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Transferability and the electron-phonon interaction: A reinterpretation of the rigid-muffin-tin approximation

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The expression for the McMillan-Hopfield constant $\eta = N(E_F)\langle I^2 \rangle$ within the rigid-muffin-tin approximation (RMTA) is reinterpreted in terms of single-channel electron-ion matrix elements $I_{l,l+1}^2$ and angular-momentum-character fractions f_l of the electronic states at the Fermi level. Reexamination of Nb- and V-based $A15$ compounds suggests that $I_{l,l+1}^2$ is more nearly an atomic property, and thus transferable from system to system, than other commonly used quantities. The fractions f_l are dependent on bonding character and crystal structure but tend to be constant within a class of compounds. Criteria for increasing η within RMTA are discussed.

I. INTRODUCTION

In his classic study of the electron-phonon interaction parameter λ and its relation to the superconducting transition temperature T_c, McMillan[1] showed that λ can be written

$$\lambda = \frac{N(E_F)\langle I^2 \rangle}{M\langle \omega^2 \rangle} \tag{1}$$

in terms of the density of states $N(E_F)$ per spin at the Fermi energy E_F, a mean-square electron-ion matrix element $\langle I^2 \rangle$, and an appropriately defined lattice stiffness $M\langle \omega^2 \rangle$. A topic of particular interest in the ensuing decade has been the discussion of high T_c metals in terms of one or the other of the factors $N(E_F)$, $\langle I^2 \rangle$, or $M\langle \omega^2 \rangle$ as most important in leading to high-temperature superconductivity. With one of these factors [say, $N(E_F)$] as the principal determinant of the high T_c, a natural procedure which could be tried to produce a higher temperature superconductor is to "transfer" this large value of $N(E_F)$ to a metal with more favorable values of $\langle I^2 \rangle$ and $M\langle \omega^2 \rangle$.

The limited data available to McMillan[1] [all empirical except for a few calculated values of $N(E_F)$] suggested that the product $N(E_F)\langle I^2 \rangle$ is roughly constant within a class of materials, in which case the search for high T_c materials should concentrate on soft lattices with small values of $M\langle \omega^2 \rangle$. Although this approach was used by several investigators in the following years, often with apparent success in understanding trends in T_c, more recently it has been called into question by a number of calculations. Based upon the "rigid-muffin-tin approximation" (RMTA) of Gaspari and Gyorffy,[2] Papaconstantopoulos *et al.*,[3] and Butler[4] have shown that, within isostructural elemental transition metals, $N(E_F)\langle I^2 \rangle$ can vary by as much as a factor of 3. Furthermore, these estimates appear to agree rather well with more recent experimental data. Thus variations of $N(E_F)$ and $\langle I^2 \rangle$ separately must be taken into account.

Another early attempt to correlate superconducting properties was made by Hopfield,[5] who introduced the notational convenience $\eta = N(E_F)\langle I^2 \rangle$ (the "McMillan-Hopfield parameter"). Analysis by Hopfield which emphasized only the *p-d* scattering led him to anticipate that, in transition metals which had a large *d* partial density of states, η would be essentially an atomic parameter. As such, η would be transferable, from element to alloy and within a class of compounds, and Hopfield used this idea in an attempt to understand superconductivity in transition-metal alloys and within $A15$ compounds. However, the startling discovery by Klein and Papaconstantopoulos[6] that the *d-f* contribution[7] to η is not only appreciable but in fact *dominant* in transition metals, and the ensuing realization that the *f* contribution is a property of the environment rather than atomic in nature, has pointed out the limited usefulness of Hopfield's approach.

There have also been suggestions that, within limited classes or subclasses of compounds, there may be an "atomic λ" which is more or less transferable. Phillips[8] suggested that, within the NaCl-structure NbN family of compounds, the sum of atomic contributions $\lambda=\lambda_A+\lambda_B$ should be a useful concept. However, RMTA calculations by Klein, Papaconstantopoulos, and Boyer[9] indicate λ_C for carbon varies by more than a factor of 5 in the compounds NbC, TaC, and HfC. This idea of "transferable λ" was then further restricted to the subclass "NaCl-structure compounds with phonon anomalies" by Haufe, Kerker, and Benneman.[10] However, at such a specialized level the concept of transferability loses much of its usefulness in understanding superconductivity as well as for predicting higher T_c materials.

In view of these largely unfruitful attempts to identify transferable quantities related to superconductivity, and also the difficulty in calculating the phonon spectrum and hence the lattice stiffness $M\langle\omega^2\rangle$, emphasis has shifted to attempting to understand the behavior of η within rigid-ion models, chiefly the RMTA. Notably, the group at the Naval Research Laboratory has published extensive RMTA calculations for elements[3,6] and for NaCl-structure[9,11] compounds and $A15$ (Ref. 12) compounds, among others. Butler[4] has provided a detailed RMTA study of the $4d$ transition metals, noting in particular the dependence of $\langle I^2\rangle$ on atomic number (i.e., valence) and volume in this class of metals. A simultaneous examination of the behavior of η across the $4d$ series was given by Pettifor,[13] who related RMTA quantities to band-structure parameters.

