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Electronic Structure of Transition Metals. II. Phonon Spectra*

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The use of the new transition-metal model potential (TMMP), developed in the preceding paper, in nearly-free-electron second-order perturbation theory of the electronic structure and properties, in particular the phonon spectra, of the transition metals is discussed. It is pointed out that, as a consequence of the strong nonlocality ($\mathcal{E}$ dependence) of the TMMP parameter, $A_2(\mathcal{E}) \propto (\mathcal{E} - \mathcal{E}_d)^{-1}$ near the position $\mathcal{E}_d$ of the d-band resonance, first-order (nearly-free-electron) perturbation theory involving the *diagonal* matrix element $\langle\vec{k}|V|\vec{k}\rangle$ of the TMMP breaks down at $\mathcal{E}_{\vec{k}} = \mathcal{E}_d$ and hence describes s-d hybridization, but second-order terms involving the *off-diagonal* matrix elements $|\langle\vec{k}|V|\vec{k}+\vec{q}\rangle|^2 \equiv |V(q)|^2$ are off resonance, i.e., $\mathcal{E}_{\vec{k}+\vec{q}} \neq \mathcal{E}_d$, and therefore small. Thus electron-phonon-interaction matrix elements, proportional to $V(q)$ in the diffraction model, can be small in the transition metals. On the basis of this property of the TMMP perturbation method, systematic trends in the lattice dynamics of simple and transition metals of the $3d$, $4d$, and $5d$ series in the Periodic Table are compared in the jellium model, and first-principles calculation of the phonon spectra of ten transition metals—Cu, Ag, Ni, Pd, Fe, Cr, Mo, W, Nb, and Ta—are performed in local TMMP approximation. The theory provides a sound basis for quantitative understanding of the lattice dynamics of these metals, and agreement with the observed phonon spectra is quite good.

I. INTRODUCTION

In the preceding paper,[1] the quantum-defect concept was extended to the transition metals and used to set up a transition-metal model potential (TMMP of the Heine-Abarenkov type[2,3] for 30 group-B (excepting the rare-earth) metals. As is well known,[4] a model-potential form factor $V(q)$ represents the Fourier transform of the effective electron-ion potential in a crystal, and in the diffraction model,[5] $V(q)$ is proportional to the electron-phonon interaction matrix element corresponding to a phonon state of wave vector $\vec{q}$. Consequently, $V(q)$ determines not only the electronic energy bands[6] of the perfect crystal but also the electronic contribution to the dynamical matrix for phonon spectrum[5,7] the electrical resistivity and thermoelectric power of the solid or liquid metal,[8] the transition temperature for superconductivity,[9] and many other aspects of the electronic structure and properties of metals. Of all these properties, the phonon spectrum is the most sensitive to the details of $V(q)$, inasmuch as it samples $|V(q)|^2$ throughout $\vec{q}$ space.

In view of this fact, we proceed in this paper to apply the TMMP method presented in the preceding paper to first-principles calculation of the phonon spectra of the following ten transition metals—Cu,[10] Ag,[11] Ni,[12] Pd,[13] Fe,[14] Cr,[15] Mo,[16] W,[17] Nb,[16] and Ta[18]—which have been measured by various workers.[10–18] The underlying assumption we make here is that the electronic contribution to the dynamical matrix can be calculated by means of *second-order perturbation theory* in $V(q)$ and the Hartree or Hartree-Fock *self-consistent field approximation*, in the manner previously reported by Animalu *et al.*[19] for the simple (nearly-free-electron) metals.

As a justification for this assumption, it should be pointed out that, as a consequence of the strong nonlocality ($\mathcal{E}$ dependence) of the TMMP parameter $[A_2(\mathcal{E}) \propto (\mathcal{E} - \mathcal{E}_d)^{-1}$ near the position $\mathcal{E}_d$ of the d-band resonance],[20] such a TMMP perturbation method breaks down in the *first order*, but the *second-order* terms which determine the electronic contribution to the phonon spectrum are small. For, in such a (nearly-free-electron) perturbation series:

$$\mathcal{E}_{\vec{k}} = T_{\vec{k}} + \langle\vec{k}|V|\vec{k}\rangle + \sum_{q\neq 0} |V(q)|^2/(T_{\vec{k}} - T_{\vec{k}+\vec{q}}), \qquad (T_{\vec{k}} \equiv \hbar^2 k^2/2m) ,$$

the *diagonal* matrix element $\langle\vec{k}|V|\vec{k}\rangle$ and the *off-diagonal* matrix elements $\langle\vec{k}|V|\vec{k}+\vec{q}\rangle \equiv V(q)$ are of the following orders of magnitude near $\mathcal{E}_d$:

$$\begin{aligned} &\langle\vec{k}|V|\vec{k}\rangle \approx C(\vec{k},\vec{k})/(\mathcal{E}_{\vec{k}} - \mathcal{E}_d) ; \\ &\langle\vec{k}|V|\vec{k}+\vec{q}\rangle \approx C(\vec{k},\vec{k}+\vec{q})/(\mathcal{E}_{\vec{k}+\vec{q}} - \mathcal{E}_d) , \end{aligned} \tag{1}$$

where V acts to the right. Thus, the former can be *on resonance* at $\mathcal{E}_{\vec{k}} = \mathcal{E}_d$, and therefore large, while the latter is *off resonance* ($\mathcal{E}_{\vec{k}+\vec{q}} \neq \mathcal{E}_d$) and therefore small. Consequently, s-d hybridization is described by first-order TMMP perturbation theory; The equation

$$\mathcal{E}_k \approx T_{\vec{k}} + \langle\vec{k}|V|\vec{k}\rangle ,$$

reduces, by virtue of Eq. (1), to the usual equation[21]:

$$(\mathcal{E}_{\vec{k}} - T_{\vec{k}})(\mathcal{E}_{\vec{k}} - \mathcal{E}_d) \approx C(\vec{k},\vec{k}) . \tag{2}$$

