

## Electronic structure of the bcc transition metals: Thermoreflectance studies of bulk V, Nb, Ta, and $\alpha\text{TaH}_x$

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Thermoreflectance studies of bulk samples of V, Nb, Ta, and  $\alpha$ -phase  $\text{TaH}_x$  are reported and the results interpreted in terms of recent band calculations. The first interband transition is identified as a transition involving the  $\Sigma$  band at  $E_F$ . An  $M_3$  critical-point transition is attributed to states at  $N$ . Significant changes induced by interstitial hydrogen in solid solution  $\alpha\text{-TaH}_x$  are observed and interpreted as due to hybridization and lowering of the  $N_1'$  eigenenergy.

The electronic structures of the bcc transition metals have been of interest to us for several years, and we have examined those metals with a variety of different optical techniques.<sup>1-5</sup> Our earliest studies involved optical studies of the absorptivity or reflectivity as a function of photon energy for  $0.1 \lesssim h\nu \lesssim 40$  eV. From those results we determined the static dielectric function,  $\tilde{\epsilon}(h\nu) = \epsilon_1 + i\epsilon_2$ , and attempted to relate experimentally observed features in  $\epsilon_2$  to band-to-band transitions predicted by theory. To gain additional insight into the electronic structures, we subsequently examined the temperature dependence of the dielectric function by using thermoreflectance techniques with thin films of V, Nb, and Cr for  $0.5 \lesssim h\nu \lesssim 5$  eV ( $0.5 \lesssim h\nu \lesssim 30$  eV for Mo). Those results were again interpreted on the basis of band calculations. Recent optical studies of alloys of Nb with Mo, Ta, V, and Zr by Black et al.,<sup>6</sup> experimental and theoretical studies of Nb-Mo alloys by Colavita *et al.*,<sup>7</sup> and preliminary investigations of the hydride systems of V, Nb, and Ta (Ref. 8) have led us to re-examine the elemental metals V, Nb, and Ta using temperature modulation of *bulk* crystals. Those results are presented in this paper. As we will show, they allow us to observe systematics within the V-Nb-Ta group and, arguing from those systematics, to shed additional light on the electronic structure of these metals and alloys. Band transitions along  $\Sigma$  and  $G$  can be identified in the experimental spectra, and a critical-point transition

can clearly be observed in Nb and related to transitions at  $N$  (an  $M_3$  critical point). The results are interpreted primarily from the band calculations of Boyer, Papaconstantopoulos, and Klein<sup>9</sup> and of Mattheiss.<sup>10</sup>

The interpretation of optical spectra of transition metals is a rather formidable task and only recently for some select cases are such spectra being successfully unraveled. The difficulty arises primarily because the optical structures of these materials are generally quite broad; sharp features are almost never observed in optical spectra for transition metals. Although we are not aware of specific theoretical studies on the subject, we believe the smearing derives mainly from the following:

(1) Lifetime broadening due to strong electron-electron interaction. The density of states in the region a few eV above  $E_F$  is particularly high in transition metals, and an optically excited electron has a very large number of channels for decaying, thereby reducing the lifetime. The experimental results for the transition metals can be compared to those for the noble metals Cu, Ag, and Au where there are only the *sp* bands with relatively low density of states a few eV above  $E_F$ , and for which the observed spectra are considerably sharper because the lifetime of the state is much greater.<sup>11</sup>

(2) The electronic wave functions tend to have purest angular momentum character at points of high symmetry, but have mixed *s-p-d* charac-

ter elsewhere.<sup>12</sup> As a result, optical transitions are often strictly forbidden at points of high symmetry and grow gradually without sharp discontinuities away from symmetry points. The strong  $k$  dependence of the electric dipole matrix elements reduces the importance of critical points (with characteristic line shapes) and distorts such other useful "fingerprints" as, for example, Fermi-surface transitions.

