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Dielectric screening and phonon frequencies of palladium, platinum, and vanadium

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In this addendum the dielectric screening and the phonon frequencies are calculated using the isotropic noninteracting *s*-*d*-band model for fcc and bcc metals. The isotropic noninteracting band models for nonrelativistic Pd and Pt are constructed considering three principal symmetry directions [100], [110], and [111], while for vanadium we construct the isotropic noninteracting band model considering three principal symmetry directions [100], [110], and [111], and three off-symmetry directions [310], [311], and [221]. The contributions to the dielectric matrix $\epsilon(\vec{q}+\vec{G}, \vec{q}+\vec{G})$, which arise due to intraband and interband transitions are calculated using the formalism of the previous papers. The Animalu transition-metal-model potential is used for the bare-ion potential in conjunction with the dielectric matrix which takes into account the local-field corrections. The results for all the three metals are found to be in reasonably good agreement with the experimental values.

I. INTRODUCTION

In the previous papers[1,2] (hereafter referred to as papers I and II) the noninteracting band models were constructed for the fcc and bcc transition metals and the formalism for the dielectric matrix which includes local-field corrections and the hybridization between different magnetic quantum numbers *m* of a *d* subband, was discussed. Using the inverse of the complete dielectric matrix, a multipole model of lattice dynamics was obtained (Refs. 3 and 4, hereafter referred to as papers III and IV) and was applied to nickel and chromium. The local-field corrections were found to be appreciable. In this paper we have tried to incorporate the effect of local-field corrections, using the formalism given in papers I–IV, in Pd, Pt, and V. Also we thought it worthwhile to investigate the effect of local fields in Pd and Pt which have a larger core size than Ni, because, as the core size increases the contribution due to local fields should increase.

The noninteracting band models and the results for the dielectric matrix are given in Sec. II. The results for phonon frequencies are given in Sec. III and are discussed in Sec. IV.

II. NONINTERACTING-BAND MODEL AND DIELECTRIC SCREENING

The isotropic noninteracting band model for Pd is constructed exactly in the same manner as discussed by Prakash and Joshi[5] taking the energy eigenvalues due to Mueller *et al.*[6] and is shown in Fig. 1. As is pointed out in paper II that in the construction of the isotropic band model the assignment of different quantum number *m* to a particular *d* subband does not remain strictly valid because of the hybridization between the *m* components of the *d* wave function. Therefore, in Fig. 1, we label the *d* subbands from 1 to 5 in the ascending order of energy, and this hybridization is taken care of in the calculations of the dielectric matrix. From Fig. 1 it is clear that the *s* band and one *d* subband are partially filled. Therefore, the number of electrons per atom in the *s* band, Z_s, and in the partially filled *d* subband, Z_{d3}, are taken to be 0.4 and

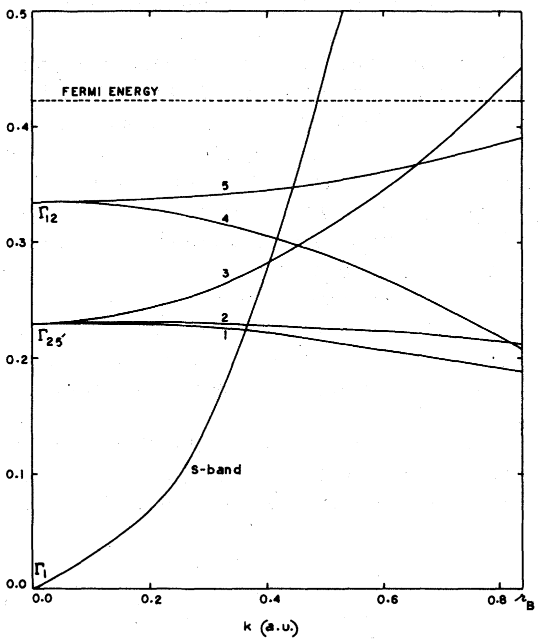

FIG. 1. Isotropic noninteracting band model for Pd. The dashed line shows the Fermi energy. The five *d* subbands are numbered from 1 to 5.

