Thermoreflectance of V, Nb, and paramagnetic Cr

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Thermoreflectance measurements of V, Nb, and Cr films were performed near 80 and 340 K to investigate the electronic properties of these metals. The thermoreflectance spectra $\Delta R/R$ were Kramers-Kronig analyzed to determine the temperature dependence of the dielectric functions. The results were compared with previous derivative measurements of Mo and with static measurements of the optical reflectance of the bcc metals. Interpretation of the structures was guided by recent band calculations. It was shown that the observed features reflect the behavior of large volumes of the Brillouin zone rather than well-defined singularities.

INTRODUCTION

The last few years have seen considerable interest in the electronic properties of the transition metals.¹ Numerous studies have been reported with the predictable outcome that our understanding of the metals has increased dramatically. The contributions of optical studies have been fundamental. For many of the transition metals, first generation optical experiments in which the reflectivity was measured over a wide energy range have been completed, $^{2-8}$ and it has been shown that, while the low-energy optical properties ($\hbar \omega \leq 10$ eV) vary significantly with the filling of the dbands, the high-energy behavior is very similar from metal to metal. The low-energy structure can be attributed to transitions within the hybridized sp and d bands within which the Fermi level lies. With the horizontal progression across the periodic table, the average energy of the dbands drops with respect to the sp bands and the Fermi level rises within them.⁹ Accompanying this, the width of the d band first increases, reaching a maximum with the Cr group, then decreases until, at the noble metals, the d bands are completely filled and lie $\geq 2 \text{ eV}$ below E_F . Similarly, with progression from 3d to 4d to 5dmetals, the d bandwidth increases. Such systematics are particularly interesting, and the interplay between theory and experiment has proved mutually beneficial. Calculations of the optical absorption from first principles (though generally without consideration of wave functions and matrix elements) are becoming more reliable.

To better understand the low-energy features observed in the bcc transition metals, we have ex-

ploited thermoderivative techniques and measured the thermoderivative of the reflectance, the thermoreflectance $\Delta R/R$. The technique is not a new one, and it has seen wide application for the noble metals,¹⁰ semiconductors,¹¹ and insulators,¹¹ but few of the transition metals have been so studied.¹² We find, in the present study, that the derivative spectra of transition metals do not possess the sharp and distinctive features observed when dealing with semiconductors since critical-point contributions are minimal. Instead, the broad structures clearly arise from large volumes of k space. Further, since the interband absorption persists to very low photon energies and generally involves states of hybridized angular momentum, line shapes cannot be calculated without detailed wave functions and matrix elements.

EXPERIMENTAL TECHNIQUE

The thermoreflectance of V, Nb, and Cr has been measured near 80 and 340 K between 0.5 and 5 eV. The general techniques of thermoderivative spectroscopy^{10,11} have been described in detail elsewhere and need be only briefly reviewed here. The samples were opaque films evaporated by electron-beam bombardment in vacua of ~10⁻⁷ Torr. They were approximately 3×25 mm, were evaporated onto quartz substrates, and had $2-5-\Omega$ electrical resistance. After evaporation, each was quickly attached to the tip of a cryofingersample-chamber, and the chamber was evacuated (working pressure ~10⁻⁶ Torr).

The thermal excursion of ~ 1 K deg was provided by a unipolar 7-Hz square wave with ~ 2 -W power dissipation. Conventional light sources (W-iodine

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lamp and 1000-W Xe arc), monochromator (Leiss double-prism), and detectors (PbS cell from 0.5 to 1.5 eV; RCA 7102 from 1 to 3 eV; EMI 6256B above 2 eV) were used. The small ac component of the reflected beam was detected with an Ithaco Model 353 lock-in amplifier, and the output signal was integrated for 100 sec. Data were taken on a point by point basis with the density of points dictated by the nature of the spectrum. The ambient temperature was measured with a thermocouple In-soldered adjacent to the sample; the measured temperature thus represents only an approximation to the actual sample temperature.

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RESULTS AND DISCUSSION

The measured thermoreflectance spectra are shown in Figs. 1–3. Also shown in Fig. 3 is $\Delta R/R$ for Mo as taken from our earlier work.⁵ Since the measured spectra scale with the temperature excursion, the magnitudes of $\Delta R/R$ are shown in arbitrary units, though it is understood that the signals are a few parts in 10³.

