Electron-phonon coupling in the transition metals: Electronic aspects*

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The electron-phonon coupling parameter λ may be written as the product of three factors: the Fermi-energy density of states, $N(E_F)$, the Fermi-surface average of the electron-phonon interaction, $\langle I^2 \rangle$, and an effective inverse lattice force constant Φ. We have calculated $\langle I^2 \rangle$ and $N(E_F)$ for 11 $4d$ transition-metal systems using the rigid muffin-tin approximation. We find a large but understandable variation in $\langle I^2 \rangle$ which is in good agreement with the empirical variation in $\langle I^2 \rangle$. $\langle I^2 \rangle$ varies approximately as the inverse second power of the atomic volume and as the first power of the amount of $l = 3$ Fermi-energy state density within the Wigner-Seitz cell. We discuss the implications of our findings in regard to the search for systems with higher superconducting transition temperatures.

I. INTRODUCTION

The primary determinant of the superconducting transition temperature T_c is the electron-phonon coupling parameter λ. It is therefore of considerable importance to attempt to predict in a qualitative way from first principles how λ varies from one material to another. Of special interest in this regard are the transition metals, their alloys, and their compounds for it is in these systems that the highest transition temperatures are found. It is probably not coincidental that these are strong scattering systems. Their electronic structure cannot be usefully viewed in terms of weakly perturbed free-electron bands. This last fact has greatly impeded our progress in understanding electron-phonon coupling in these systems.

In this paper we attempt to sort out some of the factors which strongly affect λ. We concentrate our attention on the transition metals. Our objective is to understand the variation of λ with Z, across the transition-metal series as shown in Fig. 1. These λ values were obtained empirically from McMillan's formula which relates λ to T_c,[1]

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right), \qquad (1.1)$$

using experimental values of T_c, reasonable reliable estimates of the logarithmically averaged phonon frequency $\omega_{\log}$ introduced by Allen and Dynes[2] and a value of the electron-electron Coulomb pseudopotential,[3] μ^*, equal to 0.13.

We also show in Fig. 1 the variation of the electronic density of states at the Fermi energy $N(E_F)$. It is not surprising that much of the variation in λ is related to changes in the density of states since in the BCS model $\lambda = N(E_F)V$, where V is a Fermi-surface average of an effective interaction energy between the electrons due to the exchange of phonons. The variation of $N(E_F)$ does not explain the entire variation of λ, however, as is especially evident at the ends of the series where λ is small in spite of a high density of states.

McMillan[1] showed that λ may be written as the product of two factors, $\lambda = \eta\Phi$. The first factor η measures the response of the electrons at the Fermi energy to a potential fluctuation caused by the displacement of an atom. It depends directly only upon the electronic structure at the Fermi energy. The second factor Φ measures the ease with which an atom can be displaced. It is equal to an effective inverse force constant or to $(M\langle\omega^2\rangle)^{-1}$, where M is the atomic mass and $\langle\omega^2\rangle$ is a proper average square phonon frequency.

We shall concentrate our attention upon calcu-

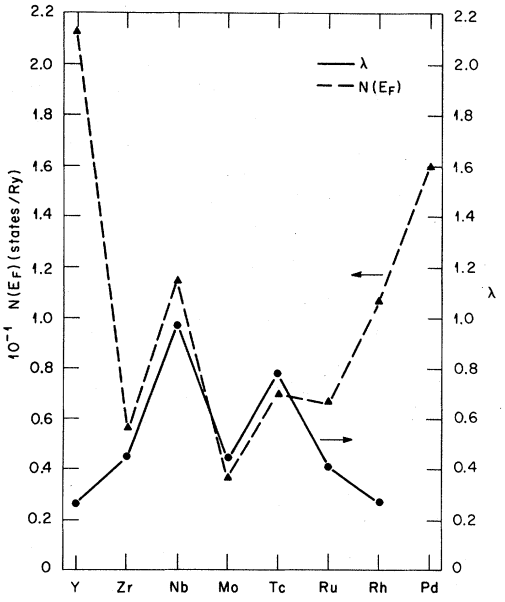

FIG. 1. Variation of electron-phonon coupling parameter λ and of Fermi-energy density of states across the transition-metal series.

lating η, the electronic component of λ, and estimate the phonon component Φ from experiment. There are two reasons for taking this approach. Firstly, we know qualitatively how the phonon component of λ varies across the transition-metal series, whereas data on the electronic component are very difficult to obtain directly from experiment. Secondly, η is easier to calculate since it depends mainly upon the Fermi-energy electronic structure whereas $\langle\omega^2\rangle$ depends in a complicated way on the electronic structure at all energies.

McMillan obtained empirical values of λ using Eq. (1.1) and measured values of T_c. He combined these values of λ with estimates of $\Phi = (M\langle\omega^2\rangle)^{-1}$ and then obtained empirical values of η for V, Nb, Ta, Mo, and W. Examination of these results led him to the conclusion that η is approximately a constant in the transition metals. Our calculations, however, indicate substantial variation in η (a factor of 6) as one crosses the transition-metal series and we believe that his observation of approximately constant η is not a general result, but is due to two facts. Firstly, systems with low η's do not have measurable T_c's and hence empirical η's are not calculable. On the other hand, transition-metal phases with very high η's appear to be unstable and hence also do not yield empirical η's.

Since the work of McMillan, there has been a substantial amount of work aimed at calculating η and explaining its variation or lact of variation with Z.[4-11] It will be easier to discuss the relationship of this work to the present paper after we have presented our results and our interpretation of them.

In a recent paper[12] it was shown that it is possible to evaluate η essentially exactly within the rigid muffin-tin approximation and the usual approximations of band theory for the cubic elements. In Sec. II we briefly review the formal results of that paper. In Sec. III we present our results for the electron-phonon interaction for the 4*d* transition metals. In Sec. IV we discuss our results and compare them with experiment and previous calculations. We also give our view on the types of systems that are likely to have high transition temperatures.

II. η FOR ELEMENTS WITH CUBIC SYMMETRY

McMillan has shown that an approximate separation of the electron-phonon coupling parameters into electronic and primarily phononic contributions can be achieved by writing $\lambda = \eta/M\langle\omega^2\rangle$ where λ, η, and $\langle\omega^2\rangle$ have the following definitions in terms of the Eliashberg function $\alpha^2(\omega)F(\omega)$:

$$\lambda = 2\int \omega^{-1}\alpha^2(\omega)F(\omega)\,d\omega, \tag{2.1}$$

$$\eta = 2M\int \omega\alpha^2(\omega)F(\omega)\,d\omega, \tag{2.2}$$

$$\langle\omega^2\rangle = \int \omega\alpha^2 F\,d\omega \Big/ \int \omega^{-1}\alpha^2 F\,d\omega\,. \tag{2.3}$$

$\alpha^2(\omega)$ is a frequency-dependent electron-phonon coupling parameter and $F(\omega)$ is the phonon density of states. $\langle\omega^2\rangle$ clearly depends upon the functional form of $\alpha^2(\omega)$ which is not known very well for the transition metals. We do know, however, that in the limit of $\omega \to 0$, $\alpha^2(\omega) \to$ constant. We also know that if the phonon mediated electron-electron interaction takes place primarily via a process in which an electron scatters off an ion causing that *same* ion to move this potential fluctuation scattering a second electron that α^2 is proportional to $1/\omega$.[13] Thus it is probably true that

$$\left(\int \omega^{-2}F\,d\omega\right)^{-1} < \langle\omega^2\rangle < \int \omega F\,d\omega \Big/ \int \omega^{-1}F\,d\omega\,.$$

For consistency with previous work we will use the $\alpha^2 =$ constant approximation, however, it should be remembered that this is probably an upper limit for $\langle\omega^2\rangle$.

η as defined in Eq. (2.2) is rigorously given (in atomic units) by

$$\eta = \frac{\Omega^2}{(2\pi)^6 N(E_F)} \int d^3k \int d^3k' \int d^3r \int d^3r'\, \nabla V(r)\cdot\nabla' V(r')\psi_k^*(r)\psi_{k'}(r)\psi_{k'}^*(r')\psi_k(r')\delta(E_k - E_F)\delta(E_{k'} - E_F)\,, \tag{2.4}$$

where Ω is the volume of a Wigner-Seitz cell, $N(E_F)$ is the Fermi energy density of states of one spin, $\psi_k(r)$ is a Bloch vector, and $\vec{u}\cdot\nabla V$ is the change in crystal potential when one nucleus suffers an infinitesimal displacement $\vec{u}$, the other nuclei being held fixed.

A very important aspect of the electron-phonon problem is the understanding of the quantity ∇V which enters (2.4). In this paper we shall employ the rigid muffin-tin approximation of Gaspari and Gyorffy.[5] In the rigid muffin-tin approximation one assumes that the total self-consistent change in crystal potential when one nucleus is moved is given by the gradient of the usual band-theory potential. We have shown[14] in calculations on Nb that the rigid muffin-tin approximation result for the matrix elements of ∇V is approximately the same as that obtained by assuming that the charge

density in the solid is a linear superposition of atomic charge densities. This has been a very useful approximation for generating band-theory potentials. Its validity has not been extensively tested, however, for generating potential changes due to atomic displacements.

