Calculation of the superconducting parameter \( \langle I^2 \rangle \) for hcp transition metals

C.-G. Jiang, G. Fletcher,* and J. L. Fry

Department of Physics, Box 19059, The University of Texas at Arlington, Arlington, Texas 76019

D. A. Papacostantopoulos

Complex Systems Theory Group, Naval Research Laboratory, Washington, D.C. 20375-5000

(Received 14 January 1991; revised manuscript received 1 April 1991)

The Fermi-surface-averaged electron-phonon interaction \( \langle I^2 \rangle \) has been computed for 12 hexagonal-close-packed transition metals in the 3d, 4d, and 5d series. The calculations were first done with a quasiorthogonal tight-binding formalism based on Fröhlich's modified tight-binding wave function. This method employed accurate Slater-Koster fits to scalar-relativistic augmented-plane-wave band structures, and scaling laws to determine gradients of Slater-Koster parameters. The second method employed the rigid-muffin-tin approximation and the augmented-plane-wave band structures. The two methods gave the same systematic trends across the series and good agreement between computed values for most elements. Differences in some cases are attributed to sensitivity of the calculation to band-structure parameters and different approximations employed. The two results were compared with empirically deduced values and other theoretical calculations. Single-atomic character, crystal structure, and the area and complexity of the Fermi surface have been found to be important in determining the behavior of \( \langle I^2 \rangle \).

I. INTRODUCTION

There has been considerable interest in predicting and calculating the superconducting transition temperature, \( T_c \), for simple metals, transition metals, and their compounds since the BCS theory\(^1\) and the more general Eliashberg-Nambu strong-coupling theory\(^2,3\) were developed. Both of these theories relate closely properties of the superconducting state to those of the normal state (e.g., phonon spectrum, electron-phonon interaction, etc.). Therefore, the calculations of \( T_c \) depend sensitively on the properties of a material, and more accurate treatment of these normal-state properties gives a reliable determination of \( T_c \).

\( T_c \), in strong-coupling theory, is determined simply by solving the linearized Eliashberg equation to obtain the point where the nonzero solution of the gap function \( \Delta(\omega) \) just appears. This is usually accomplished by an iterative numerical solution of Eliashberg's gap equation from knowledge of the Eliashberg electron-phonon coupling function, \( \alpha^2(\omega)F(\omega) \), and the Coulomb repulsive potential, \( U_C \). For simple metals falling in the weak-coupling regime, \( \alpha^2(\omega)F(\omega) \) can be written in terms of pseudopotential form factors\(^4\) and then the problem can be solved from the deduced gap edge \( \Delta(\Delta_0) \approx \Delta_0 \) by using the BCS relation \( \Delta_0 = 1.76k_BT_c \). Alternatively, McMillan has done a detailed study of the dependence of \( T_c \) on the electron-phonon interaction in metals.\(^5\) He used an iterative technique to improve the accuracy of an assumed analytic solution to the Eliashberg equation and found a simple formula for \( T_c \) in terms of three normal-state parameters:

\[
T_c = \frac{\theta}{1.45} \exp \left( -\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right) .
\]  (1)

In this equation, \( \theta \) is the Debye temperature, and \( \lambda \) and \( \mu^* \) are the electron-phonon and electron-electron coupling constants, respectively. Allen and Cohen\(^6\) have performed pseudopotential calculations for \( \lambda \) and hence \( T_c \) from McMillan's equation (1) for 16 simple metals and the alkaline earths, Ca, Sr, and Ba. They concluded that the electron-phonon interaction mechanism does a completely adequate job of explaining \( T_c \) in these metals. For transition metals McMillan showed that the electron-phonon coupling constant, \( \lambda \), can be written in the form of an electronic term divided by a phonon term:\(^7\)

\[
\lambda = \frac{n(E_F)\langle I^2 \rangle}{M\langle \omega^2 \rangle} ,
\]  (2)

