

## Electron-Phonon Interaction and Superconductivity in Transition Metals and Transition-Metal Carbides

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Using the results of self-consistent augmented-plane-wave band-structure calculations, electron mass enhancement factors and superconducting transition temperatures have been calculated for V, Nb, NbC, TaC, and HfC. Good agreement with experiment is obtained.

In order to understand better the electron-phonon (e-p) interaction and the occurrence of superconductivity in metals and compounds, it is desirable to be able to compute quantities such as electron mass enhancement factors ( $\lambda$ ) and superconducting transition temperatures ( $T_c$ ) from quantities obtained from electronic band-structure calculations. In this Letter we report on such calculations for two pure metals (V and Nb) and three compounds (NbC, TaC, and HfC), using the results of self-consistent augmented-plane-wave (APW) calculations for these materials, and a recently proposed theory of the e-p interaction.<sup>1,2</sup> We will show that our results are in good accord with experimental observations for these different types of materials. This implies that these techniques may have rather general utility.

The formulation of the e-p interaction in terms of APW quantities has been in the literature for several years<sup>3</sup> and involves quite complicated expressions because of the necessity of integrating products of APW wave functions and gradients of potentials over the Fermi surface. In a recent series of papers, Gaspari and Gyorffy<sup>1</sup> and Evans, Gaspari, and Gyorffy<sup>2</sup> have reformulated the e-p interaction into the following expression (in atomic units):

$$\langle I^2 \rangle^A = \frac{E_F}{\pi^2 n^2(E_F)} \sum_{l=0}^{\infty} \frac{2(l+1) \sin^2(\delta_{l+1}^A - \delta_l^A) n_{l+1}^A n_l^A}{n_{l+1}^{A(l)} n_l^{A(l)}}. \quad (1)$$

In Eq. (1),  $\langle I^2 \rangle^A$  is the square of the e-p matrix element averaged over the Fermi surface,  $E_F$  is the Fermi energy,  $n^A$  and  $n_l^A$  are the total and angular momentum components of the density of electronic states (DOS) at the Fermi level for site  $A$  in the unit cell,  $n_l^{A(l)}$  are effective free-scatterer densities of states defined in Refs. 1 and 2, and the  $\delta_l$  are scattering phase shifts determined from the self-consistent crystal potential. The essential ingredients in this formulation are the phase shifts and decomposed DOS which implicitly contain detailed information on the Fermi surface of the material. We note the previous work on calculating  $\lambda$  and  $T_c$  for simple metals using the pseudopotential method by Allen and Cohen,<sup>4</sup> and the work of Allen and Lee<sup>5</sup> in formulating the e-p interaction in terms of scattering phase shifts fitted to measured Fermi-surface data and applied to Cu by Nowak<sup>6</sup> using the APW formalism.

In calculating  $\lambda$  for the pure metals we follow McMillan<sup>7</sup> in writing

$$\lambda = n(E_F) \langle I^2 \rangle / M \langle \omega^2 \rangle. \quad (2)$$

For the three NaCl-structure carbides, there

are two atoms per unit cell and one must use care in deriving the equivalent expression for  $\lambda$  because of the presence of the optic mode branches. Since the metal masses are much greater than that of carbon, an accurate form for  $\lambda$  can be obtained following the idea of Phillips<sup>8</sup>:

$$\lambda_{\text{carbides}} = \frac{(n \langle I^2 \rangle)_{\text{met}}}{(M \langle \omega^2 \rangle)_{\text{met}}} + \frac{(n \langle I^2 \rangle)_{\text{carb}}}{(M \langle \omega^2 \rangle)_{\text{carb}}}. \quad (3)$$

The denominators in Eq. (3) refer to phonon averages over the metal and carbon sites, respectively. The heavy metal atom vibrations couple mainly to the electrons through zone-boundary acoustic phonons, while the much lighter carbon atoms couple primarily through the optic modes.<sup>8</sup> We emphasize that the form of Eq. (3) can be shown to be accurate only for those two-component systems having large mass differences. Gomersall and Gyorffy<sup>9</sup> have done calculations for NbN using Eq. (1) with additional approximations for the decomposed DOS's. They used an expression for  $\lambda$  similar to our Eq. (3), but having in both denominators  $\langle \omega^2 \rangle$ , averaged over *both* sites, metal and nonmetal. Their form

TABLE I. Total and angular momentum components of the densities of electronic states at the Fermi level for each site used in the calculations of  $\lambda$  and  $T_c$  for V, Nb, NbC, TaC, and HfC, in units of states/(Ry atom spin).

