Density of states, optical mass, and dc electrical resistance of Ta, W, Nb, and Mo using Slater-Koster interpolation*

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Slater-Koster interpolation has been used to fit the nonrelativistic augmented-plane-wave (APW) band calculations of Petroff and Viswanathan for Ta and W. The resulting Slater-Koster parameters have been used to calculate the density of states and optical mass. The density of states compares well with the original APW calculation, but the optical masses which have not been calculated before, seem to differ appreciably from presently available experimental data. The dc electrical resistances, which have been calculated using our values of the optical mass, agree well with experiment if an empirical coupling constant similar to McMillan's is assumed.

The Slater-Koster (SK) interpolation scheme[1] developed for fitting the energy bands of the bcc transition metals Nb, and Mo,[2] has been extended to Ta and W. We have adjusted the SK parameters to fit the nonrelativistic augmented-plane-wave (APW) band calculation of Petroff and Viswanathan,[3] and using these parameters we have calculated the density of states and optical mass. The fitting method used is identical to that in Ref. 2. The 9×9 SK matrix allows for $5d$, $6s$, and $6p$ atomic states. Table I gives the parameters of a general (three-center) fitting at 6—9 APW bands at 55 equally spaced points in the irreducible wedge of the Brillouin zone. The rms deviation for the lowest six bands is 7 mRy for Ta and 8 mRy for W. The 31 parameters include all first- and second-neighbor contributions, and the four third-neighbor integrals thought to be most important. Our results indicate that second-neighbor integrals are essential and the third-neighbor integrals are negligible. The uniquely determined two-center integrals of type ss, sp, sd, pp are consistent with a picture of atomic-wave functions overlapping in a region of predominantly negative potential.

A comment about the SK matrix used in Ref. 2 and the present work is relevant here. In the original SK matrix[1] some of the elements are imaginary. These have been made real by choosing an appropriate basis set. As a result the signs of some of the parameters are different from what would have been obtained otherwise. A change in sign of either E_{sx} or E_{sd2} resolves the discrepancy between our matrix and the original SK matrix.

The density of states $N(E)$ of W calculated by the Gilat-Raubenheimer[4] method using 5200 points in the irreducible wedge is shown in Fig. 1, and is in good agreement with the histogram results of Petroff and Viswanathan.[3] The $N(E)$ curve for Ta is extremely similar and is not shown. The d bandwidth of W shows an increase of about 3% over that of Ta, which correlates with the fact that the lattice constant of W is lower than that of Ta by about 5%. Comparisons of $N(E_F)$ and E_F are made in Table II. McMillan presents values of the unrenormalized density of states at the Fermi level for the $5d$ transition metals and their alloys.[5] These values of $N(E_F)$, which are obtained from specific-heat data after removal of the electron-phonon mass enhancement, are also shown in Table II. The density of states for W obtained from nonrelativistic band calculations, does not agree very well with McMillan's value. The value 5.04 electrons/atom Ry obtained from relativistic APW band calculations[6] gives better agreement. The discrepancy is explained by the fact that certain degeneracies are lifted by relativistic effects. These effects do not seem to be important at the Fermi surface of Ta.

The peak positions in $N(E)$ correspond closely to flat portions of the bands along symmetry directions: lower peak— G_1 band near (0.20, 0.20, 0) and Δ_1 band near (0.5, 0.5, 0) (units of $2\pi/a$); peak 2—N_2 level at 0.61 Ry; peak 3—Σ_1 band near (0.20, 0.20, 0); peak 4—N_1 level at 0.97 Ry; peak 5—N_4 level at 1.025 Ry.