It should be cautioned, however, that V is non-Hermitian and hence $|V(q)|^2$ in the second-order term is really $\langle\vec{k}|V|\vec{k}+\vec{q}\rangle\langle\vec{k}+\vec{q}|V|\vec{k}\rangle^*$, rather than simply $|\langle\vec{k}|V|\vec{k}+\vec{q}\rangle|^2$: the smallness of $V(q)$ will therefore make sense only if $V(q)$ is evaluated at a fixed off-resonance energy, e.g., in a local TMMP approximation with $\mathcal{E}=\mathcal{E}_F$ (the Fermi energy). This consideration is the essence of the TMMP perturbation method and the motivation in Ref. 1 for using local TMMP approximation to calculate the off-resonance, off-diagonal matrix elements $\langle\vec{k}|V|\vec{k}+\vec{q}\rangle$ defining the TMMP form factor $V(q)$.

The outline of this paper is as follows. In Sec. II, systematic trends in the lattice dynamics of simple and transition metals of the 3*d*, 4*d*, and 5*d* series will be compared in the jellium model. The phonon-dispersion relation in local TMMP approximation will be described in Sec. III; and numerical calculation of the phonon spectra of the ten transition metals listed above will be presented and discussed in Sec. IV. Conclusions will be drawn in Sec. V.

II. COMPARISON OF SIMPLE AND TRANSITION METALS IN THE JELLIUM MODEL

In this section, *systematic trends* in the lattice dynamics of simple and transition metals of the 3*d*, 4*d*, and 5*d* series will be *compared* in the simplest possible (albeit realistic) approximation provided by the jellium model. The motivation for this comparison is to shed some light on the effective *chemical valence* (z) of the transition metals, which determines the number of electrons that may be treated as "nearly free" in the sense of random-phase-approximation (RPA) dielectric formulation of dynamical screening in lattice dynamics.[7]

The basis of the comparison is provided by the usual sum rule connecting the longitudinal and transverse phonon frequencies in the so-called Coulomb lattice, i.e., a lattice of ions of chemical valence z interacting via long-range Coulomb potential, $(ze)^2/R$, between pairs at separation R. The sum rule is

$$\sum_s (\omega_{qs}^c)^2=\omega_p^2\ , \qquad (3)$$

where s is the longitudinal or transverse polarization-mode index and

$$\omega_p=[4\pi(ze)^2/M\Omega]^{1/2} \qquad (4)$$

is the ion-plasma frequency, Ω being the atomic volume and M the mass of the ion. Equation (3) asserts that if the frequencies are sheared equally between the three polarization modes (in the manner of Einstein's model), then the mean (Einstein) frequency, ω_E, of the Coulomb lattice is

$$\omega_E=\omega_p/\sqrt{3}\ . \qquad (5)$$

To interpret this result, physically, we compare the Einstein temperature of such a lattice, $\Theta_E=\hbar\omega_E/k_B$, with the Debye temperature (Θ_D) for three simple metals of the 3*d*, 4*d*, and 5*d* series: $\Theta_E=277$, 165, and 125 °K for Ca, Sr, and Ba, respectively, while Θ_D (experimental)$=230$, 147, and 110 °K. The differences are small, and (as expected) $\Theta_E\gtrsim\Theta_D$. The Debye temperature is a measure of the mean interatomic force (including the contribution from electron-dielectric screening) while the Einstein temperature is a measure of the "bare" (Coulombic) interatomic force. Accordingly, one can hope to improve on the agreement between the theoretical estimate of the lattice temperature (Θ_E) and the experimental lattice temperature (Θ_D) by screening the ions.

We proceed therefore to consider a new (jellium) temperature, Θ_J, defined as follows. In a jellium model, one disregards the lattice and therefore the jellium frequency which is purely longitudinal becomes $\omega_p/(\epsilon(q))^{1/2}$, where $\epsilon(q)$ is the dielectric function of the free-electron gas screening the ions. Accordingly, in a real lattice it is reasonable to suppose that the analog of Eq. (3), which leads to a Debye-like spectrum for small q, will be obtained by replacing the right-hand side of Eq. (3) by $\omega_p^2/\epsilon(q)$. If we again shear the maximum jellium frequency equally between the three modes of polarization, then we will be led to define the jellium temperature:

$$\Theta_J=\hbar\omega_p/k_B(3\epsilon(q_D))^{1/2}\ , \qquad (6)$$

where $q_D=(6\pi^2/\Omega)^{1/3}$ is the Debye wave number. Like Θ_E, this can be calculated theoretically from the physical constants of the metal displayed in Table I below. The dependence of Θ_J on the chemical valence z along an isoelectronic sequence, i.e., elements characterized by the same inert-gas core in the periodic table, is displayed graphically in Figs. 1(a)-1(c) and compared with the experimental Θ_D.