The $\Delta R/R$ spectra are complicated functions of the real and imaginary parts of the dielectric function, $\tilde{\epsilon}$, where $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$. The temperature derivative of ϵ_2 , $\Delta \epsilon_2$, is the more fundamental quantity and can be determined through a straightforward Kramers-Kronig analysis of $\Delta R/R$. Such an analysis requires a reliable set of dielectric functions, since

$$\Delta \epsilon_2 = \frac{1}{2} [k(\epsilon_1 - 1) + n\epsilon_2] (\Delta R/R) - [n(\epsilon_1 - 1) - k\epsilon_2] \Delta \theta,$$

where $\Delta \theta$ is the causal counterpart of $\Delta R/R$ and $\tilde{N} = n + ik$ is the complex index of refraction. For the analysis, we have used dielectric functions obtained in our previous static measurements.^{2,3}



FIG. 1. Thermoreflectance of V at approximately 80 and 340 K. The spectrum was also determined near 210 K; its maximum at 1.30 eV is indicated by the arrow.



FIG. 2. Thermoreflectance of Nb at approximately 80 and 340 K. The dashed curve below 0.6 eV represents the extrapolation used for our Kramers-Kronig analysis.

In the usual Kramers-Kronig analysis of R(E), it is well known that the magnitudes of ϵ_1 and ϵ_2 are dependent upon the nature of the extrapolations at high and low energy. For the derivative Kramers-Kronig analysis, the dependence is much less severe.^{13,14} Accordingly, the shapes of ϵ_2 are reliable though there were no derivative data below 0.5 eV or above ~5 eV. The results of the Kramers-Kronig analyses for Cr, V, and Nb are shown in Figs. 4 and 5. Also shown is $\Delta \epsilon_2$ for Mo. Unfortunately, the temperature modulation of the free carrier contribution to $\Delta \epsilon_2$ is large at low energy and is difficult to remove. This tends to obscure the lowest-energy derivative feature.

Numerous recent band calculations have been



FIG. 3. Thermoreflectance of Cr and Mo (from Ref. 5).



FIG. 4. Temperature derivative of ϵ_2 for Nb and V.

performed¹ for V, Nb, and Mo, and these have shown generally good agreement on many of the important features. The details still remain dependent upon the choice of starting potential (atomic configuration) and the handling of the exchange interaction. Relativistic effects in Nb and Mo are also important and tend to lift band degeneracies along certain lines. Because of the similarities in Nb, V, and Mo, we reproduce here only the bands of Nb as calculated by Mattheiss¹⁵ (Fig. 6).



FIG. 5. Temperature derivative of ϵ_2 for Cr and Mo.



FIG. 6. Energy band structure of Nb from Mattheiss (Ref. 15).

Much of the theoretical interest in Cr has been because of its antiferromagnetic ordering $(T_N$ = 312 K for bulk Cr).¹⁶ Recent calculations of the band structure of the paramagnetic phase of Cr have been performed by Rath and Callaway,¹⁷ and the derivative spectra of Cr will be interpreted in terms of those self-consistent linear-combinationof-atomic-orbitals paramagnetic bands (Fig. 7).

The lowest-energy structure in V and Nb is more prominently seen in $\Delta R/R$ than in $\Delta \epsilon_2$ because of the free carrier contribution to $\Delta \epsilon_2$. Upon cooling from 340 to 80 K, the features sharpen and shift to slightly lower energy (Figs. 1 and 2). The maximum in V shifts from 1.33 (340 K) to 1.30 (210 K) to 1.27 eV (80 K), and in Nb from 1.70 (340 K) to 1.67 eV (80 K). The other structures show less dependence on the ambient temperature. The lowenergy derivative feature corresponds to the maximum in ϵ_2 at 1.6 eV (V)and 2.4 eV (Nb) or in the absorptivity (1 - R) at 1.35 eV (V) and 1.8 eV (Nb) (see Refs. 2 and 3). Our previous identification of the origin of the structure as $\Sigma_1 - \Sigma_1$ still seems reasonable. Harmon¹⁸ has shown that the wave functions along the Σ direction are of mixed p and d character, with a greater admixture of p in the lower Σ_1 band. Such a mixing reduced the expected weakness of d-to-d transitions. Further, the involvement of states near and at E_F tends to enhance the temperature dependence of ϵ_2 . It is reasonable that the spreading of the d band increases the energy separation of the bands and moves the structure to higher energy for Nb than for V.