In this paper I present a reinterpretation of the original Gaspari-Gyorffy expression for $\langle I^2\rangle$ which results from a simple regrouping of terms. In addition to providing more physical insight into the quantities which determine $\langle I^2\rangle$, this reinterpretation has two other favorable consequences. One is that atomiclike quantities are identified, these being the electron-ion matrix elements $I_{l,l+1}$ for scattering, from partial wave l to partial wave $l+1$, by an atomic displacement. The atomiclike nature of $I_{l,l+1}$ suggests an approximate transferability which seems to hold at least in systems with common bonding characteristics. The other is that the *fraction* of states $f_l=N_l(E_F)/N(E_F)$ with angular momentum l, which multiplies $I_{l,l+1}^2$ is a much smoother quantity (in several senses to be discussed below) than the original crystalline enhancement factors. Results of various previous calculations are reviewed in terms of these ideas.

II. REARRANGEMENT OF THE GASPARI-GYORFFY EXPRESSION

Gaspari and Gyorffy derived an expression for $\langle I^2\rangle$ which can be written (in atomic units $\hbar=2m=e^2/2=1$)

$$\langle I^2\rangle=\frac{E_F}{\pi^2 N(E_F)^2}\sum_l 2(l+1)\times\sin^2(\delta_l-\delta_{l+1})\nu_l\nu_{l+1}\,, \qquad (2)$$

where δ_l is the Fermi-energy phase shift for partial wave l. The "crystalline enhancement" of the density of states is given by

$$\nu_l=N_l(E_F)/N_l^{(1)}(E_F)\,,$$

where $N_l^{(1)}(E_F)$ is the corresponding density of states for a single scatterer rather than for a lattice of scatterers. Specifically,

$$N_l^{(1)}(E_F)=\frac{\sqrt{E_F}}{\pi}(2l+1)\times\int_0^{R_S}dr\,r^2R_l^2(r,E_F)\,, \qquad (3)$$

where R_l is the radial wave function and R_S is the muffin-tin radius. The trigonometric factor in Eq. (2) arises from the RMTA matrix element

$$\int_0^{R_S}dr\,r^2R_l\frac{dV}{dr}R_{l+1}=\sin(\delta_l-\delta_{l+1})\,, \qquad (4)$$

with the radial function normalization chosen to be

$$R_l(R_S,E_F)=j_l(\kappa_F R_S)\cos\delta_l-n_l(\kappa_F R_S)\sin\delta_l\,. \qquad (5)$$

Here j_l and n_l are the spherical Bessel and Neumann function and $\kappa_F^2=E_F$.

Several features of Eq. (2) should be noted. First, the factor $\sin^2(\delta_l-\delta_{l+1})$ which is bounded between 0 and 1, depends, from Eq. (4), on the muffin-tin potential V, on its overlap with radial functions, and on the radial function normalization, which is not bounded [see Eq. (6) below]. Secondly, the rather unphysical single scatterer density of states tends to obscure the physical interpretation. Thirdly, the factor E_F, which seems to imply an overt dependence on the zero of energy, is in fact artificial, being canceled by the $\sqrt{E_F}$ factors from Eq. (3). This last feature points to the fact that the factor $(\sqrt{E_F}/\pi)$ $(2l+1)$ was *introduced* into the expression (2) to convert the *normalization integral*

$$\tau_l^2 = \int_0^{R_S} dr\, r^2 R_l^2 \tag{6}$$

to a density of states.

Although the original expression (2) may be desirable from some points of view, the following reinterpretation in many ways provides a simpler, and thereby more illuminating picture. Begin by defining a rigid-muffin-tin matrix element for the $l \rightarrow l+1$ channel by (see also Butler[4])

$$I_{l,l+1} = \int_0^{R_S} dr\, r^2 R_l \frac{dV}{dr} R_{l+1}/(\tau_l \tau_{l+1}) \; . \tag{7}$$

Evidently $I_{l,l+1}$ is independent of the normalization of the radial functions and depends only on dV/dr and the *shapes* of the radial functions. This form of matrix element has been used previously by Pickett and Gyorffy,[14] Pettifor,[13] and to some extent by Butler,[4] and was also preferred by Allen.[15] In terms of these matrix elements and the fraction f_l of states of angular momentum l, $\langle I^2 \rangle$ can be expressed as

$$\langle I^2 \rangle = \sum_l \frac{(2l+2)}{(2l+1)(2l+3)} I_{l,l+1}^2 f_l f_{l+1} \; . \tag{8}$$

This expression provides a more straightforward and useful interpretation for primarily two reasons. The first reason is that $I_{l,l+1}$ will be, to a degree to be discussed in Sec. III, an *atomic* property as it depends only on the muffin-tin potential, through its derivative dV/dr and its radial functions, but not explicitly on the crystalline arrangement of neighboring atoms. This in fact is essentially the idea of Hopfield,[5] but restricted to the muffin-tin region and making no attempt to simplify the ratios f_l out of the expression.

The second desirable feature of the summand in Eq. (8) is its dependence on energy E_F. From Eqs. (4) and (7) and the expression

$$\tau_l^2 = R_S^2 R_l (R_S, E_F)^2 \, | \dot{\gamma}_l | \; , \tag{9}$$

where $\dot{\gamma}_l$ is the energy derivative of the logarithmic derivative, $I_{l,l+1}^2$ is seen to be very smooth, varying as do δ_l and γ_l on the scale of the l and $(l+1)$ bandwidths. This energy variation has been discussed previously by Pettifor.[13] Although it is somewhat less obvious, the ratios f_l are much more smoothly varying then either its numerator or denominator alone. This is the result of (i) $N_l(E)$ and $N(E)$ having canceling van Hove singularities at the same energies, and (ii) f_l depending only on the character of eigenstates, rather than on the density of states which may vary rapidly. It follows that $\langle I^2 \rangle$ is slowly varying with energy, a characteristic which was not evident in the original Gaspari-Gyorffy expression.