From the remarkable agreement between Θ_J and Θ_D for the transition metals of the 4*d* and 5*d* series, we arrive at the surprising conclusion that the jellium model is better for the transition metals than for the simple metals of these series. The fact that Θ_J versus z is *linear* has implications for the systematics of the superconducting transition temperature (T_c) for amorphous transition-metal alloys,[22] which we shall discuss in a later publication of this series.

III. LATTICE DYNAMICS IN LOCAL TMMP APPROXIMATION

We now turn to the lattice dynamics of the transition metals in local TMMP approximation. The ten transition metals chosen for this study have fcc or bcc Bravais lattices (with one atom per unit cell). Thus in the framework of the Born-Oppenheimer

TABLE I. Parameters of the jellium model. ρ is the mass density in g/cm^3 [from C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971) p. 39]; $2\pi\nu_p = [4\pi(ze)^2/M\Omega]^{1/2}$ defines the ion-plasma frequency, ν_p (in 10^{12} Hz); $k_F = (3\pi^2 z/\Omega)^{1/3}$ (a.u.) is the free-electron Fermi wave number; $q_D = (6\pi^2/\Omega)^{1/3}$ is the Debye wave number; $\epsilon(q)$ is the Hartree dielectric function (with modification for Hubbard-Sham exchange) defined by Eq. (A7) of Ref. 1 with $e^* = e$; Θ_J is the jellium temperature (in °K) defined by Eq. (6); and $V(q_D)$ (in Ry) is the screened TMMP form factor (Appendix A of Ref. 1) evaluated at q_D, which is included here for comparison of the strength of electron-phonon interaction in simple and transition metals: It may be verified that $V(q_D)$ vs z is linear along an isoelectronic sequence (cf Θ_J vs z in Fig. 1).

	ρ	ν_p	k_F	$q_D/2k_F$	$\epsilon(q_D)$	Θ_J	$V(q_D)$
K^{+}	0.91	3.955	0.395	0.630	2.409	70.6	−0.039
Ca^{2+}	1.53	10.006	0.587	0.500	2.659	170.0	−0.090
Sc^{3+}	2.99	18.678	0.807	0.437	2.641	318.4	−0.256
Ti^{4+}	4.51	28.747	0.998	0.397	2.649	489.4	−0.387
V^{5+}	6.09	39.189	1.164	0.368	2.672	664.2	−0.521
Cr^{3+}	7.19	25.211	1.033	0.437	2.266	464.0	−0.316
Mn^{2+}	7.47	16.228	0.898	0.500	2.055	313.6	−0.188
Fe^{3+}	7.87	24.339	1.036	0.437	2.262	448.3	−0.300
Co^{2+}	8.90	16.256	0.925	0.500	2.022	316.7	−0.220
Ni^{2+}	8.91	16.534	0.930	0.500	2.016	322.6	−0.220
Cu^{+}	8.93	7.655	0.720	0.630	1.735	161.0	−0.028
Zn^{2+}	7.13	13.337	0.834	0.500	2.140	252.6	−0.206
Ga^{3+}	5.91	17.057	0.878	0.437	2.503	298.7	−0.269
Ge^{4+}	5.32	20.749	0.921	0.397	2.795	343.9	−0.327
As^{5+}	5.77	26.037	1.006	0.368	2.945	420.4	−0.403
Se^{6+}	4.81	27.361	0.993	0.347	3.269	419.3	−0.433
Rb^{+}	1.629	2.421	0.369	0.630	2.515	42.3	−0.036
Sr^{2+}	2.58	5.948	0.538	0.500	2.819	98.1	−0.074
Y^{3+}	4.48	11.539	0.736	0.437	2.810	190.7	−0.166
Zr^{4+}	6.51	18.136	0.910	0.397	2.816	299.4	−0.229
Nb^{5+}	8.58	25.559	1.069	0.368	2.827	421.1	−0.312
Mo^{6+}	10.22	32.310	1.190	0.347	2.880	527.5	−0.407
Tc^{7+}	11.50	38.850	1.290	0.329	2.944	627.3	−0.463
Ru^{4+}	12.36	22.486	1.088	0.397	2.507	393.5	−0.229
Rh^{3+}	12.42	16.696	0.986	0.437	2.329	303.1	−0.160
Pd^{2+}	12.00	10.560	0.842	0.500	2.129	200.5	−0.164
Ag^{+}	10.50	4.857	0.635	0.630	1.840	99.2	−0.024
Cd^{2+}	8.65	8.529	0.742	0.500	2.291	156.1	−0.185
In^{3+}	7.29	11.512	0.797	0.437	2.633	195.4	−0.226
Sn^{4+}	5.76	16.678	0.867	0.397	2.910	270.9	−0.280
Sb^{5+}	6.69	17.211	0.899	0.368	3.188	267.0	−0.324
Te^{6+}	6.25	19.160	0.921	0.347	3.453	285.7	−0.364
Cs^{+}	1.997	1.724	0.341	0.630	2.652	29.3	−0.031
Ba^{2+}	3.59	4.520	0.519	0.500	2.891	73.7	−0.055
La^{3+}	6.17	8.698	0.706	0.437	2.890	141.7	−0.175
Hf^{4+}	13.20	13.313	0.924	0.397	2.788	220.9	−0.247
Ta^{5+}	16.66	18.342	1.069	0.368	2.827	302.2	−0.319
W^{6+}	19.25	23.322	1.186	0.347	2.886	380.3	−0.396
Re^{7+}	21.03	27.919	1.278	0.329	2.963	449.3	−0.482
Os^{4+}	22.58	16.127	1.077	0.397	2.523	281.3	−0.257
Ir^{4+}	22.55	16.020	1.074	0.397	2.527	279.2	−0.256
Pt^{2+}	21.47	7.716	0.835	0.500	2.138	146.2	−0.240
Au^{+}	19.28	3.609	0.637	0.630	1.838	73.8	−0.032
Hg^{2+}	14.26	6.096	0.721	0.500	2.331	110.6	−0.206
Tl^{3+}	11.87	8.250	0.774	0.437	2.716	138.7	−0.236
Pb^{4+}	11.34	10.607	0.835	0.397	2.988	170.0	−0.273
Bi^{5+}	9.80	12.117	0.852	0.368	3.314	184.4	−0.300