The optical mass is inversely proportional to the Drude plasma frequency squared (Ω_p^2) which is given by

$$\Omega_p^2=\frac{4\pi e^2}{3}\sum_{kn} v_{kn}^2\delta(\epsilon_{kn}-E)\equiv\frac{4\pi e^2}{3}N(E)\langle v^2\rangle_E. \quad (1)$$

Pickett and Allen[7] have calculated Ω_p^2 for Nb and Mo by an indirect method. We evaluate Ω_p^2 for Nb and Mo directly from Eq. (1) using the interpolated bands of Ref. 2 as a check on the previously obtained[7] values. The values of Ω_p^2 for Mo differ from that cited in Ref. 7 probably because in the previous calculation,[7] a rigid-band model was assumed and the band structure of Nb used. We

TABLE I. Parameters for SK interpolation in Ta and W. The notation is that of Ref. 1, with the abbreviations d_1, d_2, d_3, d_4, and d_5 for x^2-y^2, $3z^2-r^2$, yz, zx, and xy, respectively.

	Ta	W		Ta	W
$E_{ss}(000)$	1.2512	1.4532	$E_{ss}(200)$	−0.0477	−0.0474
$E_{xx}(000)$	1.6567	1.8781	$E_{sx}(200)$	0.1064	0.1444
$E_{d_5d_5}(000)$	0.9165	0.9508	$E_{sd_2}(002)$	0.0547	0.0667
$E_{d_2d_2}(000)$	0.8352	0.8449	$E_{xx}(200)$	0.2009	0.2813
$E_{ss}(111)$	−0.0772	−0.1043	$E_{yy}(200)$	0.0027	0.0065
$E_{sx}(111)$	0.0688	0.0721	$E_{xd_5}(020)$	0.0017	−0.0056
$E_{sd_5}(111)$	0.0623	0.0716	$E_{zd_2}(002)$	−0.0960	−0.1044
$E_{xx}(111)$	0.0798	0.1129	$E_{d_5d_5}(200)$	−0.0026	−0.0100
$E_{xy}(111)$	0.0418	0.0415	$E_{d_5d_5}(002)$	0.0055	0.0062
$E_{xd_5}(111)$	−0.0485	−0.0565	$E_{d_2d_2}(002)$	−0.0663	−0.0679
$E_{xd_3}(111)$	−0.0539	−0.0597	$E_{d_1d_1}(002)$	0.0091	0.0101
$E_{xd_1}(111)$	0.0141	0.0134	$E_{ss}(220)$	−0.0047	0.0008
$E_{d_5d_5}(111)$	−0.0251	−0.0261	$E_{sd_5}(220)$	−0.0032	−0.0076
$E_{d_5d_4}(111)$	−0.0393	−0.0417	$E_{d_5d_5}(220)$	0.0053	0.0083
$E_{d_5d_2}(111)$	−0.0176	−0.0167	$E_{d_5d_2}(220)$	−0.0052	−0.0063
$E_{d_2d_2}(111)$	0.0331	−0.0344			

have also obtained Ω_p^2 for Ta and W. The plot of Ω_p^2 and $\langle v^2\rangle_E$ as a function of the energy is shown in Fig. 1. The values of $\Omega_p^2(E_F)$ are compared to the corresponding experimental values[8-16] in Table III. The experimental values of Ω_p^2 for Ta and W have been estimated by us from the values of σ_0 and τ cited by the authors. It should be emphasized that there are many experimental uncertainties involved in determining the Drude plasma frequency, and the experimental data should be treated with caution. Some of the difficulties involved in obtaining Ω_p^2 (experimentally), for transition metals have been discussed in Ref. 7. Nevertheless, we see that the discrepancy between experimental and theoretical values is quite large, and Fermi liquid effects may provide a resolution of this discrepancy. If we write

$$\Omega_{p\,\mathrm{expt}}^2 = \Omega_{p\,\mathrm{theo}}^2 (1+A), \tag{2}$$

it is possible to estimate the value of A. These values suggest that Fermi liquid effects in the transition metals under study are quite large.