Equation (2.4) can be rewritten in terms of the Fermi energy density matrix

$$\rho(r,r';E_F)=\frac{\Omega}{(2\pi)^3}\int d^3k\,\delta(E_k-E_F)\psi_k^*(r)\psi_k(r')\,, \tag{2.5}$$

as

$$\eta=N(E_F)^{-1}\int d^3r\int d^3r'\;\nabla V(r)\cdot\nabla V'(r')\times\rho(r,r';E_F)\rho(r',r;E_F)\,. \tag{2.6}$$

The Fermi-energy density matrix can be expanded in terms of radial wave functions $R_l(r)$, and cubic harmonics $K^t_{l\mu}(\hat{r})$, where t labels the irreducible representation, μ is the row of that irreducible representation, and l is the orbital quantum number:

$$\rho(\vec{r},\vec{r}';E_F)=\sum_{l,l',t}T^t_{ll'}R_l(r)R_{l'}(r')\times\sum_{\mu}K^t_{l\mu}(\hat{r})K^t_{l'\mu}(\hat{r}')\,. \tag{2.7}$$

The central results of Ref. 12 are firstly, an expression for η is terms of the coefficients $T^t_{ll'}$, and the radial wave function potential gradient matrix elements

$$V'_{l,l+1}=\int r^2\,dr\,R_l(r)\frac{dV}{dr}\,, \tag{2.8}$$

and secondly, the description of an efficient technique for evaluating these coefficients. The expression for η for cubic systems having small phase shifts for $l>2$ is

$$\eta=2N(E_f)^{-1}\Big(\sum_{l=0,1,2}(l+1)\overline{T}_{ll}\overline{T}_{l+1,l+1}V'^2_{l,l+1}+\tfrac{3}{35}V'^2_{23}(T^{25'}_{22}-T'^2_{22})(T^{25}_{33}-3T^{15}_{33}+2T^{2'}_{33})-\tfrac{12}{5}(3/7)^{1/2}V'_{12}V'_{23}(T^{25'}_{22}-T^{12}_{22})T^{15}_{13}\Big), \tag{2.9}$$

where

$$\overline{T}_{00}=T^1_{00}\,,\quad \overline{T}_{11}=T^{15}_{11}\,,\quad \overline{T}_{22}=\tfrac{3}{5}T^{25'}_{22}+\tfrac{2}{5}T^{12}_{22}\,,\quad \overline{T}_{33}=\tfrac{3}{7}T^{25}_{33}+\tfrac{3}{7}T^{15}_{33}+\tfrac{1}{7}T^{2'}_{33}\,. \tag{2.10}$$

Results of a calculation of η for Nb were presented in Ref. 12. In the following section we present results for nine other cubic $4d$ transition metal systems.

The final term in Eq. (2.9) differs by a sign from Eq. (2.26) of Ref. 12. Table II and Eq. (2.23) of Ref. 12 are correct, however, a factor of $i^{l_3-l_4}$ was mistakenly neglected in going from Eq. (2.23) to Eq. (2.25). The effect of this sign error on the final value of η or $\langle I^2\rangle$ is only a few percent in most cases.

III. CALCULATED AND EMPIRICAL VALUES OF $\langle I^2\rangle$

A. Calculated values of $\langle I^2\rangle$

Table I gives a summary of the systems on which we report in this paper. We have performed Korringa-Kohn-Rostocker (KKR) constant-energy searches of the type described in Ref. 12 for the listed potentials and energies. All potentials were constructed by the standard non-self-consistent prescription of overlapping neutral-atom charge densities. An exchange multiplier of 1.0 and a $5s^1$ atomic configuration were used for all of the potentials except for Y and Zr where a $5s^2$ configuration was used. It was shown in Ref. 12 that our Nb potential has Fermi-energy properties which hardly differ from those of a potential generated from the self-consistent $x-\alpha$ technique.

All calculations are for cubic systems even though the stable low-temperature phase of Y, Zr, Tc, and Ru is hcp. This is primarily for convenience. The expression for η is much more complicated for hcp systems involving 19 independent density-matrix coefficients. The band-structure calculation also becomes substantially more expensive for two atom per unit cell. Hopefully the average electron-phonon interaction, $\langle I^2\rangle$ defined by $\langle I^2\rangle\equiv\eta/N(E_F)$ will not be too phase dependent. In any event it is interesting and informative to follow the behavior of η, or better, $\langle I^2\rangle$ over an extensive range of Z for a single phase. Accordingly we have performed calculations on Y, Zr, Nb, Mo, Tc, and Ru assuming the bcc phase. Two additional constant-energy searches were performed for Nb at energies above and below the Fermi energy in order to investigate in a rigid band picture how η changes upon alloying. Calculations were also performed on the fcc phases of Ru, Rh, and Pd. The two calculations on Ru were performed to give an idea of how much $\langle I^2\rangle$ depends on phase. In all cases except for the extra Nb calculations the lattice parameter is chosen to give the observed volume per atom.

In Table I we also give the phase shifts at the energy for which the constant energy search was performed. δ_0 and δ_1 are both negative for all the systems shown. This indicates that the potential is repulsive for s and p electrons which are repelled from the ionic core by orthogonality requirements. This effect is diminished for Pd

TABLE I. Summary of systems for which (KKR) constant-energy searches were performed.

	Y	Zr	Nb(1)	Nb(2)	Nb(3)	Mo	Tc	Ru	Ru	Rh	Pd
Phase	bcc	bcc	bcc	bcc	bcc	bcc	bcc	bcc	fcc	fcc	fcc
Lattice parameters (a.u.)	7.6419	6.7808	6.2294	6.2294	6.2294	5.938	5.7742	5.6789	7.1549	7.172	7.327
Energy (Ry)	0.343	0.4734	0.614	0.623	0.655	0.739	0.6833	0.705	0.6712	0.576	0.46225
Electrons/atom	2.98	4.007	4.766	5.004	5.430	6.000	7.001	8.141	7.998	9.038	10.000
Phase shifts: (rad)											
δ_0	−0.47269	−0.69170	−0.84256	−0.8485	−0.86920	−0.88788	−0.77240	−0.73258	−0.68780	−0.52634	−0.32345
δ_1	−0.14033	−0.22965	−0.30399	−0.30805	−0.32226	−0.32477	−0.24744	−0.22274	−0.19937	−0.11926	−0.041757
δ_2	0.47027	0.81651	1.1351	1.2020	1.4301	1.96329	2.40951	2.52412	2.53431	2.76822	2.89337
δ_3	0.00276	0.00394	0.00555	0.00583	0.00687	0.00766	0.00510	0.00489	0.00456	0.00271	0.00143

because the ionic core is smaller and more tightly bound. The $l=3$ phase shift is essentially negligible for all of the energies and potentials. The $l=2$ phase shift on the other hand increases from 0.47 to nearly π as we cross the transition metal series. Considered individually as a function of energy, $\delta_2(E)$ for each of the potentials would show the resonant behavior characteristic of transition metals rising rapidly from a small value to a value of approximately π. This behavior is somewhat distorted in Table I where we list δ_2 as a function of Z. This distortion is due to the fact that the width of the resonance depends upon the atomic separations and upon the relative positions of the resonant energy [at which $\delta_2(E)=\frac{1}{2}\pi$] and the bottom of the s band.

Table II lists the coefficients of the Fermi-energy density matrix defined in Eq. (2.7). The radial wave functions in (2.7) are normalized so that $R_l(r)=j_l\cos\delta_l-n_l\sin\delta_l$ for r greater than the muffin-tin radius. It is probably easiest to understand the trends in these coefficients by comparing them with the single scatterer value, $(E_F)^{1/2}/\pi$, given in the last row. As shown by Gyorffy[15] the Fermi-energy density matrix may be written in terms of the scattering path operator $\tau_{LL'}$ defined by

$$\tau^{(E)}_{LL'}=\frac{1}{\Omega_{BZ}}\int d^3k\{[t^{-1}_{(E)}-G'(k,E)]^{-1}\}_{LL'}, \quad (3.1)$$

as

$$\rho(r,r';E)=-\frac{1}{\pi}\ \mathrm{Im}\sum_{LL'}\frac{R_l(r)R_{l'}(r')\tau_{LL'}(E)}{\sin\delta_l\sin\delta_{l'}} \times Y_L(\hat{r})Y_{L'}(\hat{r}'). \quad (3.2)$$

Ω_{BZ} in Eq. (3.1) indicates the volume of the Brillouin zone and we have used L to denote both the orbital quantum l and the azimuthal quantum number m. $t(E)$ is the scattering operator for scattering off a single potential and $G'(E,k)$ is the KKR structure constant matrix. The numbers in the first eight rows of Table II correspond essentially to an evaluation of the imaginary part of $\tau_{LL'}$ in a cubic harmonic basis. The single scatterer value comes from expanding Eq. (3.1) in powers of t and keeping only the first term

$$\tau^{(1)}_{LL'}=t_{LL'}(E)=(E_F)^{1/2}e^{i\delta_l}\sin\delta_l\,\delta_{ll'}\,\delta_{mm'}. \quad (3.3)$$

Thus in the single scatter approximation $T^t_{ll'}=\delta_{ll'}(E_F)^{1/2}/\pi$.