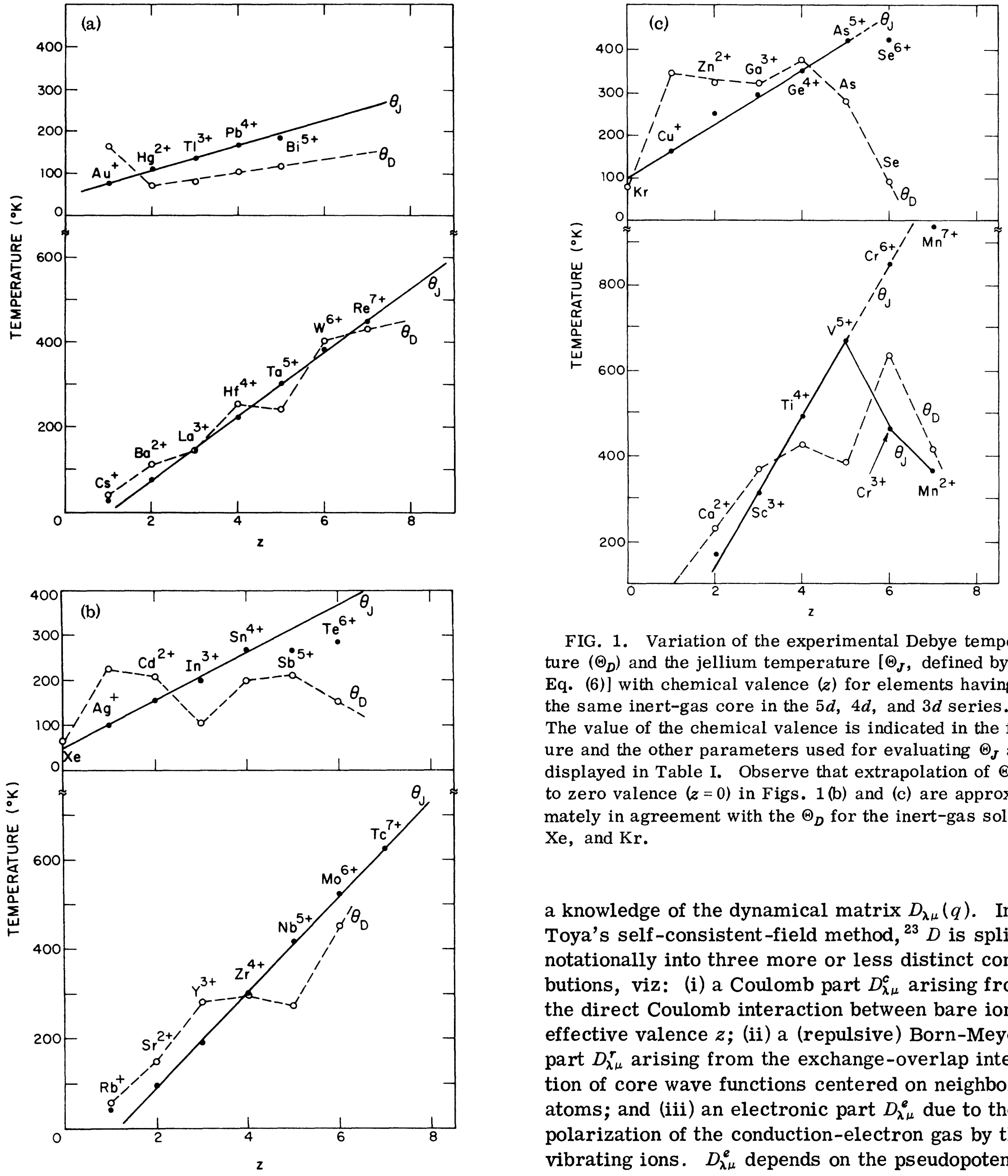

FIG. 1. Variation of the experimental Debye temperature (Θ_D) and the jellium temperature [Θ_J, defined by Eq. (6)] with chemical valence (z) for elements having the same inert-gas core in the 5d, 4d, and 3d series. The value of the chemical valence is indicated in the figure and the other parameters used for evaluating Θ_J are displayed in Table I. Observe that extrapolation of Θ_J to zero valence ($z=0$) in Figs. 1(b) and (c) are approximately in agreement with the Θ_D for the inert-gas solids, Xe, and Kr.

and harmonic approximations, the phonon dispersion relation, ω vs q, takes the form of a 3×3 matrix equation

$$[M\omega^2\delta_{\lambda\mu}-D_{\lambda\mu}(\vec{q})]\,e^{\mu}_{\vec{q}s}=0\ , \qquad (7)$$

where $e^{\mu}_{\vec{q}s}$ is the μ component ($\mu=x,\ y,\ z$) of the unit polarization vector of index s and $\vec{q}$ is the phonon wave vector restricted to the first Brillouin zone.