The Fermi liquid factor $1+A$ occurs as a multiplicative correction both in Ω_p^2 and the scattering rate $1/\tau$. Thus, in the dc limit the corrections cancel out. We now examine the dc resistance as a further experimental check on our values of Ω_p^2. The standard expression[17] for the temperature-dependent resistivity can be written

$$\rho(T) = 4\pi/\Omega_p^2 \tau_{\mathrm{dc}}\ , \tag{3}$$

where the expression[18] for τ_{dc} is

$$\frac{\hbar}{\tau_{\mathrm{dc}}} = 4\pi k_B T \int_0^\infty \frac{d\omega}{\omega} \alpha_{\mathrm{tr}}^2 F(\omega) \left(\frac{x}{\sinh x}\right)^2 , \tag{4}$$

with x equal to $\hbar\omega/2k_BT$. The subscript "tr" stands for transport and is used to distinguish the

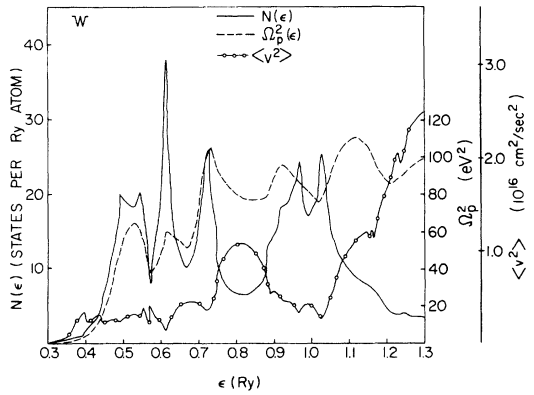

FIG. 1. Density of states $N(\epsilon)$, the Drude plasma frequency squared $\Omega_p^2(\epsilon)$ and the mean-squared velocity $\langle v^2\rangle$ in W, plotted as a function of energy. The Drude plasma frequency squared is proportional to the product $N(\epsilon)\langle v^2\rangle$. Note that $\Omega_p^2(\epsilon)$ exhibits less variation than either $N(\epsilon)$ or $\langle v^2\rangle$.

TABLE II. Fermi energy E_F (Ry) and density of states at the Fermi level $N(E_F)$ (states/Ry atom) (both spins included), of the interpolated bands compared to original APW calculations and to McMillan's values.

	Ta		W	
	E_F (Ry)	$N(E_F)$ (states/Ry-atom) (double spin)	E_F (Ry)	$N(E_F)$ (states/Ry-atom) (double spin)
Interpolated bands	0.7138	18.38	0.8569	7.51
APW bands [a]	0.7057	17.9	0.8420	7.41
Specific-heat data [b]	•••	21	•••	4.1

[a] See Ref. 3.
[b] See Ref. 5.

transport related quantities from the closely corresponding factors appearing in superconductivity theory. The relationship may be understood by referring to Eqs. (8) and (9) below. The high-temperature expansion for $1/\tau_{dc}$ can be written

$$\frac{\hbar}{\tau_{dc}} = 2\pi k_B T \lambda_{tr}\left(1 - \frac{\hbar^2\langle\omega^2\rangle_{tr}}{12(k_BT)^2}\right), \tag{5}$$

keeping terms of up to second order in the expansion of $(x/\sinh x)^2$. The parameters λ_{tr} and $\langle\omega^2\rangle_{tr}$ are defined as

$$\lambda_{tr} = 2\int_0^\infty \frac{d\omega}{\omega}\,\alpha_{tr}^2 F(\omega), \tag{6}$$

$$\langle\omega^2\rangle_{tr} = \frac{2}{\lambda_{tr}}\int_0^\infty d\omega\,\omega\,\alpha_{tr}^2 F(\omega). \tag{7}$$

The spectral function $\alpha_{tr}^2 F$ and the dimensionless number λ_{tr} are closely related to the spectral function α^2F and the coupling constant λ of superconductivity theory.[5] It is found experimentally that α^2F has the same shape as the phonon density of states F in many metals. It is reasonable to expect that this should remain true for $\alpha_{tr}^2 F$ as well, except that the low-frequency behavior should be ω^4 instead of ω^2. We can therefore directly compute ρ/λ_{tr} for a particular temperature and comparing these to the experimental values[19] of the resistivity at room temperature we obtain an empirical value of λ_{tr}. This is compared to McMillan's[5] λ in Table III. The correction factor $\langle\omega^2\rangle_{tr}/T^2$ in Eq. (5) is small at room temperature, and has been estimated using the values of $\langle\omega^2\rangle$ given in Ref. 20. The calculations for tungsten are less reliable than the others, since in this case relativistic corrections are important.