Consider first the d coefficients, $t=22\Gamma_{25'}$ and $t=22\Gamma_{12}$. If we take a weighted average of these coefficients and compare with $(E_F)^{1/2}/\pi$ we find that the effect of multiple scattering effects is to decrease the d density of states for Zr, Nb, and Mo, and to increase it for Y, Tc, Ru, Rh, and Pd.

TABLE II. Density matrix expansion coefficients $T^t_{ll'}$ in atomic units (inverse Bohr radii).

l	l'	t	Y	Zr	Nb(1)	Nb(2)	Nb(3)	Mo	Tc	Ru(bcc)	Ru(fcc)	Rh	Pd
0	0	Γ_1	0.027	0.120	0.316	0.223	0.107	0.063	0.110	0.060	0.098	0.087	0.085
1	1	Γ_{15}	0.449	0.569	0.948	0.727	0.457	0.278	0.227	0.139	0.229	0.124	0.080
2	2	$\Gamma_{25'}$	0.470	0.201	0.252	0.2071	0.0878	0.1282	0.486	0.5356	0.3186	1.0486	2.5234
2	2	Γ_{12}	0.183	0.0762	0.108	0.0739	0.0357	0.0860	0.719	1.7737	1.0422	1.1079	0.9911
3	3	Γ_{25}	2.035	1.785	2.448	1.657	0.590	0.608	1.177	0.614	1.999	2.230	1.946
3	3	Γ_{15}	0.408	0.602	0.753	0.742	0.513	0.626	2.072	1.311	0.479	0.291	0.173
3	3	$\Gamma_{2'}$	0.186	0.802	0.377	1.222	0.659	0.741	1.518	1.834	0.192	0.136	0.118
1	3	Γ_{15}	0.239	0.157	0.136	0.090	0.044	−0.056	−0.358	−0.262	−0.093	−0.080	−0.049
$(E_F)^{1/2}/\pi$			0.1864	0.2190	0.2494	0.2512	0.2576	0.2736	0.2631	0.2673	0.2608	0.2416	0.2164

We expect this because we know that multiple scattering effects broaden the relatively narrow d resonance into the full d band. Thus Pd has a Fermi energy which falls well above its narrow $l=2$ resonance. For a single scatterer the d density of states ($\approx (1/\pi)d\delta_2(E)/dE\,|_{E=E_F}$) would be very small at that energy. The true band-theory density of states is known to be quite high since the fcc transition metal density of states curves tend to have a peak near the upper band edge—hence the factor of 12 enhancement of the d density matrix coefficient for Pd. For Mo on the other hand the band-theory density of states is known to be low while the single scatterer density of states will be high due to the Mo Fermi energy falling near the resonant energy.

The $l=0$ density matrix coefficient is generally less than its single scatterer value. This is probably due in part to a hybridization effect which expels s electrons from the d bands. This effect is especially pronounced near the ends of the series for Y and for Ru, Rh, and Pd.

The p coefficients are strongly enhanced over their single scatterer values for systems to the left of Mo. For the systems to the right of Mo, T^{15}_{11} is less than its single scatterer value. The $l=3$ density of states is strongly enhanced over its single scatterer value for all systems.

This enhancement of the f-like density of states is a crucial point in understanding our results on the strength of the electron-phonon interaction. Because of the potential gradient in the electron-phonon matrix elements there is an angular momentum selection rule. l must change by ± 1 when an electron scatters off of a potential fluctuation caused by a lattice vibration. For transition metals whose Fermi-energy wave functions have primarily $l=2$ character the most important processes contributing to the electron-phonon coupling are those which involve scattering between d and f, or d and p states. In fact our calculations indicate that $d \rightarrow f$ scattering is the most important. It follows that the density of f-like states at the Fermi energy is a very important quantity for understanding superconductivity in the transition metals.

Table III lists the integrals over the Wigner-Seitz cell which are necessary to calculate the Fermi-energy density of states

$$\rho^t_{ll'} = \int_\Omega d^3r\, R_l(r) R_{l'}(r) \sum_\mu K^t_{l\mu}(\hat{r}) K^t_{l'\mu}(\hat{r}) . \qquad (3.4)$$

Thus from Eq. (2.7) we have

$$N(E_F) = \sum_{tll'} N^t_{ll'}(E_F) , \qquad (3.5)$$

where

$$N^t_{ll'}(E_F) = \rho^t_{ll'} T^t_{ll'} , \qquad (3.6)$$

is the contribution to the Fermi-energy density of states arising from irreducible representation t and angular momenta l and l'. The partial Fermi-

TABLE III. Cellular integrals of radial wave functions $\rho^t_{ll'}$ in atomic units. Entries in last row have been multiplied by 2.

l	l'	t	Y	Zr	Nb(1)	Nb(2)	Nb(3)	Mo	Tc	Ru(bcc)	Ru(fcc)	Rh	Pd
0	0	Γ_1	4.271	2.444	1.6245	1.6128	1.5710	1.3321	1.3870	1.3666	1.4239	1.7189	2.3196
1	1	Γ_{15}	5.881	3.522	2.4915	2.5002	2.5270	2.2151	2.1564	2.1604	2.1964	2.4334	2.9013
2	2	$\Gamma_{25'}$	25.993	33.098	29.5143	29.824	28.6568	18.3506	11.5068	8.3160	9.0618	5.6092	4.7296
2	2	Γ_{12}	18.590	23.330	20.6282	20.824	19.8792	12.4636	7.7555	5.5793	6.0609	3.7436	3.1576
3	3	Γ_{25}	0.1627	0.143	0.1416	0.1469	0.1669	0.1550	0.1021	0.0959	0.0625	0.0420	0.0273
3	3	Γ_{15}	0.1620	0.143	0.1409	0.1462	0.1661	0.1542	0.1017	0.0954	0.1005	0.0686	0.0455
3	3	$\Gamma_{2'}$	0.0299	0.027	0.0268	0.0278	0.3179	0.2971	0.0193	0.0181	0.0260	0.1759	0.0115
1	3	Γ_{15}	0.3117	0.2284	0.1901	0.1934	0.20512	0.2406	0.1491	0.1438	0.1366	0.1203	0.1077

TABLE IV. Density of states decomposed into contributions from different angular momenta and symmetries $N_{ll'}^{t}$ (states of one spin per rydberg).

l	l'		Y	Zr	Nb(1)	Nb(2)	Nb(3)	Mo	Tc	Ru(bcc)	Ru(fcc)	Rh	Pd
0	0	Γ_1	0.116	0.293	0.513	0.360	0.168	0.084	0.153	0.082	0.139	0.149	0.196
1	1	Γ_{15}	2.641	2.004	2.363	1.818	1.156	0.616	0.490	0.300	0.503	0.302	0.231
2	2	$\Gamma_{25'}$	12.222	6.653	7.437	6.176	2.515	2.353	5.598	4.454	2.887	5.882	11.935
2	2	Γ_{12}	3.407	1.778	2.222	1.539	0.710	1.072	5.578	9.896	6.317	4.148	3.130
3	3	Γ_{25}	0.331	0.255	0.347	0.243	0.098	0.094	0.120	0.060	0.125	0.094	0.0531
3	3	Γ_{15}	0.066	0.086	0.106	0.108	0.085	0.097	0.211	0.125	0.043	0.020	0.0079
3	3	$\Gamma_{2'}$	0.006	0.022	0.010	0.034	0.021	0.022	0.029	0.033	0.005	0.002	0.0014
1	3	Γ_{15}	0.074	0.036	0.026	0.018	0.009	−0.013	−0.053	−0.038	−0.013	−0.010	−0.0053
Total			18.863	11.127	13.024	10.296	4.762	4.325	12.126	14.912	10.006	10.587	15.549
		f_0	0.006	0.026	0.039	0.035	0.035	0.019	0.013	0.006	0.014	0.014	0.013
		f_1	0.140	0.180	0.181	0.177	0.243	0.142	0.040	0.020	0.050	0.029	0.015
		f_2	0.829	0.758	0.742	0.749	0.677	0.792	0.922	0.962	0.920	0.947	0.969
		f_3	0.021	0.033	0.036	0.037	0.043	0.049	0.030	0.0146	0.0173	0.011	0.004
$N_d^{\text{out}}/N_d^{\text{total}}$			0.152	0.123		0.106		0.058	0.030	0.020	0.015	0.005	0.0025

energy state densities $N_{ll'}^{t}$ are listed in Table IV together with the fraction of the total density of states f_l that is s-, p-, d-, or f-like. The p fraction f_1 is sizeable in the first half of the series, increasing from 14% for Y to 24% for a NbMo alloy then falling off rapidly for Tc. The f fraction is also sizable in the first half of the series increasing with Z, reaching a maximum of nearly 5% for Mo and then decreasing rapidly for Tc and Ru. Note that f_1 and f_3 are both extremely small for Pd.