where \( n(E_F) \) is the density of states at the Fermi level \( E_F \), \( \langle I^2 \rangle \) is the square of the electronic transition matrix element averaged over the Fermi surface, \( M \) is atomic mass, and \( \langle \omega^2 \rangle \) is the renormalized phonon frequency. By using Eqs. (1) and (2), and known values of \( n(E_F) \), \( M \), and \( \langle \omega^2 \rangle \) for a given material, we can either determine an empirical value of \( \langle I^2 \rangle \) through the empirical value of \( \lambda \) obtained via the experimentally measured value of \( T_c \), or determine \( T_c \) through the value of \( \lambda \) by calculating the quantity \( \langle I^2 \rangle \). The determination of the theoretical value of \( \langle I^2 \rangle \) is therefore the major part of the task to determine \( T_c \) theoretically. The purpose of this paper is to obtain \( \langle I^2 \rangle \) for hcp elements. Two basic techniques which have been used in calculating \( \langle I^2 \rangle \) are the rigid-muffin-tin approximation (RMTA) and the modified-tight-binding approximation (MTBA). Both are used here to provide not only values of \( \langle I^2 \rangle \), but also esti-
mates of their accuracy obtained by comparing the two results.

The RMTA was proposed by Gaspari and Gyorffy,7
and is based on the Bloch formulation8 of the electron-
phonon interaction in which the transition matrix be-
tween two electron states is taken between eigenfunctions
of the periodic potential. The systematic study of 3d, 4d,
and 5d transition-metal series using the RMTA has been
done by several previous researchers in cubic structures.9–12
The MTBA technique was first implemented by Mitra13
and Barišić et al.14 All the effects of the
electron-phonon interaction are represented by an
electron-phonon interaction matrix taken between
Frohlich’s modified-tight-binding bases.15,16 In the case
of transition metals the electrons are tightly bound, with
wave functions describable by localized orbitals having
nearly vanishing overlap with their nearest neighbors,
and the transitions are between two states on the Fermi
surface. These two approaches are identical to first order
in the ion displacement.17,18

Frohlich’s modified-tight-binding basis leads13,14 to the
expression of transition matrix elements in terms of a gra-
dient of Hamiltonian matrix elements in atomic bases
\( \nabla(\phi_{n}(r-R_{i})) \) in \( \phi_{n}(r-R_{i}) \). This allows use of
the Slater-Koster (SK) simplified linear combinations of
atomic-like orbitals (LCAO) scheme15,16 to describe
the variation of energy integrals due to lattice vibrations.
By employing scaling laws for the SK bond parameters
the gradient calculation may be simplified. Results for some
cubic transition metals using the MTBA were given by
Varma et al.;21 Fry et al.22 reported a systematic study
of the cubic transition metals, and Fletcher et al.23
computed \( \langle I^{2}\rangle \) and \( \langle F^{2}\rangle \) for several bcc transition metals and alloys.

While there is general agreement between values com-
puted using the RMTA and the MTBA, some differences
have been found which are thought to be due to the sensi-
tivity of some of the calculations to numerical procedures
and the details (shapes, sizes) of the Fermi surface. Since
the RMTA and MTBA are both approximations, the re-
gions of validity for these two may overlap but not be
congruent. Direct comparison of computed values of
\( \langle I^{2}\rangle \) has been possible. Experimental values deduced
through Eq. (1) are made uncertain by lack of reliable
values of \( \langle \omega^{2}\rangle \) and \( \mu^{*} \), so the agreement between the
RMTA and MTBA is perhaps a better indication of the
reliability of theoretical estimates of \( \langle I^{2}\rangle \).

Until now the MTBA has been limited to cubic sys-
tems only. This paper reports calculations of \( \langle I^{2}\rangle \) for 12
hcp transition metals using the MTBA and RMTA
methods. The plan of this paper is the following. In Sec.
II, we describe the quasiorthogonal, tight-binding formu-
lation of the electronic transition matrix in an LCAO
representation using the modified-tight-binding bases.
The final MTBA expression for \( \langle I^{2}\rangle \) in terms of transition
matrix elements is presented. In the same section we
also give a brief account of the RMTA approach. In Sec.
III we present our computed values of \( \langle I^{2}\rangle \), compare
with previous estimates, and discuss the variation of \( \langle I^{2}\rangle \)
across the 3d, 4d, and 5d transition-metal series of the
Periodic Table. Section IV contains the concluding re-
marks.

II. METHODS OF CALCULATION

The form of McMillan’s representation for \( \lambda \) given in
Eq. (2) is still valid for the hcp structure (two atoms per
unit cell) if \( M \) is the mass of a single atom and \( n(E_F) \)
the total density of states per unit cell. It is our purpose
to calculate the quantities \( \langle I^{2}\rangle \) for hcp metals. We now
describe two methods of calculation which are used in
this work.

