth and well crystallized, but contained considerable uniform lattice strain (up to 1% in V and Nb) that did not affect the reflectance.

Two of these metals, V and Cr, have been studied previously[2] by the same method, except that the films were evaporated onto room-temperature substrates instead of heated substrates. We find that the substrate heating is crucial for Cr (and Mo and W) but not for V (nor Nb). Our σ_1 and $|\sigma_2|$ are larger for Cr by as much as a factor of 2, but in essential agreement for V. The difference appears to be due to the gas-containing, fine-scale grain-boundary network that occurs in the Cr-group films at room temperature.[3,5] Actually, the previously reported[2] V results are also somewhat (up to 20%) in error, because of a mistaken extrapolation intended to account for a seeming thickness dependence presumed to be due to surface oxide coating; but, except for one (too thin) 167-Å film, the earlier results agreed with ours within experimental error (before the extrapolation).

Results from oblique reflectance[16] or Kramers-Kronig analysis[9-11,13-15] of normal reflectance are in satisfactory agreement with our conductivities. Thus, our absolute results confirm the extrapolation procedures that were chosen for the Kramers-Kronig analyses. Many ellipsometric measurements have also been reported,[4] mostly in the Soviet literature; some of these agree and some disagree, but they are too extensive to be reviewed in detail here.

III. COMPARISON WITH THEORY

The transition metals show some clear-cut trends in their electronic structure.[17] Moving horizontally across the periodic table, the energy of the *d* bands drops with respect to the low-lying *s-p* bands, and the Fermi level rises within the *d* bands. The width of the *d* bands increases, reaching a maximum with the Cr group, where the *d* bands are approximately half filled. The width then decreases until, at the noble metals, the *d* bands are completely filled, relatively narrow, and lie below the *s-p* bands at the Fermi level. Furthermore, as one progresses downward from the 3*d* to the 4*d* to the 5*d* metals, the width of the *d* bands increases.[18] The band structure of horizontally adjacent metals with the same crystal structure is quite similar, so that the rigid-band model might apply to such pairs,[17] e.g., the pairs Nb, Mo (Ref. 19) and Ta, W.[20] The systematics in the band structures of V, Cr; Nb, Mo; Ta, W have great influence on the optical properties of these metals. Transitions between individual *d* bands are responsible for much of the optical structure. Since the *d*-band width and individual band structure are similar for adjacent horizontal pairs, one would expect this structure in the optical properties to appear at similar energies. Furthermore, since the *d*-band width increases as one moves from 3*d* to 4*d* to 5*d* metals, one would expect the primary optical absorption band to increase in width moving from V to Nb to Ta and from Cr to Mo to W. This trend has been previously noted in the Cr group.[21]

It is appropriate to separate the effects of intra-

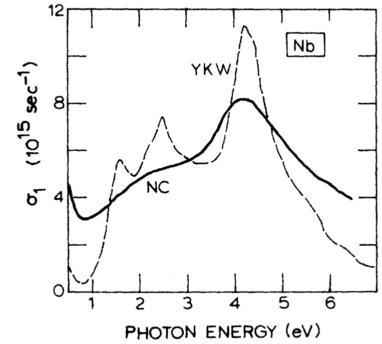

FIG. 7. Our (NC) experimental optical conductivity for Nb compared to the theoretical curve of Yamashita, Kubo, and Wakoh (YKW).

band absorption in the free-electron region of the spectrum from the interband absorption that occurs at higher energies. We used the Drude free-electron parameters derived from recent infrared measurements[22] to calculate the free-electron contribution to the total optical conductivity and find it to be insignificant above 1.0-eV photon energy. We therefore assume that our measurements are mainly within the interband portion of the spectrum, and make no attempt to subtract intraband from interband contributions to the conductivity for purposes of comparison with calculated interband optical properties.

Moruzzi, Williams, and Janak[23] calculated σ_1, the interband contribution to the optical conductivity, for V and Cr; and Laurent, Wang, and Callaway[24] for V. Both groups calculated the nonrelativistic band structure and the k-dependent matrix elements; but Moruzzi *et al.* used a self-consistent augmented-plane-wave (APW) approach with the treatment of correlation and exchange due to Kohn and Sham, while Laurent *et al.* used a self-consistent calculation employing the linear-combination-of-orbitals (LCAO) method with a basis of independent Gaussian functions and the Kohn-Sham-Gaspar local exchange potential. Their results for V are very similar, and for V the comparisons with our experimental curves resemble those published previously.[2,24] The theoretical peaks correlate with experimental peaks, but they are narrower and higher, and are shifted up in energy. Lifetime broadening of excited states equivalent to 0.5 eV would be necessary to reach agreement with the experimental results.[24] Our results for Cr are closer in magnitude to the calculation of Moruzzi *et al.* than the earlier work of Johnson and Christy,[2] but large amounts of thermal and lifetime broadening of the theoretical curve would still be required to get agreement in the magnitude of observed and calculated peaks. Yamashita, Kubo, and Wakoh[25] calculated the interband contribution to the dielectric function for Nb and Mo. Band structures and transition matrix elements were calculated throughout the Brillouin zone using a self-consistent APW model with full Slater exchange. The results (converted to conductivity) are compared to our values of σ_1 in Figs. 7 and 8. The agreement between experiment and theory is good, both in magnitude and energy for Mo and in energy for Nb. Peaks in the experimental curves can easily be associated with peaks in the theoretical curves; however, it appears that some thermal and lifetime broadening would give even better agreement, especially in the case of Nb. No calculations of σ_1 seem to exist for Ta (Ref. 26) or W.