We believe that the variation of f_3 can be partly understood in terms of the tight-binding model. It should be borne in mind that the full electronic state density within a given Wigner-Seitz cell is, in our formalism, expanded about the center of that cell. Thus if one wants to think in terms of tight-binding orbitals he must remember that an orbital which has a tail extending into a neighboring site will yield a contribution to the state density at that site. Furthermore a d orbital tail when expanded about a neighboring site will yield a non-d-state density. The rapid decrease in f_3 near the end of the transition metal series is due to the increased localization of the d orbitals. For Pd there remains hardly any d orbital "tail" which overlaps into the next cell. The increase in localization of the d orbitals is shown in Table IV where we list the ratio of the d density of states within the muffin-tin to the total d density of states, $N_d^{\text{out}}/N_d^{\text{total}}$.

This argument leaves unexplained, however, the rise in f_3 seen for Y through Mo. Apparently the tails of the d orbitals of Y, for example, do not "like" to be expanded as f states about neighboring sites. This is probably related to the r dependence of the radial wave function. As is well known the derivative of the radial wave function evaluated at the muffin-tin radius or slightly beyond is approximately zero at the bottom of the d band, while the radial wave function itself goes to zero in the interstitial region for energies near the top of the d band. In fact, since the density of states per unit volume at the Fermi energy, $\rho(r, r; E_F)$, must have the full symmetry of the lattice it follows that its normal derivative must vanish at all points on the surface of the Wigner-Seitz cell. One can show for example by considering the normal derivative in the [111] direction (where the muffin tins touch) using the formulas for $\sum_\mu K_{l\mu}^{t}(\hat{r})K_{l'\mu}^{t}(\hat{r})$ of Ref. 12 that

$$T_{00}^{1}R_0^2\gamma_0 + 3T_{11}^{15}R_1^2 + 5T_{22}^{25'}R_2^2\gamma_2 + (3.11\,T_{33}^{15} + 3.89T_{33}^{2'})R_3^2\gamma_3 + \tfrac{2}{3}(21)^{1/2}T_{13}^{15} \times R_1R_3(\gamma_1+\gamma_3) + \cdots = 0 . \quad (3.7)$$

where R_l is evaluated at the cell boundary (muffin-tin radius) and γ_l is the logarithmic derivative of R_l evaluated at the same radius. If, on the other hand, one replaces the Wigner-Seitz cell by a sphere it is clear that the following approximate boundary condition must hold:

$$\sum_l (2l+1)\overline{T}_{ll}R_l^2\gamma_l \approx 0 , \quad (3.8)$$

where $\overline{T}_{ll}$ is a density matrix coefficient averaged over irreducible representations [see Eq. (2.10)] and R_l and γ_l should be evaluated at some average cell radius r_s. Since the lth contribution to the density of states is given by

$$N_l = (2l+1)T_{ll}\int_0^{r_s} r^2\,dr\,R_l^2 = (2l+1)T_{ll}r_s^2R_l^2(r_s)\left(\frac{-d\gamma_l}{dE}\right) , \quad (3.9)$$

it follows that Eq. (3.8) is equivalent to

$$\sum_l N_l\gamma_l\left(\frac{d\gamma_l}{dE}\right)^{-1} \approx 0 . \quad (3.10)$$

TABLE V. Contributions to $\langle I^2 \rangle$ (units of 10^{-3} a.u.).

Type of contribution	Y	Zr	Nb(1)	Nb(2)	Nb(3)	Mo	Tc	Ru(bcc)	Ru(fcc)	Rh	Pd
(spherical)											
sp	0.007	0.220	0.929	0.811	1.170	0.535	0.086	0.018	0.098	0.193	0.004
pd	0.590	2.080	4.269	4.205	5.214	3.760	0.779	0.380	0.875	-0.300	0.106
d-f	1.307	4.392	8.012	9.068	9.805	19.443	17.198	10.277	13.069	8.518	2.678
(nonspherical)											
d-f	0.033	0.144	0.112	0.350	0.142	0.072	0.245	−0.114	−0.386	−0.020	0.110
p-d-f	0.156	0.312	0.325	0.331	0.305	−0.275	0.558	1.026	0.480	0.012	−0.050
$\langle I^2 \rangle$ (Total)	2.093	7.148	13.647	14.765	16.636	23.535	18.866	11.587	14.136	9.003	2.848
η(a.u.)	0.0395	0.0795	0.1777	0.1520	0.0792	0.1018	0.2288	0.1728	0.1414	0.0953	0.0443
η(eV/Å^2)	1.92	3.87	8.64	7.39	3.85	4.95	11.12	8.40	6.87	4.63	2.15

If only $l=2$ and $l=3$ are kept in the sum Eq. (3.10) one finds that

$$\frac{N_3}{N_2} \approx - \frac{\gamma_2 d\gamma_3/dE}{\gamma_3 d\gamma_2/dE} \ . \tag{3.11}$$

Now γ_3 and $d\gamma_3/dE$ do not change greatly as one crosses the transition-metal series. The ratio $-\gamma_2(d\gamma_2/dE)^{-1}$ changes considerably, however, going to zero at both the bottom and the top of the d band. N_3/N_2 given by Eq. (3.11) will therefore follow the general trend of the values of f_3 given in Table IV.

While we believe these arguments offer a qualitative explanation for the observed variation of f_3 we consider it to be very risky to use Eq. (3.11) for quantitative calculations. The reason is that the wave functions near the cell boundary contain substantial contributions from l higher than 3. Thus when we checked Eq. (3.7) for Nb, truncating at $l=3$, we found that it failed badly even though we are confident that our coefficients, $T^t_{ll'}$, are converged. The higher l components make a negligible contribution to the density of states and are not important for superconductivity due to the angular-momentum selection rule. They are, however, necessary to satisfy the boundary conditions at the surface of the Wigner-Seitz cell.

A. Contributions to $\langle I^2 \rangle$

As indicated by Eq. (2.9) there are five terms which contribute to η or to $\langle I^2 \rangle = \eta/N(E_F)$ for monatomic cubic systems. The first three terms are contained in the Gaspari-Gyorffy formula[5] which assumed spherical energy bands. The other two terms may be thought of as "nonspherical corrections."

In Table V we list the contributions to $\langle I^2 \rangle$ from Eq. (2.9). The coefficients $T^t_{ll'}$ come from Table II, the density-of-states values from Table IV and the matrix elements $V^t_{l,l+1}$ from Table I since in the rigid muffin-tin approximation $V^t_{l,l+1} = \sin(\delta_l - \delta_{l+1})$. In all cases the d-f (spherical) term is the largest followed in most cases by the p-d term. Note however, that in bcc Ru and fcc Pd the nonspherical terms are larger than the p-d term. Qualitatively, however, the nonspherical corrections do not appear to be of great importance. Only for bcc Ru does their net contribution approach 10% of the total. The p-d terms are imporant for Y, Zr, and Nb but essentially negligible for the higher Z systems.

B. Empirial values of $\langle I^2 \rangle$

Figure 2 shows the calculated values of $\langle I^2 \rangle$ together with empirical values. Empirical values

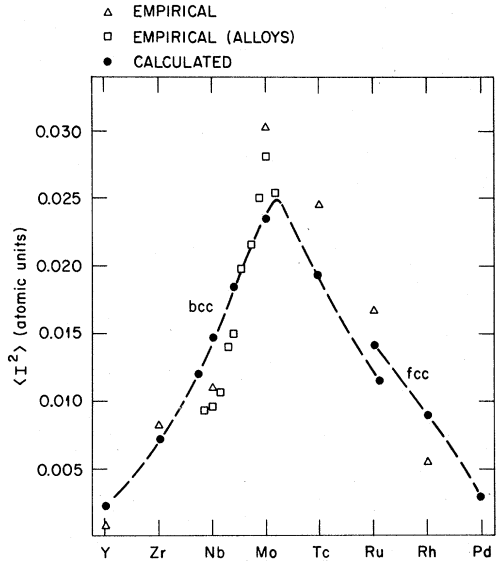

FIG. 2. Empirical and calculated values of $\langle I^2 \rangle$, the Fermi-surface average of the electron-phonon interaction. Open triangles are empirical values for elements (Table VI). Open squares are empirical values for ZrNb, NbMo, and MoRe alloys. Closed circles are calculated values for cubic phases. The two calculated points which represent ZrNb and NbMo alloys in a rigid band picture were scaled according to $\langle I^2 \rangle \propto 1/V^2$ to allow for the effect of volume on $\langle I^2 \rangle$.

TABLE VI. Empirical quantities related to 4*d* transition-metal superconductivity.