A. The modified-tight-binding approximation

Frohlich’s assumption suggests that the tight-binding
wave function corresponding to the ions slightly dis-
placed with distance \( u_{i} \), from their equilibrium position
\( R_{i}+\tau \) can be written in modified-tight-binding form,15,16
\[
\Phi_{\mu}(k,r)=\frac{1}{\sqrt{N}} \sum_{i} e^{i(k(R_{i}+\tau)}} \phi_{\mu}(r-R_{i}-\tau-u_{i}) .
\]

Assuming that the atom’s displacements \( u_{i} \) are small and
the quasiorthogonality relation for the atomic-like bases
remains valid,
\[
\langle \phi_{\mu}(r-R_{i}-\tau-u_{i})|\phi_{\nu}(r-R_{j}-\tau-u_{j})\rangle=\delta_{ij}\delta_{\tau\nu}\delta_{\mu\nu} .
\]

We can write the Bloch-like electron state in the de-
formed lattice as
\[
\Psi_{k\mu}(r)=\frac{1}{\sqrt{N}} \sum_{n,\tau} \Phi_{n\mu}(k) \phi_{\mu}(r,R_{i}-\tau-u_{i}) ,
\]
where \( \Phi_{n\mu}(k) \) are eigenfunctions and \( \phi_{\mu}(r,R_{i}) \) are
Bloch-like sums defined in (3). The electron-phonon
interaction is normally described by the scattering of an
electron in one of the above states by the lattice vibra-
tions, leading to a transition to another such state. Using
(3), (4), and (5), one can show that the electronic transi-
tion matrix which is required in the calculation of \( \langle I^{2}\rangle \)
can be written in each Cartesian direction \( \alpha \) as
\[
I_{k\mu',k\nu}=\sum_{m,n} A_{m\mu}(k)[\gamma_{mn}(k)-\gamma_{mn}(k')]A_{n\mu'}(k') ,
\]
where
\[
\gamma_{mn}(k)=\sum_{i,j} [\phi_{m}(r-R_{i}-\tau)|H|\phi_{n}(r-R_{j}-\tau)]
\times e^{-i(k(R_{i}+\tau-R_{j}-\tau')} .
\]

The energy integrals in (7) are sums of terms that are
products of angular parts (functions of the direction
cosines \( l,m,n \) of \( R_{i}+\tau \)) and radial parts (SK bond param-
ters, which are functions of distance between two
atoms). Therefore, to calculate (7) we shall write the gra-
dient operator \( \nabla_{0} \) in terms of derivatives of the energy in-
tegrals with respect to radial distance and direction
cosines. For the evaluation of the radial derivatives one must know the bond length dependence of each of the bond strength parameters. In this study, we have used the empirical scaling laws obtained by Harrison,24 where one expresses the variation of the bond strength as an inverse power of the bond length, with the power depending only upon the angular symmetry of the orbitals involved. This has been found to be quite accurate, particularly in the vicinity of the equilibrium atomic position. A detailed analysis of the validity of this scaling law can be found in Ref. 24. According to Harrison's scaling law the ss, pp, and sp bonds are taken to vary as $D^{-2}$, the dd bonds as $D^{-5}$, and the sd and pd bonds as $D^{-3.5}$, where $D$ is bond length. For hcp structures, the work to evaluate (6) and (7) is very tedious, so we have used artificial intelligence programming to carry out this task accurately.

The quantity $\langle I^2 \rangle$ can be written as

$$\langle I^2 \rangle = \frac{\sum \int_{FS} \frac{dS_k}{|\nabla_k E_{k\mu}|} \sum_{I' \mu'} \sum_{m', n'} A^*_{m' \mu'}(k) A_{n' \mu'}(k') \gamma_{m' n'}^{\alpha \alpha}(k) \sum \int_{FS} \frac{dS_{k'}}{|\nabla_k E_{k\mu'}|} A_{m' \mu'}(k') A_{n' \mu'}(k')}{\sum \int_{FS} \frac{dS_k}{|\nabla_k E_{k\mu}|} \sum_{I' \mu'} \sum_{m', n'} A^*_{m' \mu'}(k) A_{n' \mu'}(k') \gamma_{m' n'}^{\alpha \alpha}(k)}.$$  

