Angular Momentum and Transition-Metal Superconductivity*

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The relation between the systematics of superconductivity in the transition metals and the Periodic Table suggests that the transition temperature is chiefly a short-range or "chemical" property. When a local representation of phonons and an angular momentum decomposition of electron wave functions are used, the conventional description of electron-phonon interactions contains chiefly scatterings which change the angular momentum of the electron. This selection rule makes possible the writing of the electron-phonon coupling constant λ as the quotient of two parameters, each of which is of a chemical nature. This simplification is possible for materials having a high density of d states at the Fermi energy. For such materials, λ is little affected by the density of states. The theory is compared with the superconducting transition temperatures of transition metals and their alloys.

I. INTRODUCTION

THE BCS theory of superconductivity[1] with its strong coupling extension has unified many experimental data in terms of a few basic interaction parameters. In simple $(S\text{-}P)$ metals, theory has advanced to the point that estimates of the parameters entering the BCS Hamiltonian can be obtained from detailed calculations of energy-band structures, phonon energies, and the electron-phonon coupling. Calculation of the BCS parameters has so far been possible only in materials where the potential due to the ion cores is effectively weak.

While the general theory of superconductivity is generally believed to hold also for transition metals, formidable theoretical barriers prevent the calculation of BCS parameters. The behavior of electrons in transition-metal d bands is not completely understood. The atomic potential is strong. Even a good calculation of the cohesive energy of transition-metal materials has not been possible. The theoretical approach to calculating BCS parameters contains such conceptual and computational difficulties that it has never been attempted, though its formulation is being pursued.[2] Were such a calculation performed, it would contain as intermediate steps infinite details of wave functions, electron-phonon interactions, phonon modes, and Fermi-surface shape. Such details are not only necessary for such a calculation, but are also, unfortunately, sensitive to the suppositions on which such a calculation would be based.

One of the most striking features of superconductivity in transition elements and their compounds is that alchemists have developed feeling for what situations are and are not favorable from looking at the Periodic Table.[3] There have been many theoretical and "theoretical" attempts to understand this order.[4] Apparently, correlations based on a chemical description of the nature of a solid have at least a qualitative ability to predict the superconducting behavior of such materials. The implication is strong that there should be a veiwpoint on superconductivity theory which reflects the dominance of atoms and their local environments in determining superconductivity parameters. The existence of such a viewpoint would not mean that the details of the hypothetical calculation discussed above are wrong, but only that they are unnecessary to understanding the general systematics of superconductivity parameters in the transition metals. While such a chemical view cannot be universally correct—in particular cases, special detail will matter—it can be hoped to give a correct over-all view of superconductivity in the transition metals.

In Sec. II, we examine an angular momentum decomposition of the electron-phonon interaction in transition metals. Utilizing such a decomposition, one finds that the superconducting transition temperature depends chiefly on two parameters, each of which is of a chemical (or short-range) nature. (The density of states at the Fermi energy is *not* one of the parameters.) While we are at present unable to calculate either of these parameters *ab initio*, the interpolations and extrapolations possible based on these parameters provide a quantitative systemization of the behavior of T_c in transition-metal alloys and compounds. A numerical study of the variation of the parameters over the Periodic Table and the predictions of transition

[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106**, 162 (1957), referred to as BCS. A good account of most of the relevant theory is given in J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964).

[2] J. W. Garland, Phys. Rev. **153**, 460 (1967); D. C. Golibersuch, *ibid.* **157**, 532 (1967); S. K. Sinha, *ibid.* **169**, 477 (1968).

[3] B. T. Matthias, in *Proceedings of the Tenth International Conference on Low-Temperature Physics*, edited by M. P. Malkov (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967), Vol. IIA, p. 77; Phys. Rev. **97**, 74 (1955); Science **144**, 378 (1964); J. J. Engelhardt, G. W. Webb, and B. T. Matthias, *ibid.* **155**, 191 (1967).

[4] See, for example, D. Pines, Phys. Rev. **109**, 280 (1958); J. W. Garland, Phys. Rev. Letters **11**, 107 (1963); **11**, 111 (1963); B. R. Coles, Rev. Mod. Phys. **36**, 139 (1964); E. Bucher, F Heiniger, J. Muller, and J. L. Olsen, in *Low Temperature Physics; LT9*, edited by J. G. Daunt *et al.* (Plenum Press, Inc., New York, 1965), part A, p. 616; L. Pauling, Proc. Natl. Acad. Sci. U. S. **60**, 59 (1968).

temperature of alloys is given in Sec. III. A few concluding remarks are given in Sec. IV.

II. THEORY

A major problem of the calculation of the superconducting transition metal is the evaluation of the mean electron-phonon interaction parameter λ. This parameter can be defined as[5]

$$\lambda = 2 \int_0^{\omega_0} \alpha^2(\omega_q) F(\omega_q) \frac{d\omega_q}{\omega_q} = \frac{N(0)}{M} \frac{\langle \mathcal{g}^2 \rangle}{\langle \omega^2 \rangle}, \qquad (1)$$

where ω_0 is the maximum frequency of the phonon spectrum, and M is the ion mass. The function $\alpha^2(\omega_q)$ is an average electron-phonon interaction, the average being taken over all phonons having frequency ω_q and all pairs of electron-hole states near the Fermi surface connected by such phonons. The mean phonon frequency $\langle \omega^2 \rangle$ is given by

$$\langle \omega^2 \rangle = \int_0^{\omega_0} d\omega \, \omega \alpha^2(\omega) F(\omega) \Big/ \int_0^{\omega_0} d\omega \frac{\alpha^2(\omega)}{\omega} d\omega, \qquad (2)$$

where $F(\omega)$ is the phonon frequency distribution. If the change in potential due to moving an ion by an amount $\boldsymbol{\varepsilon}$ is written as $\boldsymbol{\varepsilon} \cdot \boldsymbol{\nabla} U(r)$, the average interaction parameter $\langle \mathcal{g}^2 \rangle$ is given by

$$\langle \mathcal{g}^2 \rangle = \frac{1}{3} \int \int dS_k dS_{k'} \, |\langle \psi_k | \boldsymbol{\varepsilon}_x \cdot \boldsymbol{\nabla} U(r) | \psi_{k'} \rangle|^2 \Big/$$

$$\int \int dS_k dS_{k'} \qquad (3)$$

for cubic crystals, where the integrations are carried out over the Fermi surface, and ψ_k is a Bloch wave function.