Considerable effort has been expended to identify experimental peaks in the optical conductivity of these metals with interband transitions in regions of k space at or near symmetry points and directions in the Brillouin zone. This effort is complicated by the relative flatness of the d bands, especially *away* from the symmetry directions,[19] and the resulting uncertainty in the identification of transitions that involve large volumes of k space; but surprisingly consistent models have been developed to explain similar optical features in each metal.[4] Briefly, the main peak of σ_1 (at about 2.5 eV in V and Cr, 4 eV in Nb and Mo, and 5 eV in Ta and W) is due primarily to band $3 \rightarrow 5$ transitions; and the high-energy peak (at about 6 eV in V and Cr) is due to $1 \rightarrow 6$. Structure on the low-energy side of the main peak is more prominent in Mo and W than in Nb and Ta. This difference can be understood in terms of the rigid-band model: In Cr, Mo, and W, bands 2 and 3 are below the Fermi level near the zone center, but in V, Nb, and Ta they are above it. Both the above-mentioned calculations for V (and Cr) predict transition energies almost 1 eV larger than the ob-

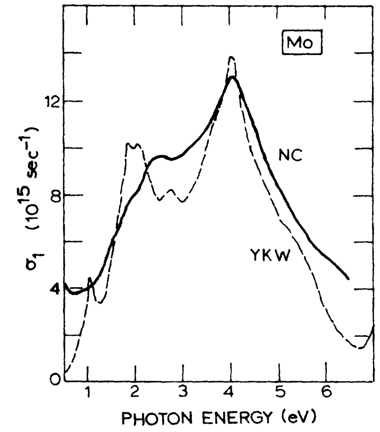

FIG. 8. Same as Fig. 7 for Mo.

served peak energies for these metals, but not a similar calculation for Nb and Mo. Since the optical features discussed above involve transitions between *d*-band states, it would appear that the theoretical models predict a too large total *d*-band width, with too much separation between individual bands. Recent work[27] on the effects of self-consistency and exchange on the band structure of V, Nb, and Ta suggests that the sensitivity of the calculated Fermi-surface shape and size to exchange parameters increases with decreasing atomic number Z. X-ray photoemission data,[28] however, indicate that the calculated[23,24] *d*-band placement below the Fermi level for V and Cr is quite good, certainly better than the agreement between these calculations and our measured optical properties. Thus it would seem that the major source of error between predicted and measured energies of the optical structure is due to placement of bands *above* the Fermi level.

The approach to the optical structure of transition metals based on the concept of "nondirect" (but not phonon-assisted) transitions,[29] in which k conservation is not an important selection rule, if of doubtful applicability.[30-32] Nevertheless, a comparison of direct and nondirect calculations for Mo (Ref. 31) with constant matrix elements showed a great similarity between the two results, as does a comparison of a nondirect optical conductivity calculation[12] for V and Cr and the direct constant-matrix-element calculation by Ganin *et al.*[22] Pickett and Allen[19] noted that most of the transitions of Mo and Nb are between relatively flat d bands which also coincide with peaks in the optical density of states, so that it is very difficult to determine if k conservation is maintained in such transitions, because the bands show no strong k dependence anyway (i.e., they are flat). Since the k-conserving and the nondirect models predict approximately the same behavior, there is no optical evidence of nondirect transitions in these metals. (An unrealistic approximation in both models was the assumption of constant matrix elements; calculation of the matrix elements throughout the Brillouin zone requires knowledge of actual wave functions, as in the calculations referred to earlier.)

IV. SUMMARY AND CONCLUSIONS

The optical properties of thin, electron-beam evaporated films of the transition metals V, Nb, Ta, Cr, Mo, and W are sensitive to film microstructure. It was found that well-crystallized films could be produced by deposition onto 700–800 °C (V, Nb, and Cr) or 1000 °C (Ta, Mo, and W) substrates. Compared to films deposited onto room-temperature or cooled (77-K) substrates, films deposited at elevated temperatures had much larger grain size. The optical reflectance of opaque well-crystallized Ta, Cr, Mo, and W films was much larger than for films deposited at room temperature (at least over most of the spectral range measured), and it agreed well with recent published bulk values for all six of the metals. For V and Nb, a fast evaporation rate was essential in order to avoid surface roughness; while for the other metals high substrate temperature was more important, so as to obtain a large-grained bcc structure.

The real and imaginary parts of the optical conductivity, obtained by inverting the transmission and reflection measurements on well-crystallized films, are believed to be representative of bulk material. Our estimates of the error in the optical constants due to instrumental uncertainties are about 1% in k and 2% in n over most of the spectral range. The satisfactory agreement between our results and the Kramers-Kronig analysis of Lynch and co-workers, would confirm the validity of their extrapolation procedures.

The intraband contribution to the optical properties is thought to be negligible over the spectral range above 1 eV. Recent first-principles calculated values of the interband contribution to the optical conductivity were compared to our results. The calculations by Moruzzi, Williams, and Janak for V and Cr and by Laurent, Wang, and Callaway for V reproduce our measured structure, but are somewhat too high and narrow, with the peak positions shifted significantly upwards in energy. The shift may be due to errors in placement of the energy bands that lie above the Fermi level. The calculations for Nb and Mo by Yamashita, Kubo, and Wakoh agree reasonably well with our measured conductivity. All these calculations seem to require the addition of an excited-state lifetime broadening of up to about $\frac{1}{2}$ eV, for unknown reasons. We conclude that all six metals are similar in the origin of their optical structure; it seems to be accounted for by direct *d*-band-to-*d*-band transitions, which occur mainly between peaks in the density of states.

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