	$n_{\text{tot}}$	$n_s$	$n_p$	$n_d$	$n_f$	
V	15.125	0.172	2.096	12.649	0.208	
Nb	12.010	0.321	1.715	9.660	0.291	
NbC	{Nb	3.938	0.039	0.073	3.714	0.114
	{C	1.687	0.085	1.452	0.130	0.019
TaC	{Ta	3.070	0.055	0.044	2.855	0.116
	{C	1.426	0.077	1.176	0.158	0.016
HfC	{Hf	0.260	0.001	0.036	0.178	0.046
	{C	0.659	0.001	0.640	0.017	0.001

of Eq. (3) had the largest contribution to  $\lambda$  coming from the nonmetal (N in their case) site. This is in disagreement with the tunneling experiment of Zeller<sup>10</sup> on isostructural TaC which showed that the main contribution to  $\lambda$  comes from the acoustic vibrations which correspond to predominantly metal atom vibrations. We will show below that our results using Eq. (3) are in agreement with experiment.

Our computations using Eq. (1) are all based on self-consistent APW calculations. For V and Nb we have extended previously reported calculations<sup>11,12</sup> to obtain the angular momentum components of the DOS; while for NbC, TaC, and

HfC we have performed new calculations<sup>13</sup> employing the  $X\alpha$  exchange and including for the latter two compounds the mass-velocity and Darwin relativistic corrections. The DOS values shown in Table I were obtained by utilizing the APW results in Mueller's "quad" scheme,<sup>14</sup> which we have suitably modified to give decomposed DOS's. Sufficient sampling of Brillouin-zone points was taken to limit statistical errors to 2% in these calculations.

In Table II we show the results of our calculations making use of Eqs. (1)–(3). We also show in this table the phonon spectral moments that we have used in our calculations for  $\lambda$ , along with the references for them. To make the calculations truly "first principles," the phonon contributions should also be computed by making use of the electronic band structure results. At present, this cannot be done accurately enough without the use of some experimental information on the phonon spectrum, but this is usually available.

To calculate  $T_c$  for V and Nb we have used McMillan's<sup>7</sup> Eq. (18) involving the Debye temperature, while for the carbides we have used the related expression involving  $\langle\omega\rangle$  as discussed by Dynes.<sup>15</sup> For V and Nb we used  $\mu^* = 0.13$  and for the carbides  $\mu^* = 0.1$  as suggested by McMillan<sup>7</sup> for transition metals and for materials with wider bands, respectively.

The theoretical results for  $\lambda$  are in remarkably

TABLE II. Square of the electron-phonon matrix element averaged over the Fermi surface  $\langle I^2 \rangle$ , second moment of the phonon spectra per site defined as  $\langle\omega^2\rangle = \langle\omega\rangle / \langle 1/\omega \rangle$ , empirical and calculated values of  $\lambda$ , and measured and calculated values of  $T_c$  for V, Nb, NbC, TaC, and HfC.

	$n(E_F)^A \langle I^2 \rangle^A$ (eV/Å <sup>2</sup> )	$\langle I^2 \rangle^A$ (eV/Å <sup>2</sup> )	$M_A \langle\omega^2\rangle^A$ (eV/Å <sup>2</sup> ) <sup>a</sup>	$\lambda_{\text{emp}}^b$	$\lambda_{\text{calc}}$	$T_{c \text{ meas}}^c$ (°K)	$T_{c \text{ calc}}$ (°K)
V	6.35	5.72	9.98	0.60	0.64	5.30	6.5
Nb	7.64	8.68	8.73	0.82	0.88	9.22	10.6
NbC	{Nb	5.87	20.24	0.61	0.45 0.18	0.63	11.1
	{C	2.56	21.30				
TaC	{Ta	6.14	26.70	0.62	0.47 0.19	0.66	11.4
	{C	3.07	27.91				
HfC	{Hf	1.08	56.57	...	0.07 0.02	~0	~0
	{C	0.25	5.27				

<sup>a</sup>Nb: Ref. 7. V: Ref. 7; R. Colella and B. W. Batterman, Phys. Rev. B 1, 3913 (1970). Carbides: W. Weber, Phys. Rev. B 8, 5082 (1973); J. L. Feldman, private communication.

<sup>b</sup>V and Nb: Ref. 7. Carbides: J. K. Hulm, M. S. Walker, and N. Pessall, Physica (Utrecht) 55, 60 (1971).

<sup>c</sup>NbC: R. H. Willens, E. Buchler, and B. T. Matthias, Phys. Rev. 159, 327 (1967). TaC: B. T. Matthias, private communication. V and Nb: Ref. 7.

good agreement with the empirical values that were obtained by solving for  $\lambda$  from the measured values of  $T_c$ , especially since  $T_c$  is such a sensitive function of  $\lambda$ , and the calculations have no adjustable parameters. In addition, our theoretical results for  $T_c$  are rather good for the values of  $\mu^*$  that we have chosen. Although the actual values of  $\mu^*$  appropriate for these materials may be somewhat different from the values that we have used, we note that  $T_c$  is much more sensitive to  $\lambda$  than to  $\mu^*$ , and it is our very good calculated values of  $\lambda$  that we wish to emphasize. In light of this, accurate calculations of  $\mu^*$  should be encouraged.