In conventional theory the phonon renormalization of the electronic density of states can be written[6]

$$N(0)_{\text{renorm}} = N(0)_{\text{bare}}(1+\lambda), \qquad (4)$$

and the superconducting transition temperature (in the absence of Coulomb interactions) can also be expressed in terms of λ. To make either of these calculations, mathematical approximations have been made which are generally viewed as unimportant. These approximations have to do with the neglect of correlation between wave vectors and frequencies to reduce an integral equation which should have depended on $\mathbf{q}$ and ω to a solvable one depending only on ω by first averaging on q. It is generally believed that these approximations are reasonable and adequate. The only major systematic error is the overemphasis in this approximation of small-q phonons. Since, for small q,

phonon frequencies scale with wave vector, this error can be compensated for by a compensating correction in $F(\omega)$. This approximation also omits any effect of energy-gap anisotropy on the transition temperature.

There exists a physical model to which the form (1) is the precise answer to the calculation of λ. Consider a solid having all but one atom fixed, and that one having a (renormalized) vibrational frequency $\bar{\omega}$. The correction to the electronic density of states due to this one ion is

$$\Delta N(0) = 1/N M \bar{\omega}^2 \langle \mathcal{g}^2 \rangle N^2(0) \equiv \lambda_{\text{one ion}} N(0), \qquad (5)$$

where $N(0)$ is the density of states of one spin per atom and N is the number of atoms in the crystal. This answer is elementary if the phonon frequencies are not renormalized, but continues to hold with renormalization. The factor of $\frac{1}{3}$ in the definition of $\langle \mathcal{g}^2 \rangle$ cancels the 3 coming from the three degenerate modes. For a crystal of N movable atoms, the results from each of the different atoms is additive, a conclusion which follows from the fact that the mathematical model with N independently moving atoms is identically a special case of the theory of Eqs. (1)–(3), in which there is only a single frequency and no wave-vector approximations are needed. Finally, the change in the density of states per ion if there is a distribution of frequencies $F(\omega)$ can be obtained by averaging (5) over frequency. The average involved is

$$\int_0^{\omega_0} \frac{1}{\omega^2} F(\omega) d\omega \Big/ \int_0^{\omega_0} F(\omega) d\omega. \qquad (6)$$

Since $\alpha(\omega)$ contains in its explicit ω dependence only the factor $1/\omega$, this averaging is the same as was done in (2). Thus a model in which each atom is regarded as independently vibrating and interacting with the electrons is equivalent to the usual superconductivity model. The omission of the correlation between ω and g in the phonon spectrum produces only a minor quantitative effect.

An understanding of the mean-square matrix element $\langle \mathcal{g}^2 \rangle$ is possible through working in an angular momentum representation. We will first examine the density of states in this representation and expand every Bloch function around one particular atom, writing

$$\psi_k = \sum_{l,m} Y_{lm}(\theta,\phi) g_{lmk}(r). \qquad (7)$$

Let the functions ψ_k be normalized to unity in the crystal volume, and let $Y_{lm}(\theta,\phi)$ be normalized to unity. Define the density of states of angular momentum l per atom (evaluated at the Fermi energy) by

$$N_l(0) = \frac{1}{\Delta} \sum_k \sum_m \int_0^{r_{\text{WS}}} |g_{lmk}(r)|^2 r^2 dr, \qquad (8)$$
$$\lim \Delta \to 0 \quad E_F < E_k < E_F + \Delta$$

where r_{WS} is the radius of a Wigner-Seitz sphere. The

[5] W. L. McMillan, Phys. Rev. **167**, 331 (1968).
[6] G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **43**, 1005 (1962) [English transl.: Soviet Phys.—JETP **16**, 780 (1963)].

total density of states in the crystal is

$$N(0)_{\text{tot}} = \frac{1}{\Delta} \sum_{\substack{k \\ \lim\Delta \to 0 \; E_F < E_k < E_F + \Delta}} 1$$

$$= \frac{1}{\Delta} \sum_{\substack{k \\ \lim\Delta \to 0 \; E_F < E_k < E_F + \Delta}} \int |\psi_k|^2 d^3r$$

$$= \frac{\text{number of cells}}{\Delta} \sum_{\substack{k \\ \lim\Delta \to 0 \quad E_F < E_k < E_F + \Delta}} \int_{\text{one cell}} |\psi|^2 d^3r, \quad (9)$$

so the density of states per atom, weighting each state according to its normalization in the cell of that atom, is

$$N(0) = \frac{1}{\Delta} \sum_{\substack{k \\ \lim\Delta \to 0 \; E_F < E_k < E_F + \Delta}} \int_{\text{one cell}} |\psi_k|^2 d^3r. \quad (10)$$

If the difference between a Wigner-Seitz cell and an atomic polyhedron is ignored, we have

$$\int_{\text{cell}} |\psi_k|^2 d^3r = \sum_{l,m} \int_0^{r\text{ws}} |g_{lmk}(r)|^2 r^2 dr, \quad (11)$$

and the total density of states per atom is then the sum of its component parts:

$$N(0) = \sum_l N_l(0). \quad (12)$$

The total density of states per atom is thus decomposable into partial-wave contributions, each being weighted by its normalization within an atomic volume.