The solution of the dispersion equation rests upon a knowledge of the dynamical matrix $D_{\lambda\mu}(q)$. In Toya's self-consistent-field method,[23] D is split notationally into three more or less distinct contributions, viz: (i) a Coulomb part $D^c_{\lambda\mu}$ arising from the direct Coulomb interaction between bare ions of effective valence z; (ii) a (repulsive) Born-Meyer part $D^r_{\lambda\mu}$ arising from the exchange-overlap interaction of core wave functions centered on neighboring atoms; and (iii) an electronic part $D^e_{\lambda\mu}$ due to the polarization of the conduction-electron gas by the vibrating ions. $D^e_{\lambda\mu}$ depends on the pseudopotential carried rigidly by the ions, i.e., on the electron-phonon coupling matrix elements.[5,7]

In a crystal with cubic symmetry, Eq. (7) factors in the principal crystallographic directions [100], [110], and [111], so that the solution may be written (symbolically)

$$\omega^2\equiv\omega_C^2+\omega_r^2-\omega_e^2\ , \qquad (8)$$

where $\omega_C^2\equiv M^{-1}D^c$, etc. If the ion cores are small, so that there is no substantial overlap between "core" wave functions centered on neighboring at-

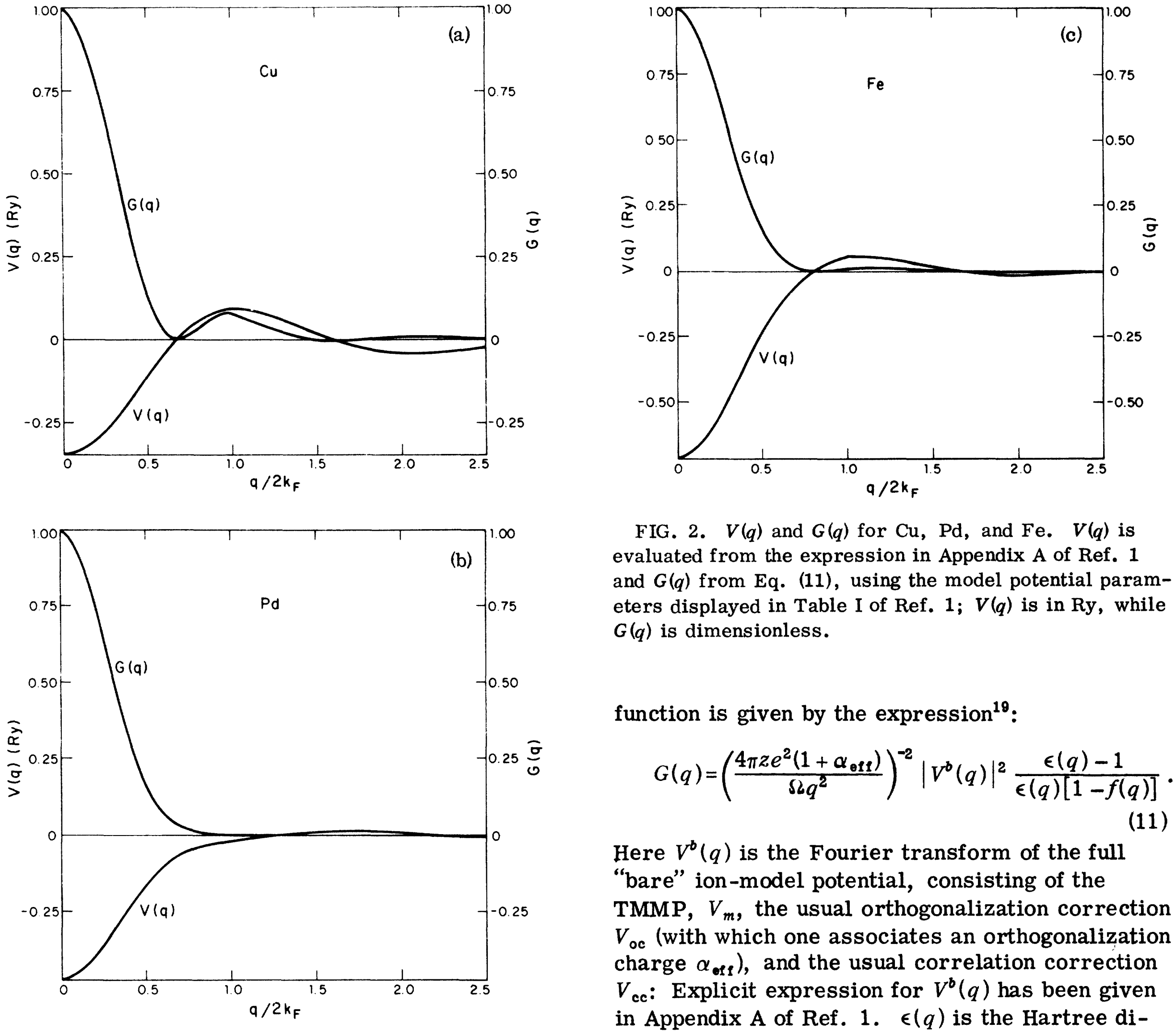

FIG. 2. $V(q)$ and $G(q)$ for Cu, Pd, and Fe. $V(q)$ is evaluated from the expression in Appendix A of Ref. 1 and $G(q)$ from Eq. (11), using the model potential parameters displayed in Table I of Ref. 1; $V(q)$ is in Ry, while $G(q)$ is dimensionless.

oms, then ω_r will be negligible in Eq. (8) and we would have simply

$$\omega^2 \equiv \omega_C^2 - \omega_e^2 \ . \qquad (9)$$

We shall return to the small-core approximation below.