Substituting (6) and (7) into (8), and using symmetry relations like $\gamma_{m n}^{\alpha \alpha} = -\gamma_{n m}^{\alpha \alpha}$, we find the final expression for $\langle I^2 \rangle$ in an LCAO representation

$$\langle I^2 \rangle = \frac{4 \sum_{m < n} \sum_{\alpha} \gamma_{m n}^{\alpha \alpha} + 2 \sum_{m} b_{m}}{\sum \int_{FS} \frac{dS_k}{|\nabla_k E_{k\mu}|} \sum_{I' \mu'} \sum_{m', n'} A^*_{m' \mu'}(k') A_{n' \mu'}(k') \gamma_{m' n'}^{\alpha \alpha}(k')}.$$  

where

$$a_{m n}^\alpha = \sum_{\mu} \int_{FS} \frac{dS_k}{|\nabla_k E_{k\mu}|} \sum_{m', n'} A^*_{m' \mu}(k) A_{n' \mu}(k) \gamma_{m' n'}^{\alpha \alpha}(k) \sum_{\mu'} \int_{FS} \frac{dS_{k'}}{|\nabla_k E_{k'\mu'}|} A_{m' \mu'}(k') A_{n' \mu'}(k'),$$

and

$$b_{m} = \sum_{\mu} \int_{FS} \frac{dS_k}{|\nabla_k E_{k\mu}|} \sum_{m', n', \alpha} A^*_{m' \mu}(k) A_{n' \mu}(k) \gamma_{m' n'}^{\alpha \alpha}(k) \sum_{\mu'} \int_{FS} \frac{dS_{k'}}{|\nabla_k E_{k'\mu'}|} A_{m' \mu'}(k') \gamma_{m' n'}^{\alpha \alpha}(k) \sum_{\mu'} \int_{FS} \frac{dS_{k'}}{|\nabla_k E_{k'\mu'}|} A_{m' \mu'}(k')^2,$$

In order to do the numerical evaluation of these surface integrals, we have divided the $\frac{1}{32}$th irreducible Brillouin zone (IBZ) into 384 tetrahedra. By checking the relation between Fermi energy and those energies of $k$ points at four vertices of each tetrahedron, we have constructed the Fermi surface in the hcp Brillouin zone and have performed surface integrations over the Fermi surface using the analytic tetrahedron method (ATM).

**B. The rigid-muffin-tin approximation**

The assumption that the muffin-tin potential moves rigidly with the atom as it vibrates is known as the rigid-muffin-tin approximation (RMTA). The RMTA was applied by Gaspari and Gyorffy7 to derive a now widely used formula for the electron-ion matrix element $\langle I^2 \rangle$, i.e.,

$$\langle I^2 \rangle = \frac{2E_F}{\pi^2 n^2(E_F)} \sum_{I} (I + 1) \sin^2(\delta_I - \delta_I R_I R_{I+1},$$

where $\delta_I$ is the scattering phase shift at $E_F$ and $R_I$ is the ratio

$$R_I = \frac{n_I(E_F)}{n_I^{1/3}(E_F)},$$

where $n_I(E_F)$ are the angular momentum components of the density of states (DOS) at $E_F$ within the muffin-tin sphere and $n_I^{1/3}(E_F)$ is the single scatterer DOS which can be computed from the radial wave functions. The above equation is exact to $l = 1$, but for $l = 2$ and higher it involves nonspherical corrections. These corrections, as shown by Butler et al.,26 are small for cubic elements. For the hcp elements we also expect the nonspherical corrections to be small and hence we have neglected them in this work.

The necessary input to the Gaspari-Gyorffy formula was generated as follows: (a) the phase shifts $\delta_I$ were found from the logarithmic derivatives of the radial wave functions that correspond to the self-consistent crystal
potential that we found from an APW calculation of each element. (b) The DOS $n(E_F)$ and $n_i(E_F)$ were computed by the tetrahedron method\textsuperscript{25} based on APW results for 45 k points in the irreducible hcp Brillouin zone. (c) The free scatterers $n_i^{11}(E_F)$ were calculated using the radial wave functions of the above crystal potential.

Finally, the accuracy of the RMTA has been questioned, especially for the new high-temperature ionic superconductors. However, in the hcp $d$-like elements that we examine here the RMTA should work well. Comparison with tight-binding results, where the RMTA is not necessarily made, provides a test of both approximation methods, and is given in the next section.