In the simple case of a monovalent metal with no band structure (free electrons), the basic density of states decomposes as

$$N(0) = 0.750/E_F = N_S + N_P + N_D + \cdots$$
$$= 0.36/E_F + 0.24/E_F + 0.13/E_F + \cdots, \quad (13)$$

where the S, P, and D terms contribute virtually everything.

If the band structure of transition metals were crudely represented by an S-P free-electron band plus a tight-binding "D" band, because the D-band wave function on a particular site comes almost entirely from D atomic orbitals, the tight binding D band will contribute almost solely to $N_D(E)$. The high densities of states of many transition metals are to be characterized as large $N_D(0)$ without alteration of N_S and N_P in this model. If one free S-P electron is assigned to niobium, then the measured $N(0)$ of 0.91 states/eV atom would be made up of 0.07, 0.04, and 0.80 for the S, P, and D contributions, with other contributions negligible.

Hybridization between the free electron and D bands will somewhat alter this simple picture. The effect of hybridization will to some extent be kept small by a cancellation visible in the following simple model. Suppose a flat "D" band is crossed by an S-P band with a constant interband matrix element V. Then the Hamiltonian matrix, with the origin of wave vector and energy taken as the crossing point, is

$$\begin{pmatrix} 0 & V \\ V & Ak \end{pmatrix}. \quad (14)$$

The two eigenstates of wave vector k have energies given by

$$E = \tfrac{1}{2}Ak \pm [(\tfrac{1}{2}Ak)^2 + V^2]^{1/2},$$

$$\psi = \frac{1}{[1+(V/E)^2]^{1/2}} \begin{pmatrix} V/E \\ 1 \end{pmatrix}. \quad (15)$$

The total density of states as a function of energy is now

$$N(E) = N_k \left| \frac{dE}{dk} \right|^{-1} A \left(1 + \frac{V^2}{E^2} \right). \quad (16)$$

From (15), the fraction of free-electron state belonging to a mixed state of energy E is $[1+(V/E)^2]^{-1}$. When this is multiplied by $N(E)$ to obtain the new density of S-P states per unit energy, the net answer is A, the unhybridized answer. In this simple model, hybridization changes the energy bands, the electron mass, and the total density of states, but not the S-P partial density of states. In reality the hybridization matrix element will not be constant, and the D bands will not be flat. S-P band structure effects are also enhanced by hybridization. It would be desirable to have a reliable absolute measure of $N_P(0)$ to eliminate the necessity for supposing $N_P(0)$ to be constant. One can only hope that the "noise" generated by the nonconstancy of $N_P(0)$ will not obscure the attempt at an over-all understanding.

The perturbation potential ∇U for a site of cubic symmetry transforms like x, y, z (Γ_4' in Bethe notation). Parity considerations then eliminate all contributions to $\langle \psi_k | \nabla U | \psi_{k'} \rangle$ from angular momentum components belonging to the same l for k and k'. The dominant part of U comes from a shifted, screened atomic potential. This potential for transition ions is strong near the core. As the distance from the atom center is increased, the bare potential decreases, and is partially screened by the d-wave functions, which, near the center of the cell, tend to move with the core. The screening is completed at a distance comparable to the size of the unit cell. The physics of the nature of ∇U might be described as a gradient of a spherical potential whose nature is chiefly determined by the number of "d" electrons on an atom, with modifications in the outer regions of the potential

depending somewhat on bonding. When, as within the transition elements and their alloys, the nature of the bonding and the volume per atom does not change, ∇U could be chiefly a property of the atomic species involved.

The simplest method of examining the nature of the average involved in evaluating λ in terms of ∇U is to sketch the calculation of the electronic specific heat. (With slightly more work, an equivalent identification can be made via superconductivity.) The change in free energy ΔF of the crystal at temperature T due to the lowest electron-phonon interaction diagram (in which one virtual phonon and electron-hole pair are excited) is

$$\Delta F = \mathcal{P}\left(\frac{\hbar}{2M\omega}\right)$$

$$\times \sum_{k,k'} \frac{|\langle k|\nabla U|k'\rangle|^2 f(E_k)[1-f(E_{k'})]}{E_k - E_{k'} - \hbar\omega_{\text{phonon}}}. \quad (17)$$

$f(E)$ is the Fermi function. In the low-temperature limit, ΔF is a constant plus a T^2 correction. This T^2 term produces a specific-heat contribution linear in temperature, so λ can be evaluated from the coefficient of this term.

It is necessary to do the sum in (17) only well enough to identify functional dependences. The T^2 term arises only from states k for which $|E_k - E_F| \sim KT$, and it is proportional to

$$\frac{1}{2M\omega^2} \sum_{\substack{k \\ |E_k - E_F|,\ |E_{k'} - E_F| < KT}} \sum_{k'} \left|\left\langle k \left|\frac{dU}{dx}\right| k'\right\rangle\right|^2, \quad (18)$$

or equivalently

$$\frac{1}{2M\omega^2}(KT)^2 4 \ \frac{1}{\Delta^2}_{\lim\Delta\to 0} \sum_{\substack{k \\ E_F < E_k}} \sum_{\substack{k' \\ E_k + \Delta\ E < _F E_{k'} < E_{k'} + \Delta}}$$

$$\times |\langle k|\varepsilon_z \cdot \nabla U|k'\rangle|^2. \quad (19)$$

Write the double sum on k and k' in an angular momentum representation about the atom in equation as

$$\sum_k \sum_{k'} \sum_{l,m} \sum_{l',m'} |\langle g_{lmk} Y_{lm}|\varepsilon_z \cdot \nabla U|g_{l'm'k'} K_{l'm'}\rangle|^2. \quad (20)$$

This matrix element vanishes unless $l = l' \pm 1$, because ∇U transforms like $P_1(\cos\theta)$ as the gradient of a spherical potential. Since U has appreciable value only within the unit cell, the radial integrations can be ended at the boundary r_{WS} of the Wigner-Seitz cell. For transition metals, the dominant wave functions in a unit cell are the D functions. These dominant functions couple only to P and F partial waves, of which in most transition metals (with possible exceptions of lanthanum and uranium) the angular momentum barrier will make the F-wave part small compared to the P-wave part.