The behavior of f_l in La (Ref. 16) is shown in Fig. 1 and it can be compared with N_l and N in Fig. 2. La is a good metal in which to illustrate this behavior because, although over most of its spectrum it is typical of a $5d$ transition metal, it possesses $4f$ $(l=3)$ bands centered 2.5 eV above E_F which provide an extreme example of the features mentioned above. Figures 1 and 2 show dramatically how the sharply structured behavior of $N_3(E)$ is translated into a smooth, almost resonance-like behavior of $f_3(E)$. Likewise, the structured d spectrum $N_2(E)$ is converted into a smoother form in $f_2(E)$ which, however, is nearly split by the f bands. [In the absence of the f bands, as in more typical transition metals, only a minor minimum in $f_2(E)$ will occur in the low density-of-states bonding-antibonding "gap."]

Deviation of $f_l(E)$ from *very* smooth behavior results primarily from hybridization, as mentioned above for the d-f interaction effect on $f_2(E)$. This effect is more clearly drawn in $f_0(E)$ and $f_1(E)$, each of which show structure due to hybridization with d bands (at -2 eV) and f bands (~ 1.5 eV). However, the resulting variation with energy in

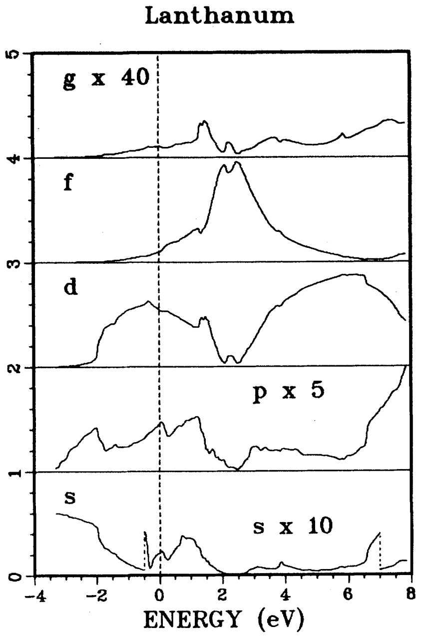

FIG. 1. The electronic density-of-states ratios f_l versus energy for fcc La, $l=0$, 1, 2, 3, 4. Successive plots are displaced by one unit $(0 \leq f_l \leq 1)$. The zero of energy is fixed at the Fermi level.

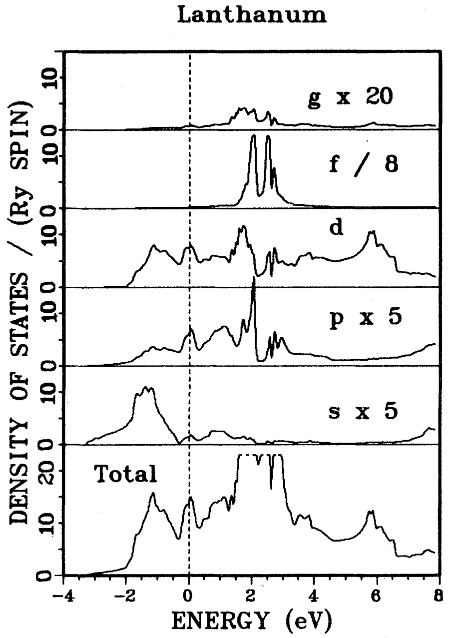

FIG. 2. The total and partial densities of states of fcc La. Rescalings of the various partial densities of states are as noted.

each case remains much smaller than that of $N_l(E)$.

To give a full picture of the present approach to $\langle I^2 \rangle$, the quantities δ_l, τ_l, and $I^2_{l,l+1}$ for La are shown in Fig. 3. [For δ_l and τ_l the $(2j+1)$-weighted averages of the corresponding fully relativistic quantities for $j=l\pm\frac{1}{2}$ have been used for $l=1$, 2, and 4. For $l=3$ this averaging results in unphysical behavior in the energy region between the $j=\frac{5}{2}$ and $j=\frac{7}{2}$ resonances, so only the $j=\frac{7}{2}$ quantities are shown in Fig. 3. The full relativistic treatment of $\langle I^2 \rangle$ will be presented elsewhere.[17]] The phase shifts for $l=0$, 1, and 2 are typical of an early 5*d* transition metal, but the sharp $l=3$ resonance (where $\delta_3=\pi/2$) at 2.1 eV gives rise to flat 4*f* bands not present (or rather, fully occupied) in heavier 5*d* transition metals. The $l=4$ phase shift is positive but less than 7×10^{-3} throughout this range.

The normalizations τ_l calculated from Eq. (6) and shown in Fig. 3(b) are proportional (except for the $\sqrt{E_F}$ factor) to the "single scatterer" density of states used in the original Gaspari-Gyorffy expression. For $l=0$, 1, and 4 these are monotonic in the interesting energy range. For $l=2$, τ_2 peaks somewhat below the *d*-band center due to the clear nonresonant form of δ_2 in Fig. 3(a). The sharp $l=3$ resonance results in a huge increase in τ_3 in the 4*f*-band region. The effect of this resonance on $I^2_{l,l+1}$ is evident in Fig. 3(c), where $I^2_{2,3}$ drops by over an order of magnitude in this region; in addition, $I^2_{2,3}$ vanishes where $\delta_2=\delta_3$. However, in the absence of the 4*f* bands, $I^2_{l,l+1}$ are smooth over the entire *d*-band region.