The interpretation of optical structure can be facilitated by examining systematic behavior in closely related transition metals or by examining the effects of alloying with either closely related or quite different elements (e.g., Nb-Mo or Nb-H). Those interpretive attempts are further aided by analogous systematic calculations which consider a group of isostructural metals with the same underlying calculational assumptions since those results predict trends which can be compared to experiment. Though there have been many calculations for the bcc metals,<sup>13</sup> we will emphasize systematics and will compare experiment to the calculations of Boyer *et al.*,<sup>9</sup> Mattheiss,<sup>10</sup> Alward *et al.*,<sup>14</sup> and Koelling<sup>15</sup> since they have calculated the bands for more than one of these bcc metals.

Experimental techniques and details can be found elsewhere and will not be repeated here. The heating system is the by-now-standard high-efficiency system developed by one of the authors.<sup>7</sup> A discussion of the thermal behavior of the thermomodulation systems will be published elsewhere and will not be repeated here.<sup>16</sup> The optical layout has been described in Refs. 3 and 11.

High-purity samples were obtained through the Ames Laboratory (USDOE) and were cut with a diamond saw into the form of thin platelets of about  $2 \times 3 \times 0.2$  mm<sup>3</sup>. They were polished to a mirror finish and electropolished in a solution of 6 vol% sulfuric acid in methanol at  $\approx 200$  K to remove the cold-worked layers from the mechanically polished surface.

The results, given in the form of spectra of relative variation of the reflectance  $\Delta R/R$  versus photon energy for  $T \approx 160$  K and  $0.5 \leq h\nu \leq 5$  eV, are shown in Fig. 1. Also shown in Fig. 1 are the results obtained previously for V and Nb films<sup>9</sup> deposited onto quartz substrates at room temperature and studied at  $\sim 80$  K (dashed spectra). The temperature difference accounts for the mismatch in energy of the maxima near  $\sim 1.5$  eV. The overall agreement is good with the bulk samples revealing considerably more detailed structure than did the films. As is now known, metal films evaporated at room temperature on flat polished insulator slabs (usually fused quartz) can be badly strained. As a result, important structures in static or modulated spectra may

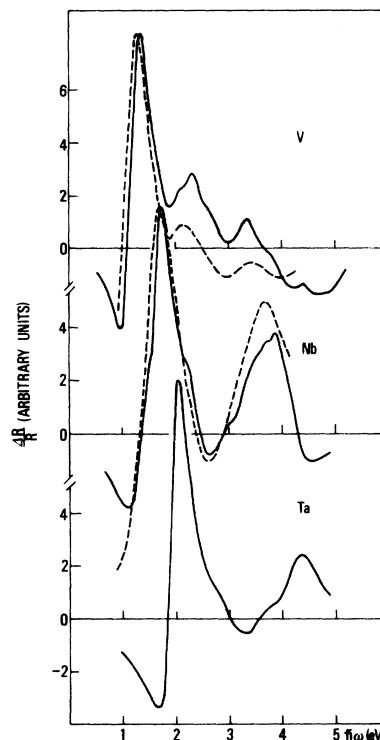


FIG. 1. Experimentally measured thermoreflectance spectra  $\Delta R/R$  shown in arbitrary units for V, Nb, and Ta bulk samples at  $T \approx 160$  K. The dashed curves are the analogous spectra for V and Nb films (Ref. 3) at  $T \approx 80$  K. The alignment of the low-energy peaks reflects the different temperature. The film spectra are less structured probably because the samples themselves were badly strained.

be washed out, as appears to be the case in our film work, or in some cases spurious structures may also appear, as can be seen by comparing our thin-film  $\Delta R/R$  results for Mo to those obtained with bulk Mo.<sup>7,17</sup> Bulk samples with sharper and more detailed spectra are clearly superior, and those results allow the identification of transitions previously overlooked.