The integrals over angles and sums on the three polarizations and m and m' yield an uninteresting multiplicative factor. The integrals and sums remaining yield

$$\frac{1}{\Delta^2}_{\lim\Delta\to 0} \sum_{\substack{k \\ E_F < E_k < E_F + \Delta}} \sum_{\substack{k' \\ E_F < E_k < E_F + \Delta}} \left|\int_0^{r_{\text{WS}}} r^2 g_{20k}^* \right.$$

$$\left. \times (\varepsilon_z \cdot \nabla U) g_{10k'} dr\right|^2. \quad (21)$$

The angular and radial form of g are determined by the energy and the atomic potential. The normalization of the g_{lmk} is k-dependent and more complicated. Multiply and divide (21) by

$$\int_0^{r_{\text{WS}}} r^2 |g_{20k}|^2 dr \int_0^{r_{\text{WS}}} r^2 |g_{10k'}|^2.$$

The factor

$$\left(\frac{dU}{dz}\right)^2 \equiv \left|\int_0^{r_{\text{WS}}} r^2 g_{20k}^*(\varepsilon_z \cdot \nabla U) g_{10k'} dr\right|^2 \bigg/$$

$$\int_0^{r_{\text{WS}}} r^2 |g_{20k}|^2 dr \int_0^{r_{\text{WS}}} r^2 |g_{10k'}|^2 dr \quad (22)$$

is the absolute square of a matrix element of the derivative of an atomic potential between two states which are normalized in an atomic volume. The form of the normalized wave functions is controlled by the atomic potential. This matrix element (22) should, like ∇U, be a property of the atomic species within the transition elements and their alloys, and is independent of k for wave vectors near the Fermi surface. Thus the sum (21) can be written

$$\left(\frac{dU}{dz}\right)^2 \left(\lim_{\Delta\to 0} \frac{1}{\Delta} \sum_{\substack{k \\ E_F < E_k < E_F + \Delta}} \int_0^{r_{\text{WS}}} r^2 |g_{10k}|^2 dr\right)$$

$$\times \left(\lim_{\Delta\to 0} \frac{1}{\Delta} \sum_{\substack{k \\ E_F < E_k < E_F + \Delta}} \int_0^{r_{\text{WS}}} r^2 |g_{20k}|^2 dr\right)$$

$$= \left(\frac{dU}{dz}\right)^2 N_P(0) N_D(0). \quad (23)$$

The total free energy at temperature T can now be written

$$F(T) - F(0) = -\tfrac{1}{3}\pi N(0)(KT)^2$$

$$- \frac{B(KT)^2}{M\omega^2}\left(\frac{dU}{dz}\right)^2 N_P(0) N_D(0), \quad (24)$$

where B is a dimensionless numerical constant involving neither phonon frequencies, nor band structure, nor the

form of ∇U. The coefficient of the T^2 term defines λ from the relation

$$F(T)-F(0)= -\tfrac{1}{3}\pi N(0)(KT)^2(1+\lambda). \qquad (25)$$

For convenience, the factor $(3B/\pi)$ will be absorbed into the definition of U.

For a single ion, the expression for the change in free energy is correct to order $(m/M)^{1/2}$, or more precisely, to the square root of a typical phonon frequency divided by the energy width of characteristic energy-band structure. The single-ion perturbation expansion will usually converge rapidly. The Green's-function theory[6] of strong electron-phonon interactions for our model is a theorem to the effect that the changes in free energy due to the vibrations of different atoms are additive.

The structure of this result is identical to the structure of the conventional result. A comparison of (5) and (25) leads to the immediate identification

$$\lambda=\frac{1}{M\omega^2}\Big(\frac{dU}{dz}\Big)^2\frac{N_P(0)N_D(0)}{N(0)}. \qquad (26)$$

This is identical in form with the usual result. In terms of the present parameters, the usual $\langle \mathcal{J}^2\rangle$ is given by

$$\langle \mathcal{J}^2\rangle=\Big(\frac{dU}{dz}\Big)^2\frac{N_P(0)N_D(0)}{N^2(0)}. \qquad (27)$$

The importance of (26) or (27) is twofold. First, *it is $(dU/dz)^2$, not $\langle \mathcal{J}^2\rangle$*, which can reasonably be expected to be a property of a single atom. Second, in the transition metals N_D is much larger than N_P. N_D is the quantity which shows the enormous variation with Fermi energy and atomic number, while N_P should be much more nearly constant. Using these two facts, we have

$$\Big(\frac{dU}{dz}\Big)^2\frac{N_P(0)N_D(0)}{N(0)}$$

$$=\Big(\frac{dU}{dz}\Big)^2 N_P\Big(\frac{N_D}{N_S+N_P+N_D\cdots}\Big)\approx\Big(\frac{dU}{dz}\Big)^2 N_P. \quad (28)$$

Therefore, the contribution to λ of a particular ion in (26) is a product of two factors, the first of which involves only a mean phonon stiffness and the second of which is chiefly a property of a single atom. The density of states $N(0)$ essentially disappears from the theory in the case of the transition metals.

If D-F scattering is also important, the theory will maintain the same structure. To the extent that the F density of states is a property of the atom, λ will still factor into a stiffness factor and an atomic term.