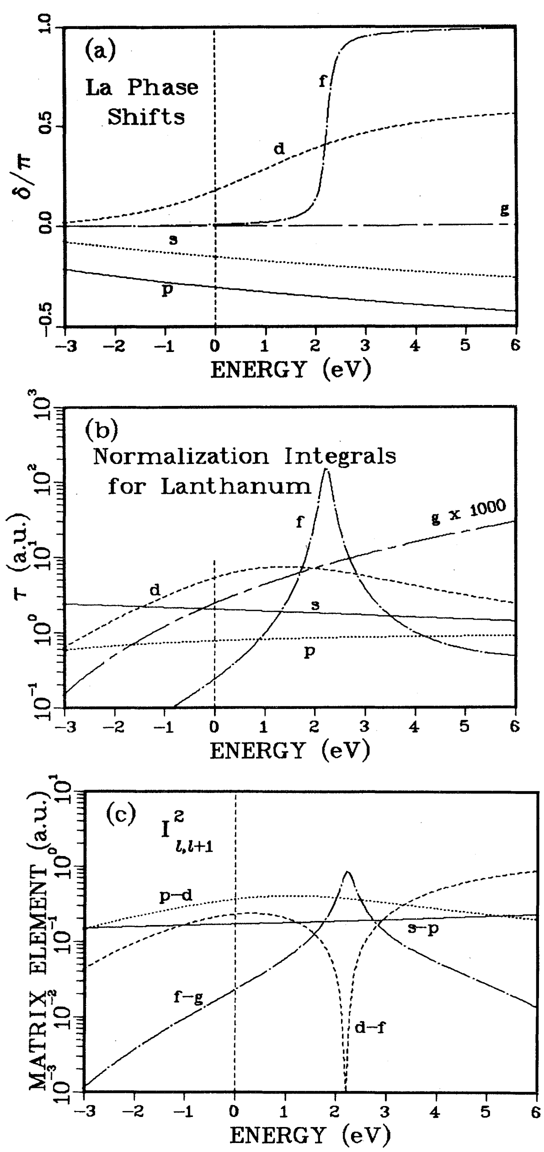

FIG. 3. La functions entering the RMTA expression for η. (a) Phase shifts δ_l relative to π. (b) Semilog plot of the normalization integrals τ_l. (c) Semilog plot of the single-channel matrix elements $I^2_{l,l+1}$. Note the zero of $I^2_{2,3}$ at the point where $\delta_2=\delta_3$.

III. TRANSFERABILITY OF $I^2_{l,l+1}$

In this section we investigate the degree to which the matrix elements $I^2_{l,l+1}$ represent atomiclike, transferable quantities. For this purpose we focus on Nb and V, for which Papaconstantopoulos, Klein, and Boyer (Refs. 3, 6, 9, 11, and 12) have carried out self-consistent band-structure determinations and calculations of η for the elemental metals, several $A15$-structure compounds, and two Nb-based NaCl-structure metals. These compounds are listed in Table I.

A feature which was not mentioned in the previous section is the dependence of the various quantities on the sphere radius R_S. As far as the RMTA itself is concerned, R_S should be fixed at the radius which most nearly reproduces the actual scattering properties. However, theoretical ambiguities can arise if spheres from distinct atoms overlap, and in the NRL calculations which will be used here, maximal nonoverlapping spheres have been used. Each of the quantities δ_l, N_l, and $N_l^{(1)}$ depend on R_S, but the ratio $\nu_l = N_l / N_l^{(1)}$ is independent of R_S to lowest order and the R_S dependence of δ_l is often weak. The resulting weak dependence of η on R_S is central to the usefulness of the RMTA in that it provides a relatively unambiguous result to compare with experiment.

The quantities f_l and $I_{l,l+1}^2$, the intermediate quantities in the interpretation of RMTA being proposed here, are separately dependent on R_S. For a comparison of these quantities in various systems, renormalization to a common radius $\bar{R}_S$ must be carried out first. This has been done as follows. For $l=0$, 1, and 2 the radial wave functions are varying slowly near R_S and the normalization correction $\Delta\tau_l^2$ is approximated by

$$\Delta\tau_l^2 = \int_{R_S}^{\bar{R}_S} r^2 dr\, R_l^2(r)$$

$$\approx R_l^2(R_S)(\bar{R}_S^3 - R_S^3)/3 \; . \tag{10}$$

In addition the radial function R_l itself is renormalized to the appropriate value at the new radius $\bar{R}_S$. Explicitly,

$$\tau_l^2(\bar{R}_S) \cong [\tau_l^2(R_S) + \Delta\tau_l^2] \left| \frac{j_l(\kappa_F \bar{R}_S)\cos\delta_l - n_l(\kappa_F \bar{R}_S)\sin\delta_l}{j_l(\kappa_F R_S)\cos\delta_1 - n_l(\kappa_F R_S)\sin\delta_l} \right|^2 . \tag{11}$$

For $l=3$ the fact that $R_3(r) \approx j_3(\kappa_F r)$ (inside as well as outside the sphere) was used to recalculate $\tau_3^2(\bar{R}_S)$ directly. No correction to the phase shifts has been considered.

The radius $\bar{R}_S$ was chosen to be midway between the elemental value of R_S and the mean of the $A15$-structure values given in Table I; these were taken as $\bar{R}_S = 2.57$ and 2.37 a.u. for Nb and V, respectively. The resulting values of $\tau_l^2(\bar{R}_S)$ in the $A15$ compounds were 5–20% increases over

TABLE I. Sphere radius R_S (a.u.), Fermi energy E_F (Ry), density of states *per metal atom* per spin $N^A(E_F)$ (Ry^{-1}), phase shifts δ_l (radians) and density-of-states ratios f_l, and enhancements ν_l, for Nb- and V-based compounds discussed in the test.