The form of the Coulomb frequencies in cubic crystals is well known (see, for example, Ref. 24, Table I). Thus in local TMMP approximation, we are primarily concerned with the calculation of the electronic contribution to the dynamical matrix, which is of the form[25]

$$[\omega_e^2(q)]_{\lambda\mu} = \omega_p^2 \sum_{\vec{H}} \frac{(\vec{q}+\vec{H})_\lambda (\vec{q}+\vec{H})_\mu}{|\vec{q}+\vec{H}|^2} G(\vec{q}+\vec{H}) - \omega_p^2 \sum_{\vec{H}\neq 0} \frac{\vec{H}_\lambda \vec{H}_\mu}{|\vec{H}|^2} G(\vec{H}) \ , \qquad (10)$$

where $\vec{H}$ is a reciprocal-lattice vector, and the G function is given by the expression[19]:

$$G(q) = \left(\frac{4\pi z e^2 (1+\alpha_{\rm eff})}{\Omega q^2} \right)^{-2} |V^b(q)|^2 \frac{\epsilon(q)-1}{\epsilon(q)[1-f(q)]} \ . \qquad (11)$$

Here $V^b(q)$ is the Fourier transform of the full "bare" ion-model potential, consisting of the TMMP, V_m, the usual orthogonalization correction $V_{\rm oc}$ (with which one associates an orthogonalization charge $\alpha_{\rm eff}$), and the usual correlation correction $V_{\rm cc}$: Explicit expression for $V^b(q)$ has been given in Appendix A of Ref. 1. $\epsilon(q)$ is the Hartree dielectric constant with the usual Hubbard-Sham modification for exchange and correlation via the function $f(q)$. Since the local TMMP approximation has been used in the derivation of Eq. (11), the screened TMMP form factor is given simply by

$$V(q) = V^b(q)/\epsilon(q) \ . \qquad (12)$$

We have discussed the motivation for using the local TMMP approximation in Sec. I. So we need only discuss the small-core approximation,[4,26] and its implications for the d-d exchange overlap contribution D^r to the dynamical matrix D in Eq. (7). To elucidate the essence, consider Fe with outer electronic shell configuration $3d^6 s^2$. In the TMMP calculation, we take $z=3$, i.e., five d electrons associated with the half-filled $3d$ shell are treated as "core" electrons: If we had used $z=8$, then we would have to include the effects of these "core" electrons in each of the three contributions, D^C, D^e, and D^r, in a self-consistent manner so as to yield the same result as $z=3$, assuming that the actual value of z is indeed 3 in the crystal. Quantitatively, the size of an ion (for given z) is measured by the ratio, $(R_c/R_a)^3 \equiv 2\alpha_{eff}$ of Ref. 3, Table 4 (for simple metals), and Ref. 1, Table I (for transition metals), where R_c is the empirical Pauling radius of the ion, and R_a is the radius of the atomic sphere. For both simple and transition metals, excepting the Group-IB-and-IIB metals—Cu, Ag, Au, Cd and Hg—this ratio is no more than 20%. For example, in Fe ($z=3$), $(R_c/R_a)^3 = 0.144$. We conclude therefore that the small-core approximation is valid for most transition metals and, for purposes of phonon-spectrum calculation, we may set $D^r \approx 0$ to obtain the final expression (9) to which the rest of this paper refers.

IV. NUMERICAL RESULTS AND COMPARISON WITH EXPERIMENTS

In this section, numerical results based on the local TMMP theory of Sec. III will be presented and compared with the observed phonon frequencies of the ten transition metals—Cu, Ag, Ni, Pd, Fe, Cr, Mo, W, Nb and Ta. The calculations of the screened TMMP form factor, $V(q)$, from Eq. (12), and the G function from Eq. (11), using the TMMP parameters displayed in Ref. 1, Table I, and the analytical expressions given in Ref. 1, Appendix A, were performed with the aid of the IBM-360 computer at Lincoln Laboratory. Typical results for Cu, Pd, and Fe are displayed in Figs. 2(a)–2(c).

The calculations of the phonon-dispersion curves in the principal crystallographic directions for the ten transition metals were based on Eqs. (9) and (10), and the Coulomb frequencies tabulated in Ref. 24, Table I. The ion plasma frequency ($\nu_p = \omega_p/2\pi$) corresponding to the valence of the transition-metal ion were taken from Table I of this paper. The results for the fcc metals—Cu, Ag, Ni and Pd—are displayed in Figs. 3(a)–3(d); and those for the bcc metals—Fe, Cr, Mo, W, Nb and Ta—are displayed in Figs. 4(a)–4(f). Experimental points for the respective metals and their sources in Refs. 10–18 are also indicated and compared with theory (continuous curves).