III. RESULTS AND DISCUSSION

A. Band structures

The MTBA and RMTA formulas for $\langle I^2 \rangle$ have been applied here to all hcp metals in the 3$d$, 4$d$, and 5$d$ transition-metal series. The first-principles band structures were self-consistent, scalar-relativistic calculations performed by the APW method at the equilibrium lattice constants. The SK fits to these band structures may be found in Ref. 27. In the MTBA work we employed only the two-centered (2C) orthogonal parameters in order to simplify the process, so comparison of computed quantities for RMTA and MTBA methods must be made with this fact in mind. The 2C-nonorthogonal SK parameters are more accurate, with a typical rms error of 5 mRy over the APW bands, while the rms error using orthogonal parameters is approximately 10 mRy. The SK parameters, band structures, and $n(E)$ plots are presented in Ref. 27, along with rms errors of the various fits.

Results for the calculation of the electron-phonon interaction sometimes depend sensitively upon the shape of bands, the Fermi energy and Fermi surface, and $n(E_F)$, so accurate determination of these quantities is important. Table I shows $E_F$ and $n(E_F)$ for the orthogonal-tight-binding (OTB), nonorthogonal-tight-binding (NOTB), and APW band structures for each element considered here. Integrals with the OTB and NOTB band structures were computed here using the ATM with 384 and then 1536 tetrahedra in the IBZ. The APW results were obtained using only 45 k points in the IBZ, since generation of many points was not practical for a systematic study of the hcp elements. Because of this, some of the computed values were not stable and are left blank in Table I in the APW columns. $E_F$ and $n(E_F)$ have also been computed independently with a different ATM program and 3078 tetrahedra in the IBZ.\textsuperscript{28} In view of the different numbers of tetrahedra used, we consider agreement between the two NOTB results excellent (see Ref. 28 for more details).

The Fermi energies computed by all these methods agree well, but $n(E)$ is a rapidly varying quantity near $E_F$ for some of the hcp metals, so greater differences occur for $n(E_F)$ with the different band structures. Using the NOTB values as a standard (better ATM calculations, better fit to first-principles band structures), the average absolute difference is about 15% for both the OTB and APW values of $n(E_F)$, with a maximum difference of about 36% for Y, where the APW DOS may not be reliable due to the small number of k points used. Since values of $\langle I^2 \rangle$ quoted below were obtained with APW and OTB band structures, a significant comparison is the corresponding $n(E_F)$ values for each element obtained from these bands. The average absolute difference is 17% between APW and OTB computed $n(E_F)$, with a maximum difference of about 70%, again for Y.

<table>
<thead>
<tr>
<th>Element</th>
<th>$c/a$</th>
<th>OTB</th>
<th>NOTB</th>
<th>APW</th>
<th>OTB</th>
<th>NOTB</th>
<th>$n(E_F)$ (states/Ry unit-cell)</th>
<th>Ref. 28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>1.59</td>
<td>0.429</td>
<td>0.430</td>
<td>0.427</td>
<td>57.1</td>
<td>61.4</td>
<td>74.7</td>
<td>61.0</td>
</tr>
<tr>
<td>Ti</td>
<td>1.59</td>
<td>0.590</td>
<td>0.590</td>
<td>0.592</td>
<td>26.7</td>
<td>23.4</td>
<td>28.9</td>
<td>24.0</td>
</tr>
<tr>
<td>Co</td>
<td>1.62</td>
<td>0.683</td>
<td>0.683</td>
<td>0.681</td>
<td>85.2</td>
<td>78.6</td>
<td>74.4</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>1.86</td>
<td>0.404</td>
<td>0.386</td>
<td>9.1</td>
<td>10.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>1.57</td>
<td>0.395</td>
<td>0.398</td>
<td>0.394</td>
<td>52.0</td>
<td>60.1</td>
<td>82.0</td>
<td>60.8</td>
</tr>
<tr>
<td>Zr</td>
<td>1.59</td>
<td>0.544</td>
<td>0.545</td>
<td>0.542</td>
<td>26.9</td>
<td>22.1</td>
<td>22.7</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>1.61</td>
<td>0.747</td>
<td>0.740</td>
<td>0.737</td>
<td>22.5</td>
<td>25.6</td>
<td>24.4</td>
<td>25.4</td>
</tr>
<tr>
<td>Ru</td>
<td>1.59</td>
<td>0.762</td>
<td>0.758</td>
<td>0.754</td>
<td>25.4</td>
<td>22.1</td>
<td>24.3</td>
<td>22.0</td>
</tr>
<tr>
<td>Cd</td>
<td>1.89</td>
<td>0.190</td>
<td>0.250</td>
<td>12.4</td>
<td>15.1</td>
<td></td>
<td></td>
<td>11.4</td>
</tr>
<tr>
<td>Hf</td>
<td>1.58</td>
<td>0.574</td>
<td>0.575</td>
<td>0.575</td>
<td>25.1</td>
<td>17.4</td>
<td>21.7</td>
<td>17.2</td>
</tr>
<tr>
<td>Re</td>
<td>1.62</td>
<td>0.800</td>
<td>0.786</td>
<td>0.783</td>
<td>17.7</td>
<td>19.0</td>
<td>18.3</td>
<td>20.0</td>
</tr>
<tr>
<td>Os</td>
<td>1.58</td>
<td>0.850</td>
<td>0.834</td>
<td>0.833</td>
<td>18.6</td>
<td>17.1</td>
<td>18.4</td>
<td>16.8</td>
</tr>
</tbody>
</table>
B. Computed values of $\langle I^2 \rangle$