	R_S	E_F	$N^A(E_F)$	δ_0	δ_1	δ_2	δ_3	f_0	f_1	f_2	f_3	ν_0	ν_1	ν_2	ν_3
NbC	2.313	0.869	4.76	−1.11	−0.51	1.30	0.0107	0.0086	0.0123	0.383	0.0288	0.193	0.150	0.361	2.571
NbN	2.308	0.849	6.43	−1.01	−0.47	1.72	0.0111	0.0057	0.0034	0.412	0.0234	0.161	0.056	0.613	2.945
Nb_3Al	2.450	0.837	16.60	−1.13	−0.50	0.86	0.0076	0.0115	0.0613	0.530	0.0123	0.965	3.257	1.707	4.248
Nb_3Ga	2.443	0.851	15.98	−1.14	−0.50	0.90	0.0082	0.0110	0.0668	0.529	0.0121	0.887	3.341	1.608	3.827
Nb_3Si	2.457	0.832	6.97	−1.12	−0.49	0.90	0.0079	0.0069	0.0557	0.560	0.0120	0.242	1.241	0.721	1.747
Nb_3Ge	2.438	0.866	8.89	−1.15	−0.51	0.92	0.0086	0.0061	0.0583	0.563	0.0126	0.271	1.597	0.967	2.108
Nb_3Sn	2.495	0.833	13.22	−1.11	−0.49	0.94	0.0083	0.0047	0.0544	0.594	0.0102	0.306	2.367	1.367	2.731
Nb_3Sb	2.482	0.874	4.33	−1.15	−0.51	1.02	0.0094	0.0046	0.0502	0.594	0.0137	0.099	0.687	0.446	1.052
Nb	2.685	0.676	9.71	−0.93	−0.36	1.14	0.0074	0.0178	0.0746	0.724	0.0128	0.807	2.923	0.681	3.846
V	2.477	0.675	12.70	−0.69	−0.17	1.03	0.0027	0.0102	0.0638	0.846	0.0071	0.549	2.841	0.634	6.936
V_3Al	2.282	0.819	15.74	−0.88	−0.28	0.95	0.0026	0.0047	0.0543	0.638	0.0056	0.365	2.698	1.003	4.288
V_3Ga	2.276	0.827	24.63	−0.88	−0.28	1.02	0.0028	0.0037	0.0565	0.652	0.0044	0.445	4.333	1.539	5.173
V_3Si	2.231	0.889	16.68	−0.94	−0.31	0.98	0.0031	0.0030	0.0568	0.629	0.0063	0.254	2.795	1.224	4.130
V_3Ge	2.253	0.871	9.56	−0.92	−0.30	1.02	0.0031	0.0038	0.0415	0.656	0.0071	0.183	1.183	0.670	2.776
V_3Sn	2.355	0.803	10.25	−0.84	−0.26	1.07	0.0029	0.0028	0.0317	0.739	0.0052	0.133	1.048	0.617	2.665

$\tau_l^2(R_S)$ for $l=0$, 1, and 3 and 5 − 10 % decreases for $l=2$. The corresponding changes in elemental Nb and V were of opposite sign in each case, since $\bar{R}_S < R_S$ in these cases. It is notable that these renormalizations resulted in bringing τ_l^2 for the $A15$ compounds closer to the corresponding elemental value only for $l=0$ and 1. For $l=2$ the renormalization worsened this "correspondence," while no clear trend appeared for $l=3$. In any case these results seem to reflect real similarities or differences between the Nb- and V-atom environments in the elements and the compounds.

In Tables I and II an extensive listing of the quantities which enter into the determination of Nb- or V- atom contributions to η is presented.[18] Both $N_l^{(1)}$ and N_l have been renormalized to $\bar{R}_S$ by multiplying by the ratio $\tau_l^2(\bar{R}_S)/\tau_l^2(R_S)$, hence η is *unaffected.* Although corrections to the phase shifts could have been incorporated, this would amount to investigating the (small) R_S dependence of η, which is not the purpose of this paper. It should be noted that the extrapolation from R_S to $\bar{R}_S$ is somewhat more uncertain in NbC and NbN than for the other cases, due to the interval $R_S - \bar{R}_S$ being twice as large.

The principal result here is the regularity in the values of $I_{l,l+1}^2$(Nb) and $I_{l,l+1}^2$(V) from system to system, greater than that of the numerator $\sin^2(\delta_l - \delta_{l+1})$ or denominator $\tau_l^2\tau_{l+1}^2$ separately, each of which is dependent on radial function normalization. The deviations of $I_{l,l+1}^2$ from perfect regularity within the $A15$ compounds are generally 5% or less, whereas $\sin^2(\delta_1 - \delta_{l+1})$ and $\tau_l^2\tau_{l+1}^2$ may vary by more than 25%. Comparing the $A15$ compounds with Nb and V, it is evident that $I_{l,l+1}^2$ of the element is smaller (for $l=1$, by nearly a factor of 2) than that of the $A15$ compound. However, for the dominant $l=2$ channel, variations in $\sin^2(\delta_l - \delta_{l+1})$ and $\tau_l^2\tau_{l+1}^2$ partially cancel, leaving $I_{l,l+1}^2$ as the most transferable quantitity. The relative constancy of $\langle I^2 \rangle$ in $A15$ compounds, described in the form $\eta \propto N(E_F)$, has been pointed out previously.[12]

The situation for the $B1$ compounds is not as clear. As mentioned previously, the extrapolation to the radius $R_S = 2.57$ a.u. may be introducing some unphysical irregularities, so only a pair of compounds is not sufficient to allow an evaluation of constancy of $I_{l,l+1}^2$ within this class. It is clear, however, that $I_{2,3}^2$ is significantly larger than in the $A15$ compounds, which may lead to comparable values of η(Nb) in spite of a lower density of states. This is discussed further below and in Sec. IV C.