A few general remarks about the calculations of the phonon spectra should be made, before turning to details applicable to the individual metals. The metals chosen for this study are grouped as follows: Cu, Ni, Fe, and Cr from the 3d series; Ag, Pd, Mo, and Nb from the 4d series; and W, and Ta from the 5d series. In each series, the TMMP parameters, $A_l (l = 0, 1, 2)$ are *linear* functions of z^2 (the square of the chemical valence z), as indicated in Figs. 4, 10, and 11 of Ref. 1. The linearity holds over a range, $R_c \lesssim R_m < R_a$, of values of the model radius R_m. These TMMP parameters could be determined, as discussed in Ref. 1, from the systematics of the atomic-spectroscopic data, but the available data for the 4d and 5d series were not sufficient to determine the position and slope of A_l vs z^2 with sufficient precision. However, it was discovered during the preliminary testing of the TMMP parameters with various properties, that the phonon spectrum could be moved up and down over a limited range by adjusting R_m and either A_0 or A_1, subject of course to the linearity of A_l vs z^2, in an isoelectronic sequence. Accordingly, the TMMP parameters in the 4d and 5d series were fixed in part by "tuning" the local TMMP model to fit the longitudinal phonon frequency at X for the fcc or at H for the bcc structures.

Bearing this fact in mind, the overall good fit to the longitudinal frequencies in Figs. 3 and 4 are not surprising. But it is most remarkable that such a fit with local TMMP theory is possible at all: it is as remarkable as the relation $\Theta_J \approx \Theta_D$ found in

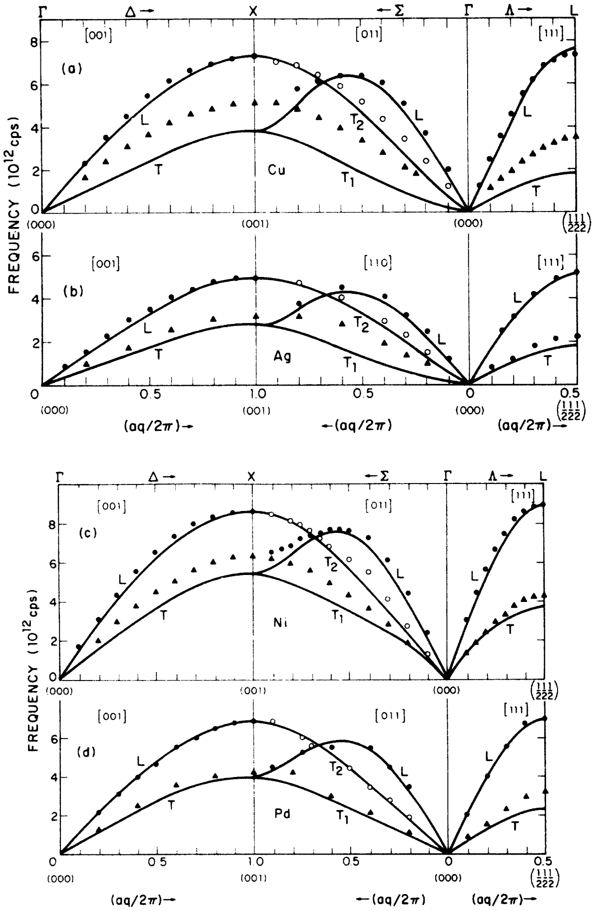

FIG. 3. Phonon dispersion curves for fcc metals, calculated (continuous curves) and measured for Cu, Ag, Ni and Pd. The experimental points are taken from Ref. 10 for Cu, Ref. 11 for Ag, Ref. 12 for Ni, and Ref. 13 for Pd. Summations in Eq. (10) were carried up to 235 reciprocal-lattice vectors.