Calculation of $\langle I^2 \rangle$ in the MTBA is more expensive than calculation of $n(E_F)$ since matrix elements are complicated and whole zone integration is required. Consequently the ATM was limited to 384 tetrahedra in each of the 24 IBZ, i.e., 9216 tetrahedra in the whole zone. On the other hand the RMTA calculation of $\langle I^2 \rangle$ employed the same 45 k points as the $n(E_F)$ calculation. We report in Table II our results for $\langle I^2 \rangle$ using both MTBA and RMTA methods, together with the empirical values for some of the elements from the studies of Hopfield and Butler. The empirical values were obtained by multiplying empirical values of $\lambda$ (which required experimental estimates of $T_c$ and $\mu^*$) by $M(\omega^2)$ and dividing by $n(E_F)$. Consequently, substantial uncertainty is associated with the empirical values of $\langle I^2 \rangle$ because they depend upon the poorly known values of the Coulomb pseudopotential $\mu^*$, and on estimates of $\langle \omega^2 \rangle$. Details of the procedures used in estimating these quantities may be found in Refs. 9 and 29. Also listed in Table II are other RMTA calculations, including those by Butler (4d) and Papaconstantopoulos et al. (3d and 4d) for hcp metals in equal density fcc or bcc structures and John et al. (5d) in the hcp structure. The latter work included spin-orbit corrections to the Gaspari-Gyorffy RMTA formula, but was based on non-self-consistent band-structure calculations.

The principal results of this paper are contained in the second and third columns of Table II. Both are theoretical calculations of $\langle I^2 \rangle$ for hcp metals using no adjustable parameters, but employing the MTBA and RMTA, respectively. Even if the MTBA and RMTA approximations were identical in principle, the limited numerical convergence and some different approximations being made in deriving the final expressions of $\langle I^2 \rangle$ of the two calculations would be expected to produce some differences. Thus we feel that reasonable agreement between the two techniques has been achieved, and note that the same systematic trends through the Periodic Table have been found. In fact a comparison of the % difference between RMTA and MTBA values of $n(E_F)$ and the % difference between corresponding values of $\langle I^2 \rangle$ shows a strong correlation. We note that on the average $\langle I^2 \rangle_{\text{RMTA}}$ is about 25% less than $\langle I^2 \rangle_{\text{MTBA}}$. Thus there are noticeable systematic differences. The largest discrepancies for $\langle I^2 \rangle$ occur near the first of each transition series: 55% for Sc and Y, followed by 25% for Ti, Zr, and Hf, where sharp structure of the DOS near $E_F$ makes the RMTA results less reliable because of the limited number of k points used. These follow the same pattern as the corresponding $n(E_F)$. We can offer no explanation for the systematic shift at this time, but attribute the correlated larger discrepancies to the numerical sensitivity of the calculations in some of the elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>hcp MTBA</th>
<th>hcp RMTA</th>
<th>Empirical estimates</th>
<th>bcc RMTA</th>
<th>fcc RMTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>0.0032</td>
<td>0.0014</td>
<td>0.0077&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.0042&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.0080&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ti</td>
<td>0.0050</td>
<td>0.0038</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.0026</td>
<td>0.0022</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.0058</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>0.0033</td>
<td>0.0015</td>
<td>0.0008&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0021&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0044&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Zr</td>
<td>0.0061</td>
<td>0.0046</td>
<td>0.0098&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.0070&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Tc</td>
<td>0.0135</td>
<td>0.0111</td>
<td>0.0244&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0189&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0212&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ru</td>
<td>0.0122</td>
<td>0.0110</td>
<td>0.0167&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0116&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.0141&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0032</td>
<td></td>
<td></td>
<td></td>
<td>0.0030&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Hf</td>
<td>0.0076</td>
<td>0.0056</td>
<td>0.0074&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re</td>
<td>0.0183</td>
<td>0.0143</td>
<td>0.0124&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os</td>
<td>0.0189</td>
<td>0.0170</td>
<td>0.0123&lt;sup&gt;d&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Hopfield, Ref. 29.
<sup>b</sup> Butler, Ref. 9.
<sup>c</sup> Papaconstantopoulos et al., Ref. 10.
<sup>d</sup> John et al., Ref. 11.
C. Systematic trends of \( \langle I^2 \rangle \) in the Periodic Table