The spectra for V, Nb, and Ta look very similar at first glance (Fig. 1). Indeed the strong resemblance is suggested by the first strong derivativelike structure (negative peaks at 0.95, 1.12, and 1.67 eV and positive peaks at 1.35, 1.75, and 2.05 eV for V, Nb, and Ta, respectively). All the spectra show a shoulder on the high-energy side (more marked in Ta than in Nb and barely perceptible in V) at  $\sim 1.75$  eV for V, 2.25 eV for Nb, and 2.75 eV for Ta. The resemblance stops there, however. Although the bands for these three metals are quite similar, the relative shifts of the energy bands bring about important differences in the higher-energy structures of the thermomodulation spectra. These

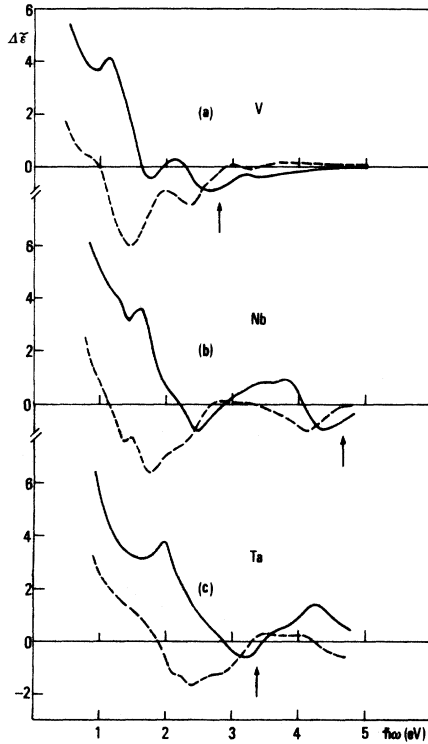


FIG. 2.  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$  for V, Nb, and Ta at  $T = 160$  K between 0.5 and 5 eV as calculated from the results of Fig. 1.  $\Delta\epsilon_1$  is shown dashed;  $\Delta\epsilon_2$  is solid.

differences can better be seen in  $\Delta\tilde{\epsilon}$  than in  $\Delta R/R$ .

The  $\Delta R/R$  spectra have been Kramers-Kronig analyzed in order to determine the temperature variations of the real and imaginary parts of the dielectric constant  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$ . As is well known, it is much easier to correlate structure in  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$  with specific interband effects than to attempt the interpretation based only in  $\Delta R/R$  because  $\Delta R/R$  is a complicated function of  $\Delta\epsilon_1$ ,  $\Delta\epsilon_2$ ,  $\epsilon_1$ , and  $\epsilon_2$ , where  $\epsilon_1$  and  $\epsilon_2$  are the static optical constants and were obtained from Refs. 1 and 2. A complete table of static and modulated data can be obtained from the authors.

The  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$  spectra for V, Nb, and Ta are shown in Fig. 2 with  $\Delta\epsilon_2$  shown as a solid line and  $\Delta\epsilon_1$  shown dashed. In the infrared below about 1 eV, both  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$  show a rapid rise with decreasing energy which reflects the temperature modulation of the free-electron part of the dielectric function, mainly through the temperature dependence of the free-electron relaxation time. At higher photon energies, modulation of interband features dominates.

The first important structure in the thermorefectance spectra is observed in the 1–2-eV energy range (peak in  $\Delta\epsilon_2$  at 1.07, 1.60, and 1.98

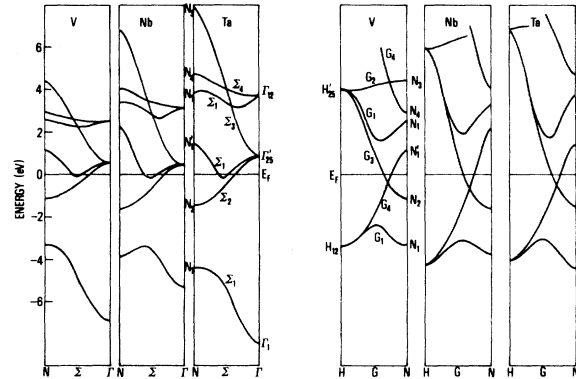


FIG. 3. Self-consistent electronic energy bands for V, Nb, and Ta along the symmetry lines  $H-G-N$  and  $\Gamma-\Sigma-N$  as calculated by Boyer, Papaconstantopoulos, and Klein (Ref. 9).