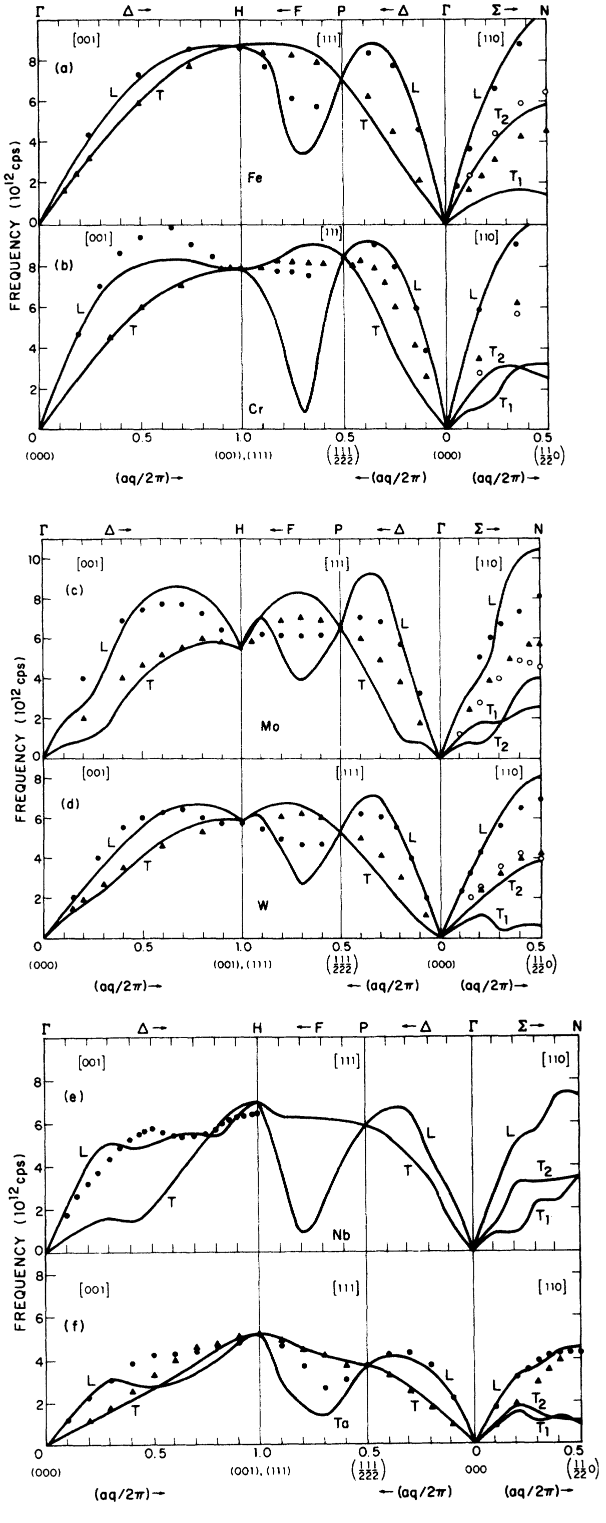

FIG. 4. Phonon dispersion curves for bcc metals, calculated (continuous curves) and measured for Fe, Cr, Mo, W, Nb, Ta. The experimental points are taken from Ref. 14 for Fe; Ref. 15 for Cr, Ref. 16 for Mo and Nb, Ref. 18 for Ta, and Ref. 17 for W. Summations [in Eq. (10)] were carried up to 326 reciprocal-lattice vectors.

the jellium model [Fig. 1(a)], for the 5*d* series. Another important point is the reproduction of the diverse features of the phonon spectra of the transition metals. The phonon spectra of Cu and Ag are similar and free from anomalies, in agreement with experiment. The phonon spectra of Ni and Pd are similar and also free from anomalies: in Pd, we also obtain good agreement between theory and experiment for the transverse branches. [Observe in passing that the form factor $V(q)$ for Pd does not cross the q axis for $q < 2k_F$ in Fig. 2(b)]. Thus both theory and experiment agree that the phonon spectra of the fcc transition metals are free from anomalies.

The situation is very different for the bcc transition metals—Fe, Cr, Mo, W, Nb, and Ta. The phonon spectrum of Fe [Fig. 4(a)] does not have anomalies, while the spectra of the other bcc metals have a variety of peculiarities. Because the spectra for the bcc metals are worked out by the same computer program, the replication of anomalies in all but Fe, is a direct evidence that these peculiarities are not spurious effects in the computation. The spectra of the group-IV*B* metals, Cr, Mo, and W, have Kohn anomalies, as Pb,[27] i.e., the longitudinal branches "soften" before reaching the zone boundary. The longitudinal and transverse [100] branches of the spectra of the group-V*B* metals, Nb and Ta, cross over (also as a result of "softening" of the longitudinal branch) before reaching the zone boundary, as Li.[19,28] These effects arise from the electronic contribution to the dynamical matrix involving the electron-phonon-interaction matrix elements.

Finally, the theory tends to disagree in details with the observed *transverse* phonon frequencies, especially in the bcc structures, near the zone boundaries. This signals the fact that some important factor must have been left out in the local TMMP approximation used in this calculation. However, it was not considered instructive to attempt to force agreement between theory and experiment at this stage of the TMMP method. Obviously, the nonlocality ($\vec{k}$ dependence as opposed to $\mathcal{E}$ dependence) of the TMMP form factors can make important contributions, but these contributions are not expected to be dominant, if our past experience[29] with simple metals is taken as an indicator. The *d-d* exchange overlap contribution may also be important, but *a priori* calculation of this contribution is, at best, nonexistent in current literature. The somewhat arbitrary choice of the chemical valence also deserves more systematic investigation, which is now in progress.

V. CONCLUSIONS

It has been shown in this paper that, as far as the phonon spectrum is concerned, the transition-metal model potential (TMMP) works in much the same way for transition metals as the Heine-Abarenkov model potential for simple metals. This is to be expected in a unified treatment of simple and transition metals which has been the keynote of the generalized quantum-defect law of Paper I: It follows naturally from the fact that the nearly-free-electron perturbation is also applicable to the transition metals. However, the *diagonal* matrix element, $\langle \vec{k} | V | \vec{k} \rangle$, normally considered unimportant for simple metals, now contains information about s-d hybridization, as discussed in Sec. I, while the *off-diagonal* matrix element, $\langle \vec{k} | V | \vec{k}+\vec{q} \rangle$ defining the TMMP form factor $V(q)$ is small, as in simple metals. Inasmuch as the fitting of the phonon spectrum, especially with regard to the features arising from the electronic contribution to the dynamical matrix, is by far the most delicate test of how accurately the electron-phonon-interaction matrix elements have been constructed, we expect the TMMP method to play a key role in future first-principles investigation of strong-coupling (transition-metal) superconductivity. The calculations of the resistivity and thermoelectric power of liquid transition metals, the binding energies, and structural phase transitions are now in progress and will be published in later articles of this series. From preliminary results of such calculations and those reported in this paper, it appears reasonably safe to suggest that the TMMP method may well provide the answer to several questions surrounding the electronic structure and properties of the transition metals.

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