It is interesting and important to understand, at least in a qualitative way, how \( \langle I^2 \rangle \) varies from one metal to another across the transition-metal series. The general trends for cubic metals have been established in previous studies\(^{9-10,21-23} \) for the 3d, 4d, and 5d series. For the cubic metals there is good agreement between computed values of \( \langle I^2 \rangle \) using RMTA and MTBA methods,\(^{22} \) so, to reduce clutter, only RMTA cubic results are shown in the figures. A suggestive curve representing \( \langle I^2 \rangle \) as an atomic property has been drawn in Fig. 2 for the 4d cubic transition metals to show the trends with atomic number. It is drawn through the points Y, Zr, and Ru where we believe from our calculations that the single atomic nature dominates the band features. This curve has been superimposed without change into Figs. 1 and 3, revealing approximately the same trend in each series: \( \langle I^2 \rangle \) increases to a maximum as the \( d \) bands and overlapping \( s \) band become half-filled, followed by a corresponding decrease as both bands fill. The distribution is approximately symmetric about the half-filled configuration in the solid, \( n d^2(n + 1)s^2 \) (i.e., Cr, Mo, W).

While \( \langle I^2 \rangle \) data are more sparse for hcp metals, RMTA and MTBA points computed here may be interpreted approximately with the same universal curve used for the cubic transition metals. As a rule, hcp values of \( \langle I^2 \rangle \) appear to be lower than cubic values, with the exception of some of the 5d transition metals. This may result from spin-orbit corrections employed in Ref. 11 or simply reflect the lack of self-consistency in the band structures in that calculation. It is difficult to deduce from formulas as complicated as Eqs. (9)–(11) (MTBA) or (12) and (13) (RMTA) how the observed trends occur, but we offer the following suggestions.

In the MTBA, band effects enter most strongly through the Fermi-surface shape and the density of states at the Fermi level [see Eq. (9)], while the atomic-like character is displayed through the gradients of 2C SK parameters which contain implicitly the effective atomic potentials. Unless unusual Fermi-surface-averaging effects occur, which may be the case for Tc, e.g., the electron-phonon coupling trends will be dominated by the gradients of the SK parameters which are expected to reflect the electron-hole symmetries about the atomic number corresponding to a half-filled shell. A similar separation of \( \langle I^2 \rangle \) into band and atomic contributions occurs in the RMTA: Band effects appear in the partial and total DOS, while the scattering phase shift and single scatterer DOS may be dominated by the muffin-tin (atomic-like) potential.

Comparing our hcp results with the results of cubic RMTA calculations in cubic structures, we find several of the elements showing their \( \langle I^2 \rangle \) values behaving as

---

**FIG. 1.** \( \langle I^2 \rangle \) in 3d transition metals. Open and solid circles are the results of the present hcp MTBA and RMTA studies, respectively. Solid squares are the cubic RMTA values from Ref. 10 of the text.