eV in V, Nb, and Ta, respectively). This structure is strongly reminiscent of a Fermi-surface transition<sup>11</sup> which, as noted elsewhere,<sup>7</sup> can be “modulated” by transition-matrix-elements effects. Possible transitions from which the observed structure can originate are  $G_1 - G_4(E_F)$ ,  $G_4(E_F) - G_3$ ,  $\Sigma_1(E_F) - \Sigma_1$ ,  $\Sigma_1(E_F) - \Sigma_3$ , and  $D_4 - D_3(E_F)$ . The partial joint density of states associated with some of these transitions is very small and these can be ruled out [e.g.,  $G_1 - G_4(E_F)$  and  $D_4 - D_3(E_F)$ ]. The other transitions are more serious candidates since not only do they involve the Fermi level (which gives extra temperature sensitivity) but also their partial joint density of states is substantial.

Referring to Figs. 1–3, the following observations lead us to prefer  $\Sigma_1(E_F) - \Sigma_3$  over  $\Sigma_1(E_F) - \Sigma_1$  and  $G_1(E_F) - G_4$ :

(1) Experimentally, the observed Fermi-surface transition shifts progressively to higher energies on going from V to Nb to Ta. The calculations of Boyer *et al.* (Fig. 3) indicate that either  $\Sigma_1 - \Sigma_1$  or  $\Sigma_1 - \Sigma_3$  would satisfy this systematic shift requirement, although the energy separation for  $\Sigma_1 - \Sigma_3$  is closer to the experimental values.

(2) Recent thermorefectance and optical studies<sup>7,18</sup> have reported that this Fermi-surface transition shifts rapidly to lower energy as Nb or Ta is alloyed with Mo or W. To first approximation, alloying with Mo or W would raise  $E_F$ . From Fig. 3, we see that as  $E_F$  moves upward the energy separation for  $\Sigma_1 - \Sigma_3$  would decrease much more quickly than that of either  $\Sigma_1 - \Sigma_1$  or  $G_1 - G_4$ .

(3) The optical studies<sup>7,18</sup> for the Nb-Mo and Ta-W systems show that the strength of the interband transition weakens appreciably as the pure

metal is diluted. The weakening would be associated with reduced matrix elements for transitions occurring ever closer to  $\Gamma$ , i.e., transitions with increasingly pure  $d$ -to- $d$  character (the states along  $\Sigma$  have mixed  $p$  character,  $\Gamma'_{25}$  is purely  $d$ ). Either  $\Sigma_1 \rightarrow \Sigma_1$  or  $\Sigma_1 \rightarrow \Sigma_3$  would be consistent with this observation, while  $G_1 \rightarrow G_4$  would show the opposite trend.

(4) Thermoreflectance studies<sup>3</sup> of thin films of V and Nb at 80 and 340 K showed that the peak in  $\Delta R/R$  shifted slightly toward higher energy as the temperature increased. (This can be seen also from Fig. 1 when the low-temperature film spectra are compared to our 160 K results.) It has been shown theoretically that when the lattice parameter is increased ( $\sim$  higher temperature), the  $\Sigma_1 \rightarrow \Sigma_3$  transition moves to slightly lower energy or is unchanged,<sup>7,19</sup> in agreement with the experimental results, whereas the  $\Sigma_1 \rightarrow \Sigma_1$  transition shifts toward higher energy. We suggest then that the dominant Fermi-surface transition giving rise to the thermomodulation feature is  $\Sigma_1(E_F) \rightarrow \Sigma_3$ . One must be careful, however, in ruling out the contributions to the static dielectric function maximum at  $\sim 2.05$  eV from states away from  $E_F$  along  $\Sigma$  and from relatively unknown volumes of  $k$  space away from the symmetry lines. The same caution holds for states along  $H-G-N$ , namely  $G_4 \rightarrow G_1$  which was previously discussed by Thomas and Thurm<sup>18</sup> in the context of their careful static-alloy studies. While those transitions are allowed and probably contribute to the first broad interband feature in  $\epsilon_2$ , they are probably not responsible for the temperature modulation features. While we could not rule them out based on these elemental metal measurements, the alloy studies of Colavita *et al.*<sup>7</sup> show the experimental features weakening and moving rapidly to lower energy as the alloy is formed, whereas the band calculations show  $G_1$  and  $G_4$  to be roughly parallel and the matrix elements should increase as one approaches  $N$  ( $N'_1$  is strongly  $p$ -like).