III. NUMEROLOGY

The results of the previous section can be summarized by writing the electron-phonon coupling parameter for transition metals [combining (26) and (28)] as

$$\lambda=\eta/A\langle\Theta^2\rangle. \qquad (29)$$

A is the atomic number, and $\langle\Theta^2\rangle$ is an average squared phonon frequency expressed in temperature units. $\langle\Theta^2\rangle$ should be understandable in short-range chemical terms once the bonding of the transition metals is understood. The parameter η is given in terms of more fundamental parameters by

$$\eta=\Big(\frac{1}{M_{\text{proton}}}\Big)\Big(\frac{\hbar}{K_{\text{Boltzmann}}}\Big)^2\Big(\frac{dU}{dz}\Big)^2 N_P(0) \qquad (30)$$

and should be predominantly a property of an atom. While it is undoubtedly true that the environment surrounding an atom in a crystal will somewhat effect η, the major dependence of η will be on the volume of the atom, which tends to remain constant if the nature of the binding is unchanged.

The first question to examine is whether η has a reasonably systematic behavior in the transition metals. Being interested primarily in high-temperature superconductors, we will follow McMillan's treatment[5] of the Coulomb pseudopotential, and thus use his expression

$$T_c=\langle\Theta^2\rangle^{1/2}\exp\Big(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\Big) \qquad (31)$$

for the transition temperature. The systematic results are not particularly sensitive to the Coulomb term μ^*, but the approximation limits consideration to transition metals which are not too magnetic.

For V, Nb, Mo, Ta, and W, McMillan's values of $\langle\Theta^2\rangle$ will be used. These substances also have known specific heats as a function of temperature[7] from which an average phonon frequency $\bar\Theta$ was determined by using the point at which the specific heat achieves half its classical value to define a $\bar\Theta$ such that a Debye specific heat had the measured values. This value of $\bar\Theta$ is approximately 1.25 times $\langle\Theta^2\rangle^{1/2}$, and this factor 1.25 was used to generate $\langle\Theta^2\rangle^{1/2}$ in the transition elements not examined by McMillan. The values of λ calculated from (31) $\langle\Theta^2\rangle^{1/2}$, the Debye temperature Θ_D, and η are given in Table I, along with the conventional $\langle\mathcal{J}^2\rangle$. The variation of η in the Periodic Table is indeed simple, and does not show the erratic behavior of $\langle\mathcal{J}^2\rangle$. The systematics of η and $\langle\mathcal{J}^2\rangle$ can be compared at a glance in Table II. That η, not $\langle\mathcal{J}^2\rangle$, was relatively simple was empirically noted by McMillan[5] for the five body-centered elements (V, Nb, Mo, Ta, W), for he pointed out that $\langle\mathcal{J}^2\rangle N(0)$ was approximately constant for these five, and η is proportional to $\langle\mathcal{J}^2\rangle N(0)$. Table II shows

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[7] The specific heats of all the transition metals except niobium were taken from Landolt-Bornstein, *Zahlannwerte und Funktionen* (Springer-Verlag, Berlin, 1961), part 4, pp. 476–479. The values for niobium were taken from J. E. Kunzler (unpublished). When corrections for the electronic specific heat were appreciable (e.g., in vanadium) only half the phonon enhancement was included.

TABLE I. Values of the various parameters of relevance to the transition temperatures of the elements. Values of Θ are from Ref. 5.

Element	$\langle\theta^2\rangle^{1/2}$ (°K)	Θ_D (°K)	λ	$\eta(10^{-6})$ [(K°)²]	$\langle\mathscr{I}^2\rangle$ [(eV/Å)²]
Ti	284	425	0.380	1.468	5.1
V	290	399	0.591	2.530	3.4
Zr	202	290	0.412	1.533	6.5
Nb	230	277	0.761	3.740	7.3
Mo	310	460	0.418	3.852	24.6
Hf	156	252	0.346	1.503	7.9
Ta	170	258	0.657	3.435	7.9
W	250	390	0.291	3.345	40.0
Re	218	415	0.489	4.327	23.3

TABLE III. Comparison of the calculated and observed transition temperatures of Ti-Zr alloys.

Alloy % Ti	% Zr	Θ_D (°K)	T_c calculated (°K)	T_c observed (°K)
100	0	425	(0.40)	0.40
75	25	327	2.27	1.18
50	50	301	2.04	1.50
25	75	295	1.10	1.20
0	100	290	(0.55)	0.55

that the behavior of η in the Periodic Table follows the same kind of smooth systematics that other physical parameters follow.

The next question of interest is whether η is approximately environment-independent in simple alloys. In most alloys, full specific-heat curves have not been measured, but instead only low-temperature Debye temperatures have been determined. For the elements, the ratio between Θ_D and $\langle\theta^2\rangle^{1/2}$ is known. This ratio changes relatively little, with the exception of rhenium, and this ratio is linearly interpolated in alloys to generate $\langle\theta^2\rangle^{1/2}$ from the measured Θ_D for alloys. The mass M used is the average mass, chosen because the low-temperature Debye specific heat measures the average mass density. It has occasionally been necessary to make systematic small shifts of alloy Debye temperatures when the experimenter found alloy data smooth and consistent with his own values of the elemental endpoints, but his endpoint values were not consistent with present best values. This is a correction for experimental systematic error. With these suppositions, T_c can be calculated for alloys from the data for elements (Table I), and the measured low-temperature Debye temperature of these alloys. (An understanding of bonding in transition metals would yield values of Θ_D for alloys and eliminate the necessity of any alloy measurements for the prediction of T_c.) As long as the fraction of D electrons at the Fermi surface on each alloy atom is the same, η can be linearly interpolated between the alloy endpoints. Table III shows a comparison between the computed transition temperatures

in Ti-Zr alloys and the measured transition temperatures.[8] The only alloy measurements which go into this prediction of T_c for the alloys are the Debye temperatures. Agreement is far from perfect, but for a theoretical estimate of the behavior of the transition temperature, it is not bad. (The experimental measurements and metallurgy are also not necessarily perfect.) The end points of this alloy sequence agree by definition, for they were used to establish η for the elements.