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
T_c (°K)	(0.0006)	0.55	9.22	0.92	7.86	0.48	(0.0002)	
Θ_D (°K)	256	290	277	460	454	550	500	270
Θ_c (°K)	210	255	288	382	(355)	382	346	290
$\langle\omega^2\rangle^{1/2}$(°K)	149	173	195	268	245	(264)	(239)	200
$\omega_{\log}$ (°K)	132	142	161	241	223	(229)	(208)	(174)
$\langle\omega^2\rangle^{1/2}/\Theta_c$	0.71	0.68	0.68	0.70	(0.69)	(0.69)	(0.69)	0.69
$\omega_{\log}/\Theta_c$	0.63	0.56	0.56	0.63	(0.63)	(0.60)	(0.60)	(0.60)
Θ_c/Θ_D	0.82	0.88	1.04	0.83	0.78	0.69	0.69	1.07
γ (mJ/mole °K^2)	10.2	2.78	7.8	1.83	4.30	3.1	4.70	9.4
λ	0.26	0.45	0.97	0.44	0.78	0.41	0.27	(0.7)
$N(E_F)$ (states/Ry)	23.3	5.53	11.41	3.66	6.96	6.33	10.66	15.9
$M\langle\omega^2\rangle$ (a.u.)	0.0722	0.100	0.129	0.252	0.218	0.258	0.215	0.156
$\langle I^2\rangle$ (a.u.)	0.00081	0.00814	0.011	0.0303	0.0244	0.0167	0.00544	
η (a.u.)	0.019	0.045	0.125	0.111	0.170	0.106	0.058	

of $\langle I^2\rangle$ require experimental estimates for T_c, $N(E_F)$, $\omega_{\log}$, $\langle\omega^2\rangle$, and μ^*. Our estimates for these quantities are given in Table VI. Since there is some uncertainty as to how best to extract the empirical quantities from the experimental data we feel obliged to give an account of how the numbers in Table VI were obtained.

1. *Transition temperature*

Superconducting transition temperatures can be measured with satisfactory accuracy. Our values for T_c are essentially the same as those quoted by McMillan[1] except for Y and Rh. For Y our value of T_c (0.0006 °K) was obtained by extrapolating the measured T_c's of Y-La alloys determined by Satoh and Ohtsuka.[16] This value of T_c when used in Eq. (1.1) with $\mu^* = 0.13$ and a value of $\omega_{\log}$ determined from the measured phonon spectrum yields a value of λ equal to 0.26 which is in good agreement with the estimate of λ by Knapp and Jones.[17] They obtained $\lambda = 0.30 \pm 0.05$ by extrapolating the high-temperature electronic heat capacity (which is not electron-phonon enhanced) to low temperature and comparing with the observed low-temperature electronic specific heat coefficient. This value is also in agreement with an extrapolation based on the high-pressure data of Wittig.[17,18] The quoted value of $T_c = 0.002$ °K for Rh was obtained from the work of Mota *et al.*[19] who extrapolated T_c measurements on Rh-Ir and Rh-Os alloys.

2. *Phonon frequencies*

According to Allen and Dynes[2] two characteristic phonon frequencies are required in order to determine η or $\langle I^2\rangle$, $\langle\omega^2\rangle$ defined by Eq. (2.3) and $\omega_{\log}$ defined by

$$\log\omega_{\log} = \int\frac{1}{\omega}\log\omega\alpha^2F\,d\omega \Big/ \int\frac{1}{\omega}\alpha^2F\,d\omega\,. \qquad (3.12)$$

Unfortunately there is little reliable information about the variation of α^2 with ω for the transition metals. The tunneling data of Shen[20] on Ta indicates that α^2 is approximately a constant whereas the very recent tunneling data of Robinson[21] and of Bostock *et al.*[22] on Nb indicates that α^2 falls off substantially for the higher frequencies. The calculations of Harmon,[23] however, indicate that α^2 is approximately constant for Nb.

In the following we shall assume for consistency and convenience that α^2=constant in calculating $\omega_{\log}$ and $\langle\omega^2\rangle$. This approximation is probably accurate to about 10% for $\langle\omega^2\rangle^{1/2}$. It is probably also an overestimate due to two effects. Firstly, as pointed out by Appel and Kohn[13] it is probably not unreasonable to suppose that the phonon mediated electron-electron interaction is primarily a local effect with both electrons interacting with the same ion. This assumption leads to $\alpha^2 \propto 1/\omega$. Secondly, in the transition metals with high T_c's, (e.g., Nb and Tc) one finds anomalous dips in the phonon spectra.[24] It is thought that these dips are caused by the electron-phonon interaction. If this is in fact the case it is reasonable to believe that α^2 is anomalously large for the phonon modes which show the dips. This correlation between large α^2 and reduced ω would act to reduce $\langle\omega^2\rangle$ and $\omega_{\log}$.

For Y,[25] Zr,[26] Nb,[27] Mo,[27] Tc,[28] Pd,[29] and [27] Nb-Mo solid-solution alloys the phonon spectrum has been determined by inealstic neutron scattering. There is also a limited amount of neutron-scattering data on Ru.[24] For Y, Zr, Nb, and Mo, $\omega_{\log}$ and $\langle\omega^2\rangle$ were calculated by fitting a Born-Von Kármán model dynamical matrix to the experimental phonon spectra.[30] For Nb and Mo, these $\langle\omega^2\rangle$ values are in good agreement with those obtained by Weber[31]

using a shell model to fit the phonon spectra. Our $\langle\omega^2\rangle$ and $\omega_{\log}$ values are, however, somewhat higher than those quoted by Allen and Dynes. $\langle\omega^2\rangle$ for Pd was taken from Ref. 9 and $\omega_{\log}$ estimated as 0.87 $\langle\omega^2\rangle$.

Although the phonon spectrum of technetium has been measured, a force-constant fit is not yet available so we estimated $\langle\omega^2\rangle$ and $\omega_{\log}$ by the following procedure: we assume that the acoustic modes have a Debye like density of states with a maximum frequency of 331 °K and that the optical-mode frequencies are uniformly distributed between 192 and 331 °K. These particular frequencies were chosen to agree with the phonon measurements of Smith.[28] The same procedure when applied to Y turned out to be in error by only 5%

For Ru and Rh, phonon spectra are not yet available. For these elements we have estimated $\langle\omega^2\rangle$ and $\omega_{\log}$ from characteristic phonon frequencies associated with specific-heat measurements. It is traditional in reporting results of low-temperature specific heat measurements to quote a Debye temperature Θ_D obtained by fitting the specific heat to the formula

$$C_v = \gamma T + \beta T^3 , \tag{3.13}$$

where β is related to Θ_D through $\beta = 12\pi^4 R/5\Theta_D^3$, R being the gas constant. This procedure does not yield a satisfactory measure of typical phonon frequencies for two reasons. Firstly, Eq. (3.13) does not apply until really low temperatures are reached. In Nb for example the fit must be done at temperatures less than 3 °K.[32,33] At these low temperatures the second term in Eq. (3.13) is quite small compared to the first so that it is difficult to get a precise measure of Θ_D. The second problem is that Θ_D, even if obtained accurately, is not a good measure of typical phonon frequencies, but only of the very lowest ones. Thus when we compare $\langle\omega^2\rangle^{1/2}$ obtained from neutron scattering to Θ_D we find that the ratio varies from 0.57 to 0.71. There is a 25% difference in these ratios which would translate into a 55% difference if we were comparing $\langle\omega^2\rangle$ values. The Θ_D values in Table VI were obtained from the compilation by Heiniger *et al.*[34] except for[35] Y and Tc.[36]

It is possible to obtain a more reliable estimate of $\langle\omega^2\rangle$ if specific heat measurements at higher temperatures are available. In particular the *temperature-dependent* Debye temperature determined by setting the Debye specific heat function equal to the experimentally determined lattice specific heat tends to a constant for temperatures above about $\frac{1}{3}$ of the Debye temperature. Values of this quantity are available for all of the 4*d* transition metals except Tc (Refs. 37–43). We have listed them in Table VI as Θ_c. For the cases where we can compare, the ratio of $\langle\omega^2\rangle^{1/2}$ to Θ_c is very close to 0.69. Thus for Ru and Rh we have used this ratio to calculate $\langle\omega^2\rangle$ from the experimental Θ_c. We have also calculated $\omega_{\log}$ from Θ_c for Ru, Rh, and Pd by multiplying Θ_c by 0.60. There seems to be more variation in the ratio of $\omega_{\log}$ to Θ_c than in the ratio of $\langle\omega^2\rangle^{1/2}$ to Θ_c. Fortunately, empirical values of η and $\langle I^2\rangle$ are rather insensitive to variations in $\omega_{\log}$.

3. *Empirical values of* λ *and* $N(E_F)$

By using the listed values of T_c and $\omega_{\log}$ one can calculate the exponent appearing in Eq. (1.1). In order to calculate λ one must assume a value for μ^*. For want of better information we follow McMillan and use $\mu^* = 0.13$ for all of the 4*d* transition metals. The resultant values of λ are given in Table VI. Our empirical value for λ for Y is consistent with the estimate of Knapp and Jones.[17] Our estimates for λ are generally slightly higher than those of McMillan due to $\omega_{\log}/1.2$ being generally less than $\Theta_D/1.45$. For Pd we do not calculate an empirical value of λ since we do not believe that Pd is a superconductor at any temperature. Knapp and Jones have, however, obtained a value for the electronic specific-heat enhancement of 0.7. This electronic specific-heat enhancement is probably due at least partly to persistent spin fluctuations.[44–46]

From the observed electronic specific heat coefficients[34,36,47,48] one can calculate the unenhanced electronic specific-heat coefficient, $\gamma^0 = \gamma/(1+\lambda)$, and from it one can calculate the unenhanced or band-theory Fermi-energy density of states. For Mo, Nb, Rh, and Pd these empirical values of $N(E_F)$ can be compared with our calculated values in Table IV. The agreement is extremely good for Rh and Pd and acceptable for Nb and Mo. For Nb the calculated $N(E_F)$ seems to be 10% too low while for Mo it is about 18% too high. The empirical density of states of Tc (6.94 states/Ry) is about 13% higher than the value calculated by Faulkner.[49] The empirical $N(E_F)$ value for Ru is in good agreement with the calculation by Jepsen *et al.*,[50] but the empirical value for Zr is about 20% lower than their calculated value.