Evans and co-workers<sup>2,16</sup> have done calculations on transition metals using Eq. (1) but with approximations for the decomposed DOS's, quantities for which they did not have calculated values, and their results for  $\lambda$  were within a factor of 2 or so of the empirical values. As we have shown here, the use of the calculated decomposed DOS's, which are readily available from band-structure calculations, gives much better agreement with experiment.

For the carbides, the major contribution to  $\lambda$  comes from the metal site [first term in Eq. (3)], and corresponds to the coupling of mainly the acoustic modes to the electrons. This agrees with Zeller's<sup>10</sup> experiment on TaC. Our calculated value of  $\lambda$  for HfC is very small, and HfC is predicted to be nonsuperconducting as is observed experimentally.

In comparing the pure metals and the carbides, we note that the large values of  $\lambda$  are obtained when the product  $n(E_F)\langle I^2 \rangle$  is large. NbC and TaC have smaller values of  $n(E_F)$  than the pure metals, but they have larger values of  $\langle I^2 \rangle$ , resulting in comparable values of  $\lambda$  for the four materials. These results provide a striking example of the interplay between the DOS at the Fermi level and the e-p interaction in determining superconductivity in materials.

The band-structure results for the carbides<sup>13</sup> indicate strong ionic bonding in these metals, with the carbon atoms having an excess of negative charge. This is likely the reason for the large e-p interaction in these compounds, as the conduction electrons have a strong tendency to screen the bare ionic charges when the atoms are displaced. Although HfC has a strong ionic bond,<sup>13</sup> and the Hf site has a large e-p interaction, the eight valence electrons per molecule places the Fermi level at a minimum in the DOS so that HfC has very weak metallic properties and no

superconductivity. No special soft-mode mechanism needs to be invoked to explain superconductivity in NbC and TaC, but rather their phonon anomalies<sup>17</sup> and high  $T_c$ 's are both consequences of their large e-p interactions.

In conclusion, it is encouraging that accurate electronic band structure calculations can give a good account of the parameters which enter into the theory of superconductivity, since these same calculations can be used to relate superconductivity to the physical and chemical properties of materials.

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<sup>1</sup>G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. **28**, 801 (1972).

<sup>2</sup>R. Evans, G. D. Gaspari, and B. L. Gyorffy, J. Phys. F: Metal Phys. **3**, 39 (1973).

<sup>3</sup>D. G. Golibersuch, Phys. Rev. **157**, 532 (1967); S. K. Sinha, Phys. Rev. **169**, 477 (1968).

<sup>4</sup>P. B. Allen and M. L. Cohen, Phys. Rev. **187**, 525 (1969).

<sup>5</sup>P. B. Allen and M. J. G. Lee, Phys. Rev. B **5**, 3848 (1972).

<sup>6</sup>D. Nowak, Phys. Rev. B **6**, 3691 (1972).

<sup>7</sup>W. L. McMillan, Phys. Rev. **167**, 331 (1968).

<sup>8</sup>J. C. Phillips, in *Superconductivity in d- and f-Band Metals*, AIP Conference Proceedings No. 4, edited by D. H. Douglass, Jr. (American Institute of Physics, New York, 1972).

<sup>9</sup>I. R. Gomersall and B. L. Gyorffy, J. Phys. F: Metal Phys. **3**, L138 (1973).

<sup>10</sup>H. R. Zeller, Phys. Rev. B **5**, 1813 (1972).

<sup>11</sup>D. A. Papaconstantopoulos, J. R. Anderson, and J. W. McCaffrey, Phys. Rev. B **5**, 1214 (1972).

<sup>12</sup>J. R. Anderson, D. A. Papaconstantopoulos, J. W. McCaffrey, and J. E. Schirber, Phys. Rev. B **7**, 5115 (1973).

<sup>13</sup>B. M. Klein and D. A. Papaconstantopoulos, to be published.

<sup>14</sup>F. M. Mueller, J. W. Garland, M. H. Cohen, and K. H. Bennemann, Ann. Phys. (New York) **67**, 19 (1971).

<sup>15</sup>R. C. Dynes, Solid State Commun. **10**, 615 (1972).

<sup>16</sup>R. Evans, V. K. Ratti, and B. L. Gyorffy, J. Phys. F: Metal Phys. **3**, L199 (1973).

<sup>17</sup>See H. G. Smith, in *Superconductivity in d- and f-Band Metals*, AIP Conference Proceedings No. 4, edited by D. H. Douglass, Jr. (American Institute of Physics, New York, 1972), for a discussion of this point and additional references.