Some results for Zr-Nb alloys are shown in Table IV. Agreement here is rather good,[9] particularly in view of the fact that the alloys are bcc, while the evaluation of η for Zr was for the hexagonal structure of the element. Zr-Rh alloys are not capable of simple theoretical interpretation, for the Fermi-surface D electrons in an alloy having such different atoms will not be equally shared between the atoms. One can, however, plot the apparent η determined from the measured T_c to observe its dependence on concentration. The numbers relevant to such a calculation[10] in Zr-Rh are given in Table V, and the plot of η versus alloy concentration for Zr-Nb and Zr-Rh is given in Fig. 1. That the Zr-Nb alloys fall on a straight line connecting Zr and Nb was evident already from the agreement between the observed and calculated T_c. The striking feature of this graph is the difference between Nb and Rh. In spite of the fact that the addition of a little rhodium to zirconium raises the transition temperature immensely (Table V), as does the addition of niobium, Fig. 1 clearly suggests that pure Rh is a poor candidate for superconductivity. Indeed, Rh is not a superconductor. The absence of superconductivity in Rh is caused by the large Coulomb

TABLE II. Variation of $\eta(10^{-6})$ and $\langle\mathscr{I}^2\rangle$ arranged according to the Periodic Table. The values are from Table I. The upper values are η, the lower values (in parentheses) are for $\langle\mathscr{I}^2\rangle$.

Ti	V	Cr	Mη
1.47	2.53	...	...
(5.1)	(3.4)	...	...
Zr	Nb	Mo	Tc
1.53	3.74	3.85	...
(6.5)	(7.3)	(24.6)	...
Hf	Ta	W	Re
1.50	3.44	3.35	4.33
(7.9)	(7.9)	(40.0)	(23.3)

TABLE IV. Comparison of calculated and observed transition temperatures for Zr-Nb alloys.

Alloy % Zr	% Nb	Θ_D (°K)	T_c calculated (°K)	T_c observed (°K)
100	0	290	(0.55)	0.55
50	50	238	9.9	9.3
25	75	246	11.6	10.8
0	100	277	(9.22)	9.22

[8] E. Bucher, F. Heiniger, J. Muheim, and J. Muller, Rev. Mod. Phys. 36, 146 (1964). The values of Θ_D necessary to compute T_c were also taken from this paper.
[9] Experimental numbers for this alloy system are from F. Heiniger, E. Bucher, and J. Muller, Physik Kondensierten Materie 5, 243 (1966).
[10] G. Dummer, Z. Physik 186, 249 (1965).

TABLE V. Transition temperatures and Θ_D for Zr-Rh alloys.

Alloy	% Rh	0	3	4	5	6	7
T_c (°K)			0.55	3.1	3.8	4.8	5.7	5.9
Θ_D (°K)			290	244	226	210	196	192

interactions.[11] Since we have not allowed each atom to have its own Coulomb interaction, the plot of Fig. 1 represents the large Coulomb interactions in Rh as negative η for that element. This plot, however, suggests the failure of a rigid-band picture, and indicates that Rh is already showing large Coulomb interactions when present in small concentrations in bcc Zr alloys. The fact that Zr is hexagonal and all the other alloys shown bcc causes no obvious systematic error.

Calculated and measured[12] transition temperatures for Nb-Mo alloys are shown in Table VI. Agreement is not ideal, but quite tolerable for the larger T_c. Of particular relevance to the lack of complete agreement are the facts that (a) very low transition temperatures are a delicate enough balance between Coulomb and electron-phonon effects that they are harder to predict and (b) the density of states in this alloy sequence plunges to such a low value in the 60–90% Mo range that the justification for regarding N_D as large compared to N_P is lacking.

The systematics of the $5d$ transition-metal alloys[13] between hafnium, tantalum, and tungsten shown in Table VII are in reasonable accord with theory. The behavior is very similar to that of the analogous $4d$ alloys, with a shift of minimum transition temperature from the interior of the sequence to the terminal member tungsten. It would be interesting to see whether the monotonic trend predicted by theory exists in experiment.

Insufficient data exists to analyze the behavior of the $3d$ elements. The Debye temperatures are not known

TABLE VI. Comparison of calculated and observed transition temperatures in the Nb-Mo system.

Alloy	% Nb	% Mo	Θ_D (°K)	T_c calculated (°K)	T_c observed (°K)
	100	0	277	(9.22)	9.22
	85	15	312	5.9	5.85
	60	40	371	2.4	0.60
	40	60	429	0.7	0.05
	30	70	442	0.6	0.02
	20	80	461	0.4	0.09
	10	90	487	0.3	0.03
	0	100	460	(0.92)	0.92

[11] J. R. Schrieffer and N. F. Berk, Phys. Rev. Letters **17**, 433 (1966); and in *Proceedings of the Tenth International Conference on Low-Temperature Physics*, edited by M. P. Malkov (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967), Vol. IIA, p. 150.

[12] Values of Θ and T_c from B. W. Veal and J. K. Hulm, Ann. Acad. Sci. Fennicae **A210**, 108 (1966).