4. *Empirical values of* $\langle I^2\rangle$

By multiplying the empirical values of λ by $\langle\omega^2\rangle$ and dividing by $N(E_F)$ one may obtain empirical values of $\langle I^2\rangle$ which are listed in Table VI and plotted in Fig. 2. Note that $\langle I^2\rangle$ varies by a factor of about 40, increasing rapidly from Y to Mo, and then declining rapidly for higher Z. We have also included in Fig. 2 empirical values of $\langle I^2\rangle$ de-

termined by Weber for Nb-Mo alloys. Weber's estimates of $\langle I^2 \rangle$ for Nb and Mo disagree slightly with our empirical values because we used $\omega_{\log}/1.2$ rather than $\Theta_D/1.45$ as the pre-exponential factor in the T_c equation. $\langle I^2 \rangle$ is also plotted for the alloys $Nb_{0.87}Zr_{0.13}$, and $Mo_{0.85}Re_{0.15}$. For the NbZr alloy, γ and T_c were obtained from the work of Masuda *et al.*[51] and Heiniger *et al.*[34] while the phonon data were taken from the work of Wakabayashi *et al.*[52] For the MoRe alloy, γ and T_c measurements of Morin and Maita[53] were used while the phonon data were obtained from the work of Smith.[28]

III. CONCLUSIONS AND DISCUSSION

A. Calculated and empirical values of $\langle I^2 \rangle$

In general the agreement between the calculated and empirical values of $\langle I^2 \rangle$ is quite good considering the uncertainties in each. The principal uncertainties in the calculated values of $\langle I^2 \rangle$ arise from the use of the rigid muffin-tin approximation and our lack of knowledge of the phase dependence of $\langle I^2 \rangle$. The existence of some phase dependence is clear from our calculations on bcc and fcc Ru. The principal uncertainties in the empirical values of $\langle I^2 \rangle$ arise from uncertainties in $\langle \omega^2 \rangle$ and μ^*. One should also not rule out the possibility of persistent spin fluctuations decreasing T_c in Y, Nb, and Rh. The existence of this effect seems to be fairly well established in Pd.

If one chooses to view these calculations as a test of the rigid muffin-tin approximation he has to admit that the rigid muffin-tin approximation agrees with the empirical data almost within "experimental" uncertainties. Consider Mo, for example, the empirical value of $\langle I^2 \rangle$ is 25% higher than the calculated value, but the two values can be brought into agreement by a small downward adjustment of μ^* and a small upward adjustment of $\langle \omega^2 \rangle$, both adjustments being well within experimental uncertainties.

Nb is somewhat harder to bring into agreement. Benneman and Garland[52] have suggested that μ^* for Nb should be 0.16 (including a small spin fluctuation contribution). Use of this value in calculating the empirical $\langle I^2 \rangle$ would account for about one-half of the observed discrepancy. It would also reduce the discrepancy between the empirical and calculated $N(E_F)$ values and it would give a larger value for λ.

It is likely that much of the discrepancy between the empirical and calculated values for $\langle I^2 \rangle$ is due to the *ad hoc* manner in which the rigid muffin-tin approximation treats the problem of screening. It is also likely, however, that theories which treat only the screening aspects of the electron-phonon interaction while ignoring the more mundane electronic structure aspects will fail when applied to the transition metals. There is clearly a need for improvement in the accuracy of the experimental numbers in order to provide a more stringent test of the calculations. Most helpful would be accurate determinations of μ^* and $\langle \omega^2 \rangle$.

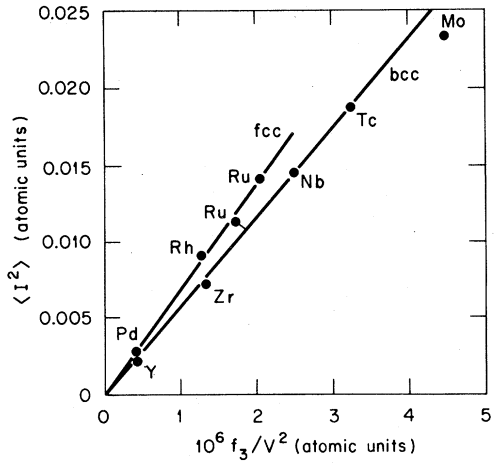

FIG. 3. Plot of $\langle I^2 \rangle$ showing approximate proportionality to f_3/V^2. f_3 is the ratio of $l=3$ Fermi-energy density of states to total density of states. V is atomic volume.

The results for Y and Rh are interesting. In both cases the calculated $\langle I^2 \rangle$ exceeds the empirical value. It has been suggested that persistent spin fluctuations are responsible for the absence of observable superconductivity in these elements as well as in Pd.[44-46] Our calculations do not rule out a small spin fluctuation effect. They do indicate however that the main reason for low T_c's in these elements is their low values of $\langle I^2 \rangle$. Pd, for example, is probably not a superconductor at any temperature due to persistent spin fluctuations. If, however, we calculate T_c ignoring spin fluctuation effects using our calculated value of $\langle I^2 \rangle$ and empirical values of $N(E_F)$ and $\langle \omega^2 \rangle$ and $\mu^* = 0.13$ we obtain $\lambda = 0.29$ and a value of T_c of only 0.01 °K. If the mass enhancement of Pd is indeed 0.7 our calculations would indicate that approximately one-half of it results from persistent spin fluctuations.

B. Variation of $\langle I^2 \rangle$

Since both empirical and calculated values of $\langle I^2 \rangle$ have such a large variation (a factor of 40) as one crosses the 4*d* transition-metal series compared to $M\langle \omega^2 \rangle$ (a factor of 4), and $N(E_F)$ (a factor of 6), it is very important to understand the origin of this variation. The variation in the calculated

values of $\langle I^2\rangle$ arises primarily from two effects. The first effect is the rapid decrease in atomic volume at the beginning of the transition-metal series followed by the minimum which occurs for Ru followed by a slight increase in volume for Rh and a somewhat larger increase for Pd. We find that $\langle I^2\rangle$ is roughly proportional to the inverse second power of the atomic volume V. The second important effect is the variation of f_3, the fraction of the Fermi-energy density of states arising from states with $l=3$. From Table IV we see that f_3 decreases rapidly in the latter half of the series. We find that $\langle I^2\rangle$ is roughly proportional to f_3. The dependence of $\langle I^2\rangle$ on f_3 and V is illustrated in Fig. 3 where we have plotted calculated values of $\langle I^2\rangle$ versus f_3/V^2.

The simple dependence of $\langle I^2\rangle$ on f_3 and V may seem improbable considering the complicated integrals of Eqs. (2.4)–(2.6). This result can be understood in a qualitative way, however. Consider the spherical $d \rightarrow f$ term in Eq. (2.9). Since this is the most important term especially in the latter half of the transition metal series we have in the rigid muffin-tin approximation

$$\langle I^2\rangle \approx 6N(E_F)^{-2}\overline{T}_{22}\,\overline{T}_{33}\sin^2(\delta_2-\delta_3)\,. \tag{4.1}$$

However, $\overline{T}_{22}$ and $\overline{T}_{33}$ are related to the $l=2$ and $l=3$ density of states, respectively, through

$$N_2 \approx 5\overline{T}_{22}\int_0^{r_{WS}} r^2R_2^2(r)\,dr \tag{4.2}$$

and

$$N_3 \approx 7\overline{T}_{33}\int_0^{r_{WS}} r^2R_3^2(r)\,dr\,, \tag{4.3}$$

where r_{WS} is the Wigner-Seitz radius. Thus we can write $\langle I^2\rangle$ in terms of f_2 and f_3 as

$$\langle I^2\rangle \approx \tfrac{6}{35}f_2f_3\sin^2(\delta_2-\delta_3)\Big/\left(\int r^2R_2^2\,dr\int r^2R_3^2\,dr\right). \tag{4.4}$$

The origin of the linear dependence of $\langle I^2\rangle$ on f_3 is obvious from Eq. (4.4), but it may still seem surprising that there is not a strong dependence on Z arising from the factor $\sin^2(\delta_2-\delta_3)$ which is strongly peaked near the center of the series. It turns out that this dependence is roughly cancelled by the integral of R_2^2 in the denominator.[6] Since δ_3 is generally negligible, consider the ratio $\sin^2\delta_2/\int R_2^2(r)r^2\,dr$. $\sin^2\delta_2$ will have a resonance behavior peaking where $\delta_2(E_F)\approx\frac{1}{2}\pi$, but $\int r^2R_2^2(r)\,dr$ will show a similar behavior since for tightly bound d electrons

$$\int r^2R_2^2(r)\,dr \approx E_F^{-1/2}\frac{d\delta_2(E)}{dE}\,. \tag{4.5}$$

In fact, if we assume a resonance formula for $\delta_2(E)$ such that $\tan\delta_2(E)=\Gamma/(E_d-E)$ it is easy to show that $d\delta_2/dE=\sin^2\delta_2(E)/\Gamma$. Thus we have for a resonant phase shift δ_2 that

$$\sin^2\delta_2(E_F)\Big/\int R_2^2(r)r^2\,dr \simeq \Gamma E_F^{1/2}\,, \tag{4.6}$$

where Γ is the width of the resonance. Γ and E_F vary with Z but not nearly so rapidly as $\sin^2\delta_2(E_F)$.