In addition to variations in $I_{l,l+1}^2$ two possibilities remain for producing a larger Nb or V contributon to η. The obvious possibility is to find a compound with a larger value of $N(E_F)$ per atom. This approach leads to a well-known instability toward formation of a material with a smaller value of $N(E_F)$. Rather than placing a very large number of electrons at the highest occupied energy, the compound will tend to (a) distort to a lower symmetry, thereby moving some electrons to lower en-

TABLE II. Normalization integrals τ_l^2 (a.u.), $\sin^2(\delta_1 - \delta_{l+1}) \equiv S_{l,l+1}^2$, $I_{l,l+1}^2$ (eV/Å)^2, $\eta_{l,l+1}^A$ and η^A (eV/Å)^2, and $\langle I^2 \rangle^A$ (eV/Å)^2. Note the definition $\eta^A \equiv N(E_F)^A \langle I^2 \rangle^A$, with $N(E_F)^A$ defined in the caption to Table I.

	τ_0^2	τ_1^2	τ_2^2	τ_3^2	$S_{0,1}^2$	$S_{1,2}^2$	$S_{2,3}^2$	$I_{0,1}^2$	$I_{1,2}^2$	$I_{2,3}^2$	$\eta_{0,1}^A$	$\eta_{1,2}^A$	$\eta_{2,3}^A$	η^A	$\langle I^2 \rangle^A$
NbC	0.715	0.436	3.40	0.0257	0.32	0.95	0.92	675	421	7000	0.02	0.18	4.62	4.82	13.8
NbN	0.770	0.449	2.95	0.0249	0.26	0.67	0.98	505	333	8850	0.00	0.06	6.91	6.97	14.8
Nb_3Al	0.676	0.358	3.54	0.0235	0.35	0.95	0.56	966	498	4480	0.55	5.27	6.09	11.91	9.8
Nb_3Ga	0.677	0.363	3.58	0.0246	0.36	0.97	0.61	956	495	4580	0.55	5.48	5.90	11.93	10.2
Nb_3Si	0.688	0.359	3.73	0.0235	0.35	0.97	0.61	929	478	4570	0.12	2.04	2.69	4.85	9.5
Nb_3Ge	0.671	0.366	3.49	0.0256	0.36	0.98	0.62	959	508	4600	0.15	2.91	3.65	6.71	10.3
Nb_3Sn	0.694	0.349	3.98	0.0242	0.34	0.98	0.64	932	466	4400	0.15	3.91	4.44	8.50	8.7
Nb_3Sb	0.678	0.355	3.88	0.0271	0.35	1.00	0.72	963	480	4490	0.05	1.22	2.00	3.26	10.2
Nb	0.819	0.316	7.90	0.0176	0.29	1.00	0.82	743	262	3900	0.47	2.72	4.42	7.61	10.7
V	0.900	0.363	12.97	0.0071	0.25	0.87	0.73	495	122	5230	0.20	1.64	5.06	6.90	7.4
V_3Al	0.704	0.366	6.96	0.0101	0.32	0.89	0.66	822	231	6220	0.16	2.47	4.38	7.01	6.1
V_3Ga	0.706	0.370	7.21	0.0104	0.32	0.93	0.72	808	230	6400	0.20	4.09	5.72	10.02	5.5
V_3Si	0.658	0.376	5.71	0.0122	0.34	0.92	0.69	919	284	6500	0.13	3.32	5.45	8.90	7.3
V_3Ge	0.676	0.376	6.31	0.0117	0.33	0.94	0.73	869	262	6480	0.07	1.34	3.64	5.05	7.2
V_3Sn	0.746	0.362	8.62	0.0101	0.30	0.94	0.77	733	200	5840	0.03	0.94	2.92	3.90	5.2

ergy and lowering $N(E_F)$ (the band Jahn-Teller effect), (b) crystallize in an unrelated structure with a smaller value of $N(E_F)$, or (c) phase separate into distinct compounds with lower values of $N(E_F)$.

The alternative choice is to increase η by shifting the character of states at E_F, that is, altering the fractions f_l to maximize $\langle I^2 \rangle$. An extreme example of this effect is to shift (somehow) the *s* and *p* character (or an equal amount of *d* character) in Nb to *f* character, thereby taking advantage of the stronger *d*-*f* scattering described by $I_{2,3}^2$ in Table II, and in this particular example increasing $\langle I^2 \rangle$ by a factor of 8. It is not immediately clear how such a shift is to be accomplished, although a change of crystal structure and/or bonding character is probably required.