[13] Values of Θ and T_c from E. F. Bucher, F. Heiniger, and J. Muller, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio*, edited by J. G. Daunt et al. (Plenum Press, Inc., New York, 1965), p. 1095.
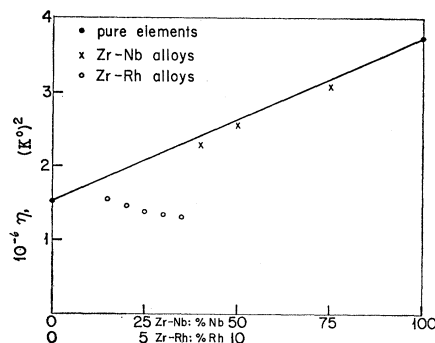

FIG. 1. Values of η for Zr-Nb and Zr-Rh alloys. The theory interpolates the values for Zr-Nb alloys on the straight line drawn connecting the elements at the end points.

for the Vi-V alloys. Since T_c follows[14] the same pattern as Zr-Nb, the expected similarity in trends in Θ_D between $3d$ and $4d$ elements suggests that Ti-V alloys will indeed be easily described by present theory. In the V-Cr alloys,[15] the parameter η is not known for Cr because chromium is magnetic rather than superconducting. A small systematic calibration error in Θ_D also seems likely here, since the very systematic alloy data behavior of Θ_D given by one author does not extrapolate to the "best value" for pure vanadium given by others. If η for Cr is about the same as η for V, expected on the basis of the $4d$ and $5d$ elements, the rapid drop in T_c as Cr is added to V will be understandable in terms of the rapid rise in Θ_D, just as in the 4-d and 5-d sequences.

The behavior of rhenium and its alloys with tungsten and molybdenum is difficult to evaluate. Rhenium (hcp) has a rather different lattice vibration spectrum from that of the other elements discussed so far. Its low-temperature Debye temperature is about 30% higher than would be expected from its high-temperature Debye temperature, as compared to other transition metals. A major question which this large difference introduces is how the low-temperature Θ_D for alloys (particularly those with crystal structures other than hcp), should be scaled to obtain $\langle \Theta^2 \rangle$. Seeing no resolu-

TABLE VII. Comparison of calculated and observed transition temperatures in the Hf-Ta-W system.

Alloy	Θ_D (°K)	T calculated (°K)	T_c observed (°K)
100% Hf	252	(0.09)	0.09
30-70 Hf-Ta	209	4.2	6.8
100% Ta	258	(4.48)	4.48
84-16 Ta-W	265	3.8	1.8
60-40 Ta-W	291	2.0	
40-60 Ta-W	317	0.85	Not investigated
20-80 Ta-W	354	0.16	below 1.2°K
100% W	390	(0.012)	0.012

[14] C. H. Cheng, K. P. Gupta, E. C. van Reuth, and P. A. Beck, Phys. Rev. **127**, 2030 (1962).

[15] Data on T_c and Θ_D are given in Ref. 5, quoting K. Andres and E. Bucher (private communication).

tion to this problem, we have presented η for the Mo-Re [16] and W-Re [13,17] systems using a universal factor $\langle\theta^2\rangle^{1/2} = 0.675\Theta_D$ in Fig. 2. Data on technicium (whose Debye temperature is only approximately known[18]) and on[16] $Mo_{0.50}Tc_{0.50}$ are also shown. The difference between the pure Tc and pure Re points would be completely explained if Re alone, and not Tc, has an anomalously high low-temperature Debye temperature. The three points Mo:$Mo_{0.50}Tc_{0.50}$:Tc lie on a straight line as expected, though with the sparseness of data little weight should be attached to this fact. The values for η in Mo-Re and Tc-Re agree with each other within experimental error in the bcc phase region (below 30% Re). Such agreement is easy to understand if Re carries both its own η and its unique bonding effect on lattice frequencies into the two hosts. With the change in crystal structure, this sytem drops back to the straight-line interpolation between the end points. Further high-temperature specific-heat measurements will be necessary to determine whether this system follows or contains exceptions to the proposed interpolation.

Finally, let us examine the systematics of some β-tungsten compounds of vanadium and niobium. In the β-tungsten structure of V_3Si and Nb_3Sn, both the volume per transition-metal ion and the nearest-neighbor transition-metal distance have decreased by about 15% from the values of the bcc pure metals. A change of η from the pure metals is therefore to be expected. While the theory of Sec. II was not designed for compounds, its application to systems such as V_3X can be justified if it can be argued that almost all of the Fermi-surface density of states is associated with the V atom. Such an association might be possible when the material has a very high electronic density of states, but the atom X has no D levels near the Fermi energy.
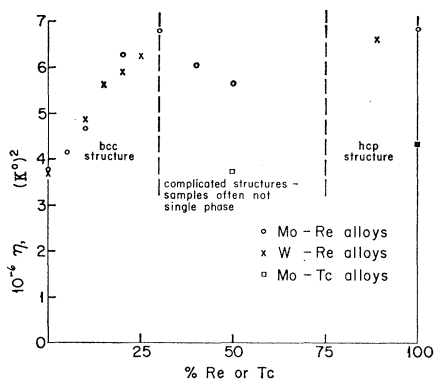

FIG. 2. Values of η for W-Re, Mo-Re, and Mo-Tc alloys. These values were all calculated using $\langle\theta^2\rangle^{1/2} = 0.075\Theta_D$ (see text) and should not be directly compared with values quoted in other tables.

[16] F. J. Morin and J. P. Maita, Phys. Rev. **129**, 115 (1963).

[17] Values of T_c from Ref. 5, E. Bucher (private communication).

[18] The Debye temperature of 375°K for technicium was supplied by B. T. Matthias (private communication).

TABLE VIII. Parameters for V_3X compounds and calculated transition temperatures obtained from these parameters.