The remaining factor in Eq. (4.4) is the cellular integral of the $l=3$ radial wave functions $\int_0^{r_{WS}} r^2R_3^2(r)\,dr$. This factor has a very strong volume dependence since $R_3(r)\approx j_3(\sqrt{E}r)\approx(\sqrt{E}r)^3/105$. Thus the integral may be roughly approximated as

$$\int_0^{r_{WS}} r^2R_3^2(r)\,dr \approx 10^{-5}E^3r_{WS}^9\,. \tag{4.7}$$

It is the very small value of this integral compared to the similar integral for the $l=1$ radial wave functions that causes $d \rightarrow f$ scattering to be more important than $d \rightarrow p$ scattering. It is also the strong volume dependence of this integral that is primarily responsible for the volume dependence of $\langle I^2\rangle$. Combining Eqs. (4.4), (4.6), and (4.7) we obtain a very rough estimate of $\langle I^2\rangle$,

$$\langle I^2\rangle \simeq 1.25\times10^6(f_2\Gamma/E_F^{5/2}V)f_3/V^2\,. \tag{4.8}$$

Evaluation of the quantity $\Gamma/E_F^{5/2}V$ for the transition-metal systems considered here yields $\Gamma/E_F^{5/2}V\approx4\times10^{-3}$ so that

$$\langle I^2\rangle \simeq 5\times10^3f_2f_3/V^2\,, \tag{4.9}$$

which is in reasonably good agreement with the slopes of the lines through the data points in Fig. 3. Although the above arguments are qualitatively correct the strict proportionality of $\langle I^2\rangle$ to f_3/V^2

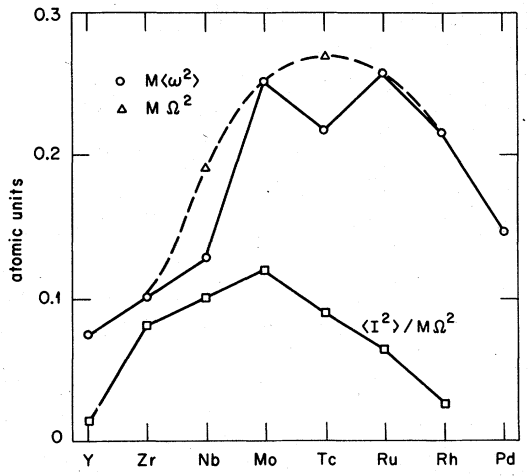

FIG. 4. Plot of $M\langle\omega^2\rangle$ and of the unrenormalized phonon frequencies $M\Omega^2$. Values of $M\Omega^2$ are somewhat speculative. Also shown is $\langle I^2\rangle/M\Omega^2$.

observed in Fig. 3 is somewhat fortuitous since for low Z, $\Gamma/E_F^{5/2}V$ is less than 4×10^{-3} but this is compensated by contributions from $p \rightarrow d$ scattering.

Physically, the approximate proportionality of $\langle I^2\rangle$ to f_3/V^2 arises from the angular-momentum selection rule and from the fact that a transition-metal ion is a compact resonant scatterer. It would be reassuring if we could check this result experimentally. Two types of experiments would be useful in their regard. To check on the volume dependence of $\langle I^2\rangle$ it would be useful to have measurements of T_c, γ, and Θ_c under pressure. To check on the dominance of $d \rightarrow f$ scattering it would be useful to have extensive measurements of the electron-phonon contribution to the phonon linewidth. If our calculations are correct this linewidth which measures the strength of the electron-phonon coupling should show peaks for those q's which connect points on the Fermi surface having large d- and large f-state densities.

C. Variation of $\langle\omega^2\rangle$ and λ

So far we have only discussed the electronic component of the electron-phonon coupling parameter. We feel that the results illustrated in Fig. 2 justify some confidence that a basic understanding of this quantity is emerging for the transition metals. There remains, however, the problem of understanding the phononic component of λ. Table VI lists empirical values of $\langle\omega^2\rangle$. These are also plotted in Fig. 4. At present it is not possible to calculate phonon frequencies from first principles for transition metals. We are forced therefore to resort to a qualitative and somewhat speculative discussion.

Most properties related to nonmagnetic transition-metal bonding when plotted versus Z follow a rather smooth curve having a extrenum near $Z=6$ or slightly beyond. This is generally interpreted in terms of the filling of the d band. The lower d orbitals are bonding in character and the upper ones are antibonding although strictly speaking the transition from bonding to antibonding need not occur when the d band is exactly half-filled since whether or not an additional d electron contributes a net bonding effect depends upon the position of the Fermi energy relative to the d state of the free atom among other things.

The average square phonon frequency $\langle\omega^2\rangle$ does not seem to follow a smooth curve, however. $M\langle\omega^2\rangle$ for Nb and Tc is lower than the rather arbitrary smooth curve labeled $M\Omega^2$ that we have drawn through the mean-square frequencies of the other elements. Nb and Tc both have high superconducting transition temperatures and it is generally believed that there is a softening of the phonons due to the stronger electron-phonon interaction in these systems.

A qualitative explanation of the variation of λ with Z in the transition-metal series can be constructed along the following lines. λ is the product of three factors, $N(E_F)$, $\langle I^2\rangle$, and $(M\langle\omega^2\rangle)^{-1}$. $\langle I^2\rangle$ has the variation shown in Fig. 2. The main origin of this variation can be traced to the variation of the volume per atom and to the $l=3$ component of the Fermi-energy density of states. Some of this variation is however cancelled out by a similar variation of $M\Omega^2$ (Fig. 4). The variation of $M\Omega^2$ with Z being caused by the progressive filling of the d band. If we divide $\langle I^2\rangle$ by $M\Omega^2$ we get a curve like the lower one of Fig. 4. In principle this curve would describe the variation of λ with Z if all of the transition metals had the same Fermi-energy density of states and the same phonon frequency "renormalization." The effect of the density of states seems to enter two ways. It enters as a simple multiplicative factor and it also appears to be involved in the phonon "renormalization" which reduces Ω^2 to $\langle\omega^2\rangle$. The connection between phonon "renormalization" and the Fermi-energy density of states is not completely straightforward however. When Zr is added to Nb, T_c, λ, and $N(E_F)$ increase substantially. The "renormalization" effect, however, does not seen to be enhanced. It seems in fact that if one allows for the expected softening due to having fewer d electrons per atom that the phonon "renormalization" is in fact decreased.[52]

There is a final piece of experimental evidence which we believe supports our basic picture describing the variation of λ with Z. Collver and Hammond have measured T_c's, of "amorphous" transition-metal alloys.[54] These T_c's show much less variation with Z than those for the crystalline state. In addition, they have a single peak which occurs between Mo and Tc. It is difficult to analyze these results in detail since nothing is known about the Fermi-energy densities of states or phonon frequencies for these alloys. It is reasonable to believe, however, that the primary effect of destroying the crystalline order is to reduce the structure in the density of states. The remaining variation in λ is due to $\langle I^2\rangle/M\langle\omega^2\rangle$ (or possibly $\langle I^2\rangle/M\langle\Omega^2\rangle$) and this quantity we would predict to have a single maximum falling between Mo and Tc in general agreement with the observed variation in T_c.

D. Relation of this work to some previous work

Many people have tried to systematize the variations in T_c for the transition metals. We shall only

comment on that work which is directly related to our own. We have made extensive use of McMillan's idea that λ can be regarded as the product of electronic and phononic factors.[1] We disagree with his conclusion that the electronic factor is essentially constant, however. Table VI indicates a factor of 6.5 difference between η for bcc Tc and η for bcc Y. The empirical η's show an even larger variation (a factor of 9). Nb and Mo, the two 4*d* elements which McMillan considered, *do* have rather similar values for η (both calculated and empirical). This is due to two compensating effects. $\langle I^2\rangle$ increases rapidly in going from Nb to Mo but this is offset by a decrease in $N(E_F)$. This compensation does not however, appear to be a general effect.

Hopfield[4] was the first to point out the importance of the angular momentum selection rule due to the potential gradient in the electron-phonon interaction. Hopfield obtained the result

$$\lambda \approx \left(\frac{dV}{dX}\right)^2 \frac{N_p(E_F)N_d(E_F)}{N(E_F)M\langle\omega^2\rangle}, \tag{4.10}$$

where dV/dX is a potential gradient and N_p, N_d, and N are the p, d, and total Fermi-energy densities of states. Hopfield considered $N(E_F)$ to be approximately equal to $N_d(E_F)$, and $N_p(E_F)$ to be approximately a constant independent of Z, thus he obtained

$$\lambda \approx C\left(\frac{dV}{dX}\right)^2 \Big/ M\langle\omega^2\rangle. \tag{4.11}$$

We believe that Hopfield erred in two details. Firstly, he did not anticipate the importance of $d \rightarrow f$ scattering. Secondly, he did not realize that for the type of calculation he envisioned the entire density of states within a cell must be expanded about the center of that cell. Thus, the amount of p or f density of states at the Fermi energy depends strongly on the number and nature of the d states on the neighboring sites.