A possible example of this effect may be provided by the refractory compounds NbC and NbN, which are currently understood in terms of a much more covalent type of bonding[19,20] than the primarily metallic bcc elements and *A*15 compounds. As a result f_3 *is twice as large,* and f_1 much smaller for Nb in these compounds than in the other in Table I. Since Nb has no atomic *f* states, f_3 results primarily from the Nb-site decomposition of neighboring atom states,[4,13] and covalent bonding (i.e., strong overlap extending into the Nb sphere) with C or N*p* states evidently enhances the Nb $l=3$ character of states of E_F in these compounds. Of course, $\langle I^2 \rangle$ will be maximized if as much weight as possible is shifted into the channel $\bar{l}$ with maximum $I_{\bar{l},\bar{l}+1}^2$ such that $f_{\bar{l}}=f_{\bar{l}+1}$, with other fractions f_l vanishing. However, such shifts may well lead to small values of $N(E_F)$, or if not, the resulting increase in the electron-phonon interaction can lead to a "covalent instability" as discussed previously.[21,22]

IV. DISCUSSION AND CONCLUSIONS

A. Elemental transition metals

Expressing $\eta=N(E_F)\langle I^2 \rangle$ with $\langle I^2 \rangle$ given by Eq. (8) leads to a simple understanding of the variation of T_c in transition metals and their alloys. Both $I_{l,l+1}^2$ and f_l vary smoothly with Fermi-level position (equivalent to the mean valence or alloy concentration in the rigid-band model), so rapid changes in T_c such as occur in the NbMo alloy system[23] result from variations in $N(E_F)$, with some contribution due to changes in $\langle \omega^2 \rangle$. On the larger scale, however, Butler[4] has found $\langle I^2 \rangle$ to vary by a factor of 40 within the 4*d* transition series, in large part due to the factor f_3. On this point there is little to add to his thorough discussion except to recall the interesting crystal-structure effects found in Ru. Fur Ru (which is actually hcp) Butler carrier out both bcc and fcc calculations, finding f_3 and $\langle I^2 \rangle$ to be about 20% larger in the fcc phase. However, $N(E_F)$ is smaller by 33%, leading to a smaller value of η in the fcc phase. The differences in f_3 between the two phases are no doubt related to the nearest-neighbor distances and coordination numbers, but such detailed relationships are not well understood at present.

The present picture provides a new viewpoint on the differences in the $l=3$ effects between V and Nb. In the important *df* channel $I_{2,3}^2$ is one-third larger in V than in Nb, with the smallness of τ_3^2 in V more than compensating for the less favorable values of τ_2^2 and $\sin^2(\delta_2-\delta_3)$. The average matrix element $\langle I^2 \rangle$, however, is only two-thirds that of Nb. Although this is due partly to large values of $I_{0,1}^2$ and $I_{1,2}^2$ in Nb, it is the larger value of f_3 in Nb which is primarily responsible. This illustrates that the presence of a larger f_3 will be accompanied by a larger τ_3, and hence smaller $I_{2,3}^2$ and that the relative importance of these effects is not necessarily reflected in the crystalline enhancement ν_3 (which is nearly twice as large in V as in Nb).

B. *A*15 compounds

It can be noted from Table II that within each of the Nb_3X and V_3X classes, the values of $I_{l,l+1}^2$ are virtually constant. The Nb_3X class includes *X* atoms with valences of 3, 4, and 5 leading to differing positions of the Fermi level and variations of $N(E_F)$ by a factor of 4. Nb_3Sn and Nb_3Sb, with T_c's which differ by 2 orders of magnitude (18.2 and 0.2 K, respectively), illustrate dramatically how their differences in η arise solely from the differences in $N(E_F)$. More to the point of this study, however, is the *degree of regularity* of $I_{l,l+1}^2$ and f_l which is not apparent in the ν_l nor always in the factors of $\sin^2(\delta_l-\delta_{l+1})$ (see Tables I and II).

It has been established in several *A*15 compounds[24] that T_c is sensitive to the degree of disorder (as measured by the residual resistivity). The main effect of disorder in the low-disorder regime is to broaden the electron states ("lifetime effects"). The effect on η and on T_c if the electron-phonon spectral function α^2F is not altered by the disorder, can be accounted for by using Lorentzian-broadened values of $N(E_F)$ and $\langle I^2 \rangle$. As was pointed out above, however, $\langle I^2(E) \rangle$ is a smooth function which will be insensitive to broadening. On the other hand, many unusual properties of $A15$ compounds have been interpreted in terms of sharp structure in $N(E)$ and such structure has been verified by band-structure calculations.[12,25] The present interpretation of the RMTA makes it clear that the extreme sensitivity of T_c to disorder must be reflecting the fine structure.

C. NbC AND NbN

These $B1$ (NaCl-structure) compounds differ from the $A15$ compounds in having a more strongly covalent (metal d state with nonmetal p state) and ionic (metal-to-nonmetal charge transfer of the order of one electron) bonding, rather than primarily metallic bonding. This difference is reflected in the Fermi energy falling nearer the d resonance ($\delta_2 = \pi/2$) and results in a value of $I_{2,3}^2$ that is 80−90 % larger than in Nb and the Nb-based $A15$ compounds. Another apparent consequence (in this case) of the strong bonding is the low value of $N(E_F)$, which leads to a rather unimpressive value of η_{Nb} in spite of $\langle I^2 \rangle$ being 40−50 % larger than in the $A15$ compounds. These compounds do illustrate, however, that a change in bonding character can lead to substantial increases in $\langle I^2 \rangle$ relative to those in $A15$ compounds, and there remains the possibility that compounds with larger values of η may be found.