**FIG. 2.** \( \langle I^2 \rangle \) in 4d transition metals. Open and solid circles are the results of the present hcp MTBA and RMTA studies, respectively. Solid squares are the cubic RMTA values from Ref. 9 of the text.

**FIG. 3.** \( \langle I^2 \rangle \) in 5d transition metals. Open and solid circles are the results of the present hcp MTBA and RMTA studies, respectively. Solid squares are the RMTA values for hcp metals reported in Ref. 11 of the text.
atomic in nature, since there is very close agreement between hcp and cubic values. Butler\textsuperscript{26} has done calculations for Ru both in bcc and fcc structures using the RMTA. The \( \langle I^2 \rangle \) values of his calculations are 0.0116 and 0.0141 Ry\(^2\)/a.u.\(^2\) for bcc and fcc phases, respectively, which are close to our hcp value of 0.0122 Ry\(^2\)/a.u.\(^2\). This suggests that \( \langle I^2 \rangle \) for Ru is strongly of single atomic character. The largest discrepancy found between our MTBA and RMTA bcc values is for Tc. This may be a consequence of the importance of band effects, as suggested in Ref. 30. We found the area of the Fermi surface of Tc to be the largest among the transition metals and very complicated, a factor which may account for the observed differences.

Since superconducting transition temperature \( T_c \) is influenced directly by the value of \( \lambda \) given by Eq. (2) it should be emphasized that the product \( n \langle E_F \rangle \langle I^2 \rangle \) is more directly connected to \( T_c \). At this level the atomic in nature quantities \( \langle I^2 \rangle \) are modulated by \( n \langle E_F \rangle \) which brings into the picture the different band-structure effects for different elements and crystal structures.

IV. CONCLUSION

We have computed the Fermi-surface-averaged electron-phonon interaction in hcp transition metals using the MTBA and RMTA expressions. While there is acceptable agreement between the two results, especially considering the various numerical constraints placed upon the calculations, the RMTA values were systematically lower by about 25\%. Both methods found the same systematic trends across the Periodic Table which appear to be similar to the trends seen in the cubic metals. Exceptions to the trends are attributed to special Fermi-surface or band effects. Scalar-relativistic effects were included in the band structures, but explicit corrections to the RMTA and MTBA formulas were not made. The basic assumptions of the RMTA and MTBA are not necessarily the same. One uses a muffin-tin potential which is assumed to move rigidly during a lattice vibration, while the other makes no assumption about the form of the potential, but assumes scaling laws for the change in integrals of the potential. Additional computational details make it remarkable that the level of agreement found in Table II is possible, and suggest that we may have fairly reliable (\( \pm 25\% \)) theoretical estimates of \( \langle I^2 \rangle \) for the transition metals. Since the MTBA method may more easily be extended to crystals with arbitrary numbers of atoms and arbitrary symmetry, agreement with the RMTA for hcp, bcc, and fcc metals suggests it as a method of choice for future studies in complex systems. New techniques\textsuperscript{31} for measuring \( \langle I^2 \rangle \) directly may further serve to check existing calculations and provide a better theoretical understanding of the electron-phonon interaction in metals.

ACKNOWLEDGMENTS

We would like to thank L.L. Boyer for making a modification of the density-of-states program used in the ATM calculations. Computational facilities were provided by The University of Texas Center for High Performance Computing. Work at The University of Texas at Arlington was supported by The Robert A. Welch Foundation under Grant No. Y-707.

---

\textsuperscript{*}Present address: Department of Physics, Texas Technical University, TX 79409.

\textsuperscript{1}J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 106, 162 (1957); 108, 1175 (1957).


\textsuperscript{3}Y. Nambu, Phys. Rev. 117, 648 (1960).

\textsuperscript{4}J. P. Carbotte and R. C. Dynes, Phys. Rev. 172, 476 (1968).

\textsuperscript{5}W. L. McMillan, Phys. Rev. 167, 331 (1968).


\textsuperscript{8}F. Bloch, Z. Phys. 52, 555 (1928).


\textsuperscript{15}H. Fröhlich, in Perspectives in Modern Physics, edited by R. E. Marshak (Interscience, New York, 1966).


\textsuperscript{17}R. A. Deegan, Phys. Rev. B 5, 1183 (1972).


\textsuperscript{20}M. Miasek, Phys. Rev. 107, 92 (1957).