The  $p$  character of  $N'_1$ , the  $d$  character of  $N_2$ , and the shape of the bands in the vicinity of  $N$  suggest that an  $M_3$  critical-point transition should be observed by thermoreflectance studies, particularly since the deformation potential for  $N_2 \rightarrow N'_1$  transition is large. The experimental results for Nb reveal the characteristic line shape near 4.5 eV for an  $M_3$  critical point (see arrow Fig. 2). That  $M_3$  identification is confirmed by re-examining the composition-modulation studies of Black *et al.* for Nb-Mo or by fitting the line shape observed in temperature-modulation studies of the Nb-Mo alloys. We believe that these results reflect the first observa-

tions of a critical point in any transition-metal studies. A rather crude line-shape analysis results in an electronic lifetime of  $\Gamma \approx 0.2$  eV which, though approximate, nevertheless confirms the model which attributes the very broad character of interband optical features to lifetime broadening.

The  $M_3$  critical point is also present in the spectra of V and Ta but is less discernible because of greater overlap with other nearby optical features. We interpret the line shapes of  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$  at  $\sim 2.8$  eV in V and 3.15 eV in Ta as indicative of an  $M_3$  critical point, i.e.,  $N_2 \rightarrow N'_1$  transitions. This identification is in fairly good quantitative agreement with the calculated band structures and, moreover, is consistent with the predicted systematics regarding the eigenenergies at  $N$ .

In Fig. 4 we show the thermoreflectance spectra obtained for three  $\alpha$ -phase  $\text{TaH}_x$  samples at  $T \approx 320$  K (hydrogen orders at lower temperatures but occurs as a solid solution in the metal lattice at 320 K). These samples were prepared, as dis-

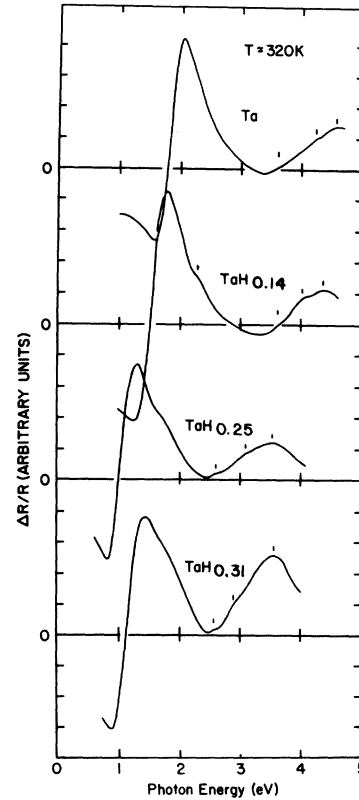


FIG. 4. Thermoreflectance spectra of several compositions of  $\text{TaH}_x$  where H appears interstitially in solid solution at 320 K. The characteristic features observed in Ta metal are observed to shift to lower energy as the hydrogen concentration increases.

TABLE I. Comparison of experimental to predicted interband optical transitions. Energies are given in electron volts.