Gyorffy, Gaspari, and Evans[5,6] introduced the idea of calculating the electron-phonon matrix elements in the rigid muffin-tin approximation and showed that they could be written in a closed form involving the phase shifts. Their original estimates of λ, however, suffer from their having had to approximate N_l for $l \neq 2$ by its single scatterer value. This approximation can be in error by almost an order of magnitude.

Klein, Papaconstantopoulos, and Boyer[7-9] have performed a number of calculations on transition metals and transition-metal compounds using the Gaspari-Gyorffy theory. Their calculations do not include the nonspherical terms of Eq. (2.9), but these terms are rather small for the cubic elements. Our results for η are in good agreement with theirs for Nb, but somewhat lower for Pd.

Brinboim and Gutfreund[10,11] have tried a different apporach to calculating λ for the transition metals. Their work is based on that of Appel and Kohn.[13] Appel and Kohn showed that one could avoid the Fermi surface integrals that we have performed if he is willing to make the "contact" approximation. The contact approximation is equivalent to setting certain Fermi-surface integrals to zero, i.e., one assumes that

$$\int_{FS} dS_k\, v_k^{-1} e^{i\vec{k}\cdot\vec{R}_n} = N(E_F)\delta(\vec{R}_n), \tag{4.12}$$

where $\vec{R}_n$ is a lattice vector, and v_k is the magnitude of the Fermi velocity. We have evaluated these integrals for $\vec{R}_n$ not equal to zero and have found them to be non-negligible. For Nb we estimate that the "contact" approximation leads to an underestimate of $\langle I^2\rangle$ of about a factor of 2.

Probably a more serious source of error in the work of Gutfreund and Birnboim is the replacement of the Wannier functions of Appel and Kohn by rather arbitrary atomic wave functions. The error associated with this approximation is difficult to estimate. We believe, however, that the physical picture that emerges from the local approach is equivalent to the one which emerges from the present work. In particular some readers may prefer to think of the $d \rightarrow f$ scattering which arises in the KKR or augmented-plane-wave picture in terms of a scattering between tight-binding d orbitals sitting on neighboring sites.

One important difference between our work and that of Brinhoim and Gutfreund is that we assume the validity of the Bloch formulation of the electron-phonon interaction.[53] They abandoned the Bloch formulation in favor of a tight-binding formulation because the Bloch formulation appeared to give a value of λ an order of magnitude too large. We believe that the source of this discrepancy lies not in the Bloch formulation of the electron-phonon interaction but in their other approximations.

The very recent work of Pettifor[54] is quite interesting. He has made calculations of η for the 4*d* transition metals following Gaspari and Gyorffy. Some of his results are qualitatively similar to those reported here. Pettifor avoids any calculation of the energy bands and is able to estimate the partial p and f densities of states by means of an antiresonance formula for the p states and an equation equivalent to Eq. (3.11) for the f states. The Z dependence which he obtains for the ratio N_3/N_2 is qualitatively similar to that which we obtain in the sense that he finds N_3/N_2 to be quite small for the higher Z members of the se-

ries. Eq. (3.10) cannot be quantitative, however, because of the neglect of the higher l components of the radial wave functions. We find that Pettifor's values of f_3 are larger than ours (except for Mo) sometimes by a factor of almost 3. This overestimate of N_3/N_2 makes his values of η somewhat larger than ours. Pettifor reduces these values of η by means of arguments related to screening of the rigid muffin-tin matrix elements. A similar reduction applied to our rigid muffin-tin calculations would lead to somewhat poorer agreement with the empirical values of $\langle I^2\rangle$ or η.

E. To obtain a high T_c

Ultimately the theorist would like to be able to predict new systems which have high superconducting transition temperatures and which are stable (or at least metastable) at low temperature and atmospheric pressure. Although we have studied only a limited class of systems we offer the following considerations concerning systems involving transition metals which are likely to have high T_c's.

The electron-phonon coupling parameter λ is the product of three factors: $\langle I^2\rangle$, $N(E_F)$, and $(M\langle\omega^2\rangle)^{-1}$. Clearly we want all three to be as large as possible. This is not a trivial matter to accomplish, however, since a modification of the system which leads to an increase in one of the factors often causes a decrease in one of the others.

We have seen that $\langle I^2\rangle$, in systems which have primarily d electrons at the Fermi energy depends strongly on the amount of non-d (p or f) Fermi-energy density of states and (especially if the scattering is primarily $d \rightarrow f$) on the volume per atom. Thus to obtain a high value for $\langle I^2\rangle$ one wants delocalized d orbitals and a small volume per atom. These two properties are usually associated with strong bonding which generally implies a high value of $\langle\omega^2\rangle$. Thus the factor of 40 variation in $\langle I^2\rangle$ across the 4-d series seen in Fig. 2 is partly offset by the variation in $M\langle\omega^2\rangle$ or $M\Omega^2$ (Fig. 4). In addition, strong bonding tends to reduce $N(E_F)$ by spreading out the d band.

From Fig. 4 we can see that the increase in $\langle I^2\rangle$ near the center of the series dominates the increase in $\langle\omega^2\rangle$. Thus the rule of thumb in the transition metals is that the highest T_c's will be found near the center of the series for those systems which have a high Fermi-energy density of states. It should be remembered that $N(E_F)$ enters λ in two ways, directly as a multiplicative factor, and indirectly through its effect on $\langle\omega^2\rangle$. It is therefore a fairly simple matter to predict transition-metal systems which would in principle have higher T_c's than those heretofore observed. An hcp alloy of composition $Mo_{0.3}Tc_{0.7}$, for example, should be on a peak in $N(E_F)$[50] (assuming a rigid band model) and consequently have a very high transition temperature since $\langle I^2\rangle/M\Omega^2$ is high in this region. Unfortunately the hcp phase appears to be unstable for Z less than 6.9.[55] This instability is probably not coincidental since a phase having a half-filled d band and a high Fermi energy density of states is likely to be unstable compared to a phase which splits the d band into bonding and antibonding sub-bands with a near gap in the center of the band (viz., the bcc phase).

It is sometimes stated that the bcc phase is conducive to high T_c. Our view is somewhat different. We suggest that the strong d-d bonding which occurs near the center of the series is conducive to strong electron-phonon coupling. This strong directional bonding also leads to the stability of the bcc phase. Our calculations which have been restricted to cubic phases seem to suggest that the fcc phase is somewhat more favorable than the bcc phase for high T_c. This may, however, be an artifact of the rigid muffin-tin approximation which truncates the potential at different radii for the two phases. In our view the effect of crystal structure on T_c in the transition metals will enter primarily through its effect on the Fermi-energy density of states and on the fraction of that density of states which has $l=3$ character.

Finally, we would like to speculate on the possibility of finding systems in which the advantage of having a high $\langle I^2\rangle$ is not offset by a concommitant high $\langle\omega^2\rangle$. The connection between high $\langle I^2\rangle$ and strong bonding originates in the angular-momentum selection rule in the electron-phonon interaction. For the transition metals the scattering is primarily $d \rightarrow f$ where the f density of states arises from the tails of the d orbitals centered on neighboring sites. Thus in the transition metals an increase in the f density of states can be achieved only by increasing the overlap of the d orbitals and hence the strength of the interatomic binding.

In the early rare earths and actinides, however, the situation is different. In these systems the f density of states in a given cell arises primarily from the atomic f orbitals centered on the site at the origin. Let us consider $d \rightarrow f$ scattering for such a system. Using Eq. (4.4) and remembering that both the d and f orbitals are tightly bound so that

$$\int r^2 R_3^2\, dr \approx [\Gamma_3 (E_F)^{1/2}]^{-1} \sin^2\delta_3 ,$$

where Γ_3 is the width of the f resonance we obtain

$$\langle I^2\rangle \approx \tfrac{6}{35} f_2 f_3 E_F \Gamma_2 \Gamma_3 \left(\frac{E_3 - E_F}{\Gamma_3} - \frac{E_2 - E_F}{\Gamma_2}\right)^2 , \quad (4.13)$$

where E_2 and E_3 are the d and f resonance energies. The volume does not enter Eq. (4.13) explicitly, however, it does enter indirectly through the resonance widths Γ_2 and Γ_3. It is impossible without doing an energy-band calculation to estimate $\langle I^2 \rangle$ for this class of system with any confidence. A rough estimate indicates that values of $\langle I^2 \rangle$ comparable to the highest found in the transition metals might be achieved under favorable circumstances. In addition to $d \rightarrow f$ scattering there will also be $f \rightarrow g$ scattering analagous to the $d \rightarrow f$ scattering in the transition metals. Such a large value of $\langle I^2 \rangle$ coupled with a very large $N(E_F)$ (which is likely in such a system) and a comparatively low $M\langle \omega^2 \rangle$ could lead to very strong electron-phonon coupling.

Unfortunately, few high T_c phases are known among the rare earths and actinides. It is possible that even if strong electron-phonon coupling exists in these systems superconductivity may be prevented or T_c drastically reduced by exchange effects.

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