The predominance of Nb-based compounds in high T_c materials is still not completely understood. It is clearly *not* due to $\langle I^2 \rangle_{\text{Nb}}$, since $\langle I^2 \rangle$ peaks strongly at Mo rather than at Nb in the 4*d* series.[4] The evidence suggests[25] this predominance is due instead to the tendency of Nb-based (and similar) compounds to form phases with strongly split bonding and antibonding d bands. For Nb, with its slightly less than half-filled d shell, the Fermi level is left in a favorable region for large values of $N(E_F)$. The half-filled d shell Mo instead leaves E_F in the low density-of-states "gap."

The bcc transition-metal alloys and the $A15$ compounds are prime examples of this behavior. This point of view suggests that Mo will only be useful in raising T_c if a d electron is transferred onto another atom, transforming Mo into "pseudo-Nb." Exactly this behavior occurs[26] in the Chevrel phase compounds $M\text{Mo}_6\text{S}_8$ and $M\text{Mo}_6\text{Se}_8$ (M=metal atom, e.g., Pb, Sn,...), for which d bonding between neighboring Mo atoms is strong. An electron is transferred from each Mo to the chalcogen atoms and E_F falls in a region of high density of states just below the bonding-antibonding gap. For PbMo_6S_8, $T_c = 15$ K results.

This behavior is violated in Mo-chalcogen compounds in which $d-d$ bonding is less dominant, and such compounds tend toward semimetallic or semiconducting character. It is also violated in the $B1$-structure compounds such as those discussed above, where metal d, nonmetal p bonding dominates and no $d-d$ bonding-antibonding gap occurs. Approximately one electron is transferred[11] off the metal atom in the Nb-based compounds, and similar behavior is expected in their Mo-based counterparts, since Nb and Mo are expected to form good rigid-band systems. A rigid-band picture suggests $N(E_F)$ in MoC should be 10% *larger*[11] than in NbC, and the results of Butler[4] suggest $\langle I^2 \rangle_{\text{Mo}}$ will be somewhat larger than $\langle I^2 \rangle_{\text{Nb}}$ (as in the elements). Indeed, it is found that T_c is 30% larger in MoC (14.3 K versus ~11 K).

The same argument suggests T_c of MoN should be considerably larger than that of NbN ($T_c = 16$ K). Rigid-band behavior suggests a 20% increase[9(b)] in $N(E_f)$; however, $\langle I^2 \rangle_{\text{Mo}}$ may be slightly less in MoN since E_F already lies slightly above the d resonance in NbN (see Table I). The few studies of molybdenum nitrides reported in the literature[27] have not unambiguously established the existence of $B1$-structure MoN. Although negative results often go unreported, there are at least two reasons why an extensive search for this material may have not been undertaken. The first is the *apparent* dominance of Nb-based compounds in high T_c superconductors, as mentioned above, which makes the substitution of Mo for Nb in these compounds unappealing. The second reason is the electron-atom ratio of MoN ($e/a = 5.5$), which violates the "Matthias rule"[28] that high T_c materials cluster around $e/a = 4.75$ and 6.5 with a deep intermediate valley. The Matthias rule can be understood in terms of the structure in $N(E)$ in materials dominated by $d-d$ bonding, and it is of considerable interest to establish whether this guideline is violated in the $B1$ structure. Finally, the lack of stability of MoN itself is suggestive of a strong electron-phonon interaction in this compound. The phonon spectrum will also affect the value of T_c but such considerations are beyond the scope of the present paper.

D. A caveat

Allen and Dynes[22] have noted that, although soft lattices may contribute somewhat to high values of T_c, known metals with high T_c achieve this primarily through a large value of η. Within the RMTA, higher values of η in transition-metal compounds thus seem to rely on a larger $N(E_F)$ or $I_{2,3}^2$ or on larger f_3 ratios. The $l=3$ character arises from tails of states on neighboring atoms, and an $l=3$ expansion of these tails requires (i) they behave approximately as $j_3(\kappa r)$ as seen from a neighboring atom, as pointed out previously by Butler,[4] and (ii) they are expandable in $l=3$ angular functions. These requirements might be expected to point the way to crystal structures and chemical configurations with larger values of f_3, and perhaps η. The NaCl-structure compounds, it should be noted, have Nb f_3 ratios *twice as large* as for the $A15$ compounds, much of which probably derives from C or N p states.

However, the contribution to η involving f_3 arises in real space from near the sphere boundary, where the RMTA model of the screened potential is most approximate. Indeed it has been noted[3] that T_c's of elemental metals seem to show better agreement with measured values if $\eta_{2,3}$ is (somewhat arbitrarily) divided by two.[29] It is at first glance surprising that this df contribution, from near R_S, is not sensitive to the value of R_S, although the present treatment of RMTA clarifies this point (neither f_3 nor $I_{2,3}^2$ is sensitive to R_S). We want merely to caution here that requirements (i) and (ii) above are necessary to maximize f_3 *within* RMTA, but that the RMTA is least certain here. It seems likely that the inclusion of the nonrigid potential[30] and the concomitant relaxing of the $l \Longleftrightarrow l+1$ selection rule in a more rigorous theory may be necessary to lead to a more fundamental understanding of the best mechanism by which to increase η.

For f-band metals with *atomic* contributions to the $l=3$ quantities, that is, rare earths and actinides, Butler[4] has suggested that the f bands may be useful in reaching large η values. Calculations[17,31,32] for La, Ce, and Th do not confirm these expectations, however, and the discussion of Sec. II shows why narrow f bands will not lead to large η's, in spite of extremely large densities of states.

Note added in proof. Calculations of T_c for NbN and NbC have been presented by W.E. Pickett, B.M. Klein, and D. A Papaconstantopoulos [Physica 107B, 667 (1981)].

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