Compound	Θ_D (°K)	$\langle\theta^2\rangle^{1/2}$ (°K)	λ calculated	T_c calculated (°K)	T_c observed (°K)	$N(0)$
V_3Si	330	343	0.845	17.6	17.1	2.09
V_3Ge	405	421	0.451	2.1	6.0	1.06
V_3Ga	310	322	0.776	13.5	16.5	2.84
V_3Au	350	364	0.390	0.7	0.7	1.40

The general character of the lattice vibration spectrum will also be changed. As long as the distribution of lattice frequencies was approximately fixed, any measure of the lattice vibration frequencies was adequate. With two atoms per unit cell of different masses and chemical natures, different measures of lattice frequencies will not scale together, a point which we must simply ignore at our present state of knowledge.

To make intercomparisons of various β-tungsten materials, it has been necessary to characterize the phonon spectrum by the one commonly measured experimental quantity Θ_D. The full specific-heat curves have been measured[19] for Nb_3Sn and V_3Si. For Nb_3Sn, the low-temperature Debye temperature[20] is 228°K and the high-temperature $\bar{\Theta}$ (obtained from the measured specific heat by subtracting an extrapolated electronic contribution) is 304°K. For V_3Si, equivalent numbers are 330 and 485°K. The ratios of these temperatures are 0.75 and 0.68, and the difference between these two ratios is a measure of the error attributable to regarding the materials as having a common frequency spectrum. These differences are comparable to those present in the pure elements, and the full specific-heat curves for all the compounds would be necessary to resolve the problem. It will here be assumed that for V_3X compounds $\langle\theta^2\rangle^{1/2}$ is $0.707\bar{\Theta} = 1.04\Theta_D$. Table VIII shows calculations of the transition temperatures of V_3X materials based on this supposition, $\mu^* = 0.13$, and an assumed η for vanadium in V_3X of 4.49. This value of η is 1.77 times the value for η in the pure element. The last column shows the electronic density of states at the Fermi level for these materials.[9] Note that the present calculation describes correctly the order and approximate magnitudes of T_c, while if the electronic density-of-states factors were the important consideration, two pairs would be reversed. If the same factor 1.77 is used to scale the bcc value of η for niobium to the β-tungsten values, the transition temperatures of Nb_3X compounds can be calculated from their specific heats. The calculated temperature for Nb_3Sn based on its $\langle\Theta^2\rangle^{1/2}$ of 243°K is 21°K. The measured transition temperature is 18.0°K.

The complexities of the phonon modes and distributions in materials having several atoms of quite different masses per unit cell should keep one from literally

[19] J. E. Kunzler (private communication).

[20] L. J. Vielund and A. W. Wicklund, Phys. Rev. **166**, 424 (1968).

believing the theoretical estimates even if the basic theory were perfect. (Similar considerations prevent a useful analysis of systems like Ti-Hf alloys.) These results do suggest, however, that the systematics of superconductivity in the β-tungsten structure appears favorable to superconductivity, for typical transition elements exhibit in this structure about a factor of 1.8 increase in η over the values for close-packed or bcc structures.

IV. CONCLUSION

By using a local representation of phonons and an angular momentum description of Bloch waves, it has been possible to characterize the strength of the electron-phonon interaction in transition metals by two parameters of a short-range or chemical nature. One of these parameters, the mean vibrational frequency, is a characteristic of the bonding; the other is an atomic property expected to be weakly environment-dependent within a given type of bonding. The theory described is another in a line of theoretical and empirical attempts to understand the systematics of super-conductivity in transition metals.[4,5] Because at present the calculation of η *ab initio* is difficult, the theory can be tested only by examining its agreement with experiment. The most useful additional experimental information would be determinations of the specific heats of alloys at intermediate temperatures to provide a better estimate of the mean vibrational frequency. The number of additional systems to which the theory might be hoped to apply directly is circumscribed by the present necessity of presuming only one vibrational frequency and an equal partitioning of Fermi-surface electrons between all transition-metal ions.

In order that the Coulomb interaction not be the dominant problem in determining T_c, it has been necessary to restrict attention to only half the transition metals. Use of isotope effect information would extend the range of the theory to include a variation of the Coulomb pseudopotential. In this regard, the large Coulomb interaction of rhodium when present in small concentrations in zirconium is particularly interesting.

A major difference between the present attempt at systematization in the transition metals and past attempts is the use of the angular momentum repre-

sentation to argue that $N(0)$ is *not* the major parameter of interest. It is the trends of vibrational frequencies which are of theoretical interest, a point already empirically noted. The correlation between mean vibrational frequencies and the mean density of states at the Fermi energy is quite strong, which makes it difficult to demonstrate definitely the relative irrelevance of $N(0)$. The transition temperatures of V_3X compounds do exhibit features which are inexplicable as $N(0)$ effects and explicable in present theory, but the application of present theory to these compounds requires a good bit of faith. The general correlations between super-conductivity[21] and hardness or melting point[22] become qualitatively understandable if $N(0)$ is irrelevant, but again do not prove this irrelevance. It is perhaps worth noting that because Coulomb interactions of the type $(D+D \rightarrow D+D)$ take place, a high N_D can increase Coulomb interactions with no compensating change in the electron-phonon interaction.

A second possible comparison of theory with experiment is through experimental details of the electron-phonon interaction. The present structure of theory indicates that those parts of the Fermi surface which are characterized by being chiefly S-P in character will have abnormally *short* relaxation times. Since such parts also can be expected to have light masses compared to the average mass, the frequency dependence of the electrical conductivity (in the dc to near infrared range) can provide some check of the theory. The anisotropy of the superconducting energy gap, in conjunction with calculated energy bands and wave functions, can similarly be used to check the importance of P-D scattering.

ACKNOWLEDGMENTS

[21] B. T. Matthias, Phys. Letters **25A**, 226 (1967).
[22] B. T. Matthias, W. H. Zachariesen, G. W. Webb, and J. J. Engelhardt, Phys. Rev. Letters **18**, 781 (1967).