	$\Sigma_1(E_F) \rightarrow \Sigma_3$	$G_4(E_F) \rightarrow G_1$	$N_2 \rightarrow N'_1$
V			
Alward <i>et al.</i> , Ref. 14	2.16	2.27	2.73
Boyer <i>et al.</i> , Ref. 9	2.40	1.90	2.20
Koelling, Ref. 15	1.70	1.84	2.70
Present results	1.07	1.60	2.80
Nb			
Alward <i>et al.</i> , Ref. 14	1.93	1.70	1.82
Boyer <i>et al.</i> , Ref. 9	2.25	2.45	3.80
Koelling, Ref. 15	2.07	2.18	4.00
Mattheiss, Ref. 10	1.60	2.05	4.00
Present results	1.60	2.12	4.53
Ta			
Alward <i>et al.</i> , Ref. 14	2.05	2.05	2.16
Boyer <i>et al.</i> , Ref. 9	3.50	2.35	2.80
Koelling, Ref. 15	2.36	2.37	3.30
Mattheiss, Ref. 10	3.00	2.40	2.65
Present results	2.00	2.37	3.16

cussed in Ref. 8, by charging pure Ta in an H atmosphere. The samples were subsequently polished and electropolished, the latter process possibly increasing the hydrogen content above the nominal concentration determined from gas evolution analysis. The first derivative structure moves toward lower energies on adding hydrogen. This behavior is very similar to what is observed when Ta is alloyed with W (Ref. 18) and when Nb is alloyed with Mo. The shift rate is also comparable (roughly 0.01 eV/at. % solute). The similarity with group VB-group VIB alloys ends there, however. The high-energy features of the spectrum move very quickly toward lower energies on adding hydrogen while they move much more slowly or are stationary when W is added<sup>18</sup> to Ta (or Mo to Nb). On adding hydrogen (which enters the metal matrix interstitially in the  $\alpha$  phase) the Fermi level shifts somewhat in order to accommodate the extra electrons. This explains the "red shift" of the leading peak much in the same way as for the Nb-Mo alloy. The volume expansion of the lattice plays a secondary role since the transition energy would shift very little (and in the opposite direction<sup>3</sup>).

The TaH<sub>x</sub> spectra show that with increasing H concentration, the  $M_3$  critical point structure near 3.2 eV moves rapidly toward lower energy. Such a shift is consistent with the lowering in energy of the  $N'_1$  state due to hybridization of that  $p$ -like wave function with the hydrogen states. Preliminary calculations of Switendick<sup>20</sup> for NbH<sub>x</sub> indicate that upon adding hydrogen to Nb to form

ordered Nb hydrides, significant changes occur in the band structure along (110) as  $N'_1$  is drawn toward  $E_F$ . This lowering of  $N'_1$  is not observed in substitutional Nb-Mo or Ta-W alloys.

Our conclusions are summarized in Table I. From Table I it can be seen that energy separations extracted from the calculations of Mattheiss [non-self-consistent augmented plane wave (APW)],<sup>10</sup> Koelling (self-consistent relativistic APW),<sup>15</sup> and Boyer *et al.* (self-consistent APW)<sup>9</sup> are in reasonably good agreement with the experimental results. However, the nonlocal empirical pseudopotential method (EPM) of Alward *et al.*<sup>14</sup> does not produce bands which are consistent either with the APW calculations or with our results. For instance, Alward *et al.* predict the  $N_2 \rightarrow N'_1$  critical point in Nb at 1.82 eV while we find it at 4.5 eV (their ordering of the bands at  $N$  differs from those of the others), and the trends predicted by the EPM method on going from V to Ta are not observed experimentally.

The experimental spectra show additional possible critical points. For instance, V and Nb may have  $M_3$  critical points at about 1.82 and 2.5 eV, respectively, and Nb and Ta show  $M_1$  critical points at 4.0 and 4.42 eV. It is not possible to make attributions for these transitions at present since they probably arise from regions of  $k$  space removed from high-symmetry points. Nonsymmetry transitions are undoubtedly important in interband optical absorption in the transition metals and their alloys, but are very difficult to assess, and their importance, to-

gether with the importance of matrix elements, continues to be a challenge in the field.

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