The empirical coupling constants λ_{tr} from resistance and λ from superconductivity are very similar in magnitude for these metals. This is not particularly surprising because theory gives closely related expressions for these numbers, namely,

$$\lambda = \sum_{kk'} \frac{|M_{kk'}|^2}{\hbar\omega_{k-k'}}\delta(\epsilon_k)\delta(\epsilon_{k'}) \Big/ \sum_k \delta(\epsilon_k), \tag{8}$$

$$\lambda_{tr} = \sum_{kk'} \frac{(v_{kx}-v_{k'x})^2|M_{kk'}|^2}{\hbar\omega_{k-k'}}\delta(\epsilon_k)\delta(\epsilon_{k'}) \Big/ 2\sum_k v_{kx}^2\delta(\epsilon_k), \tag{9}$$

TABLE III. The Drude plasma frequency Ω_p (eV) and the average Fermi velocity $\langle v^2\rangle_{E_F}^{1/2}$ (10^8 cm/sec) calculated from the interpolated bands (for interpolated bands of Nb, Mo, see Ref. 2) are compared with experimental data. The Silin parameter A is also tabulated. The values of λ_{tr} (empirical) and λ (McMillan) are compared.

	Nb	Mo	Ta	W
Ω_p (theo) (eV)	8.87	8.24	9.44	8.78
Ω_p (expt) (eV)	4.8 [a]	5.9 [b]	7.01 [c]	6.6 [d]
	5.7 [e]			5.2 ± 1.6 [f]
	7.9 [g]			
A	−0.7	−0.5	−0.5	−0.4
	−0.6			−0.7 ± 0.2
	−0.2			
$\langle v^2\rangle_{E_F}^{1/2}$ (10^8 cm/sec)	0.61	0.86	0.67	0.96
$\langle\omega^2\rangle_{tr}^{1/2}$ (°K) (Ref. 20)	183	251	148	220
$\rho(295)$ (expt) ($\mu\Omega$ cm)	14.5	5.3	13.1	5.3
λ_{tr} (empirical)	1.15	0.47	1.08	0.25
λ (McMillan)	0.82	0.41	0.65	0.28

[a] See Ref. 11.
[b] See Refs. 12–14.
[c] See Ref. 8.
[d] See Ref. 9.
[e] See Ref. 15.
[f] See Ref. 10.
[g] See Ref. 16.

where $M_{kk'}$ is the electron-phonon matrix element, $\omega_{k-k'}$ is the phonon frequency, and sums over all phonon branches and electron bands and spin are implied. The δ functions imply that the summations are restricted to the Fermi surface. Equation (9) results from a variational treatment[21] of the Boltzmann equation, assuming that the distribution function ϕ_k is proportional to $\vec{v}_k \cdot \vec{E}$. The error made in this variational approximation is similar in nature and accuracy to the isotropic (or "dirty") approximation implicit in the McMillan theory[5] relating T_c to λ given by (8). In the special case of a spherical Fermi surface, Eq. (9) differs from (8) only by the familiar factor $(1-\cos\theta)$ which weights large angle scattering more strongly than small. Thus λ_{tr} is similar in magnitude to λ, and it is not possible to tell *a priori* which number is larger. We urge band theorists to provide theoretical values of Ω_p^2 or $\langle v^2 \rangle$ for other transitions metals so that λ_{tr} can be extracted from experiment. We also urge theorists doing calculations of λ to calculate λ_{tr} simultaneously as a test on the procedures used as a step towards a microscopic understanding of transport in these materials.

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