The energy bands of Cr and Mo have been shown to be very similar in the absence of spin-orbit splitting and magnetic ordering. In addition, they have the same general features as those of V and Nb. The position of the Fermi level within the



FIG. 7. Energy bands in paramagnetic Cr from Rath and Callaway (Ref. 17).

bands has an important influence on the low-energy optical properties. The Σ transitions identified as being responsible for the first structure in $\Delta R/R$ for V and Nb are still possible for Cr and Mo, though they might be expected to appear at higher energy and be weaker since the respective Fermi levels are no longer involved, but additional structure due to transitions along Δ also come into play. The degeneracy of the Δ_5 bands in Cr is lifted by relativistic effects in Mo and W, and the optical features associated with the $\Delta'_2(\Delta_7)$ $\rightarrow \Delta_5(\Delta_6, \Delta_7)$ transitions reflect the changes. In Cr, only a single feature is observed in R or $\Delta R/R$; in Mo, static measurements failed to resolve the splitting of the initial states,³ but the derivative spectra clearly showed the separation⁵ (see Fig. 3); in W, the spin-orbit splitting is $\sim 0.5 \text{ eV}$, and static measurements⁴ were able to resolve structures in R and ϵ_2 . Hence, the assignment of the first structure in Cr as $\Delta'_2 \rightarrow \Delta_5$ seems secure.

The identification of the second derivative structure in V and Nb and the third in Cr and Mo is difficult, but large volumes of k space are certainly involved. In their recent relativistic-augmentedplane-wave calculations for Mo, Koelling et al.¹⁹ concluded that the experimental feature in ϵ_2 at 4.1 eV was built up from transitions between bands along F, G, and Σ . Cr would be expected to have an analogous structure in ϵ_2 , but the extrapolation of those transitions to the Cr bands of Rath and Callaway is thwarted: Examination shows the band separation at F to be about 2 eV, at G to be 2.6 eV, and along Σ to be about 2.3 eV. Few new "high-symmetry" candidates present themselves. Transitions like $P_4 - P_3$ are allowed by selection rules, have large joint densities of states, and would probably have non-negligible matrix elements since P_4 wave functions are $\approx 100\% d$ -like

and those at P_3 are 20% *p*-like, 80% *d*-like.¹⁸ Nevertheless, though the energy difference is approximately correct in Cr(~3.5 eV), it is too great to account for the features in the other bcc metals, based upon existing energy bands for those metals. Probably, then, the *P* transitions are of minimal importance. Transitions like $\Delta_{3,4} - \Delta_6$ can also be discounted by analogy to Mo and W since, if such transitions were evident in Cr, they could be expected to carry over to Mo and W and result in pairs of structures, the separation of which would grow with the spin-orbit splitting. No such features were observed.

The recent calculations of Pickett and Allen²⁰ indicate that the d bands in the transition metals Nb and Mo tend to be flatter away from symmetry lines than along them. Their calculations showed that major contributions to the ϵ_2 structure in Nb near 4.3 eV and in Mo near 4.1 eV arose from the region around $k = (\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$. Though there have been no calculations of a similar nature for V and paramagnetic Cr, one might expect that the experimental features in Cr near 3.5 eV ($\Delta \epsilon_2$) or 3.3 eV (σ), and in V near 2.5 eV ($\Delta \epsilon_2$) or 2.35 (ϵ_2) could be explained by transitions in that part of the Brillouin zone. The consequence of the Pickett-Allen calculations was that structures which is observed in the experimental spectra can arise from off-symmetry parts of the zone.

It is clear from our measurements that the derivative features in the transition metals are broad, thereby indicating that large volumes of k space are contributing to the structures. It is also apparent that the last word is not in as far as calculations are concerned, and identifications such as those put forth tentatively here are subject to improvement. This refining must come after good agreement with experimental data is achieved; such agreement must result from the inclusion of matrix elements in the calculations. The derivative spectra reported here provide yet another set of experimental data to which the theorist must compare his calculations.

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