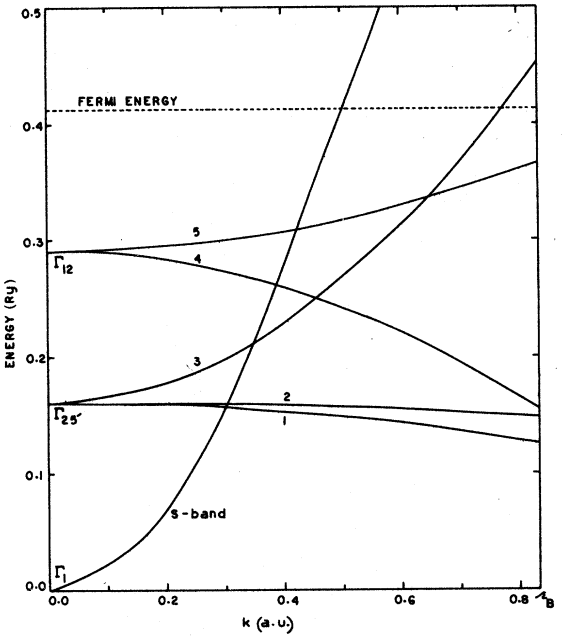

FIG. 2. Isotropic noninteracting band model for Pt. The description is the same as of Fig. 1.

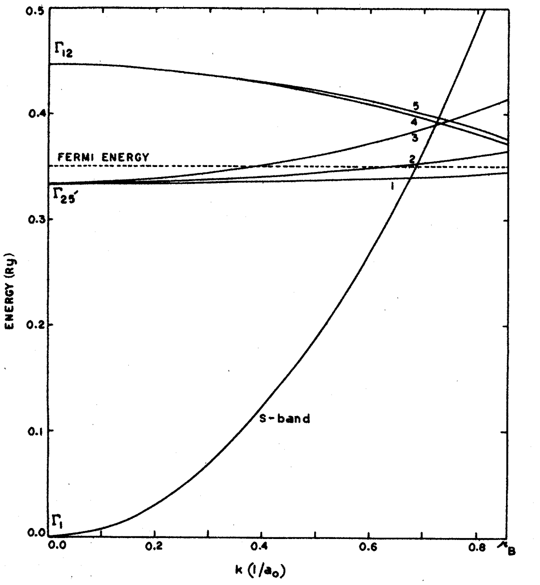

FIG. 3. Isotropic noninteracting band model for V. The description is the same as of Fig. 1.

1.6, respectively, in agreement with the de Haas–van Alphen studies of Pd.[7,8]

The isotropic noninteracting band model for Pt is shown in Fig. 2 and is constructed in the same way as for Pd using the nonrelativistic energy-band-structure calculations of Smith.[9] Z_s and Z_{d3} for Pt are taken to be 0.4 and 1.6, respectively, which is again in agreement with the de Haas–Van Alphen studies of Pt.[10] The *d* bandwidths of Pd and Pt obtained from the isotropic band model are comparable with the average of the *d* bandwidths in the [100], [110], and [111] directions obtained from the detailed band-structure calculations of Mueller *et al.* and Smith, respectively.

The general features of the band-structure calculations of vanadium[11,12] are the same as those of paramagnetic chromium.[13] Therefore, exactly the same procedure, as in paper II, is followed for constructing the isotropic noninteracting *s*-*d* band model for vanadium using the detailed band-structure calculations due to Yasui *et al.*,[11] where the coefficient of Slater exchange potential is taken to be one and the orthogonalized plane wave and the modified tight-binding method are used for *s* and *d* electrons. The isotropic band model for V is shown in Fig. 3. The *d*-band width of the isotropic band model is comparable with the *d*-band width in the detailed band-structure calculations of Yasui *et al.* The occupied *s*-*d* bandwidth is 0.357 Ry which is in reasonable agreement with the experimental value[14] 0.47. The electronic configuration of vanadium is taken to be $3d^4 4s^1$ which is also used by Yasui *et al.* and is similar to that of chromium.

In our isotropic band model given in Fig. 3 two *d* subbands and the *s* band are partially filled, one *d* subband is completely filled and rest of the two *d* subbands are completely empty. The completely filled and completely empty bands are assigned two electrons and no electron per atom, respectively. Therefore, the remaining two *d* electrons are distributed among the partially filled *d* subbands in the ratio of the volume occupied by them. Z_{d2} and Z_{d3} for vanadium are 1.5856 and 0.4144, respectively. The effective masses and the Fermi radii of the *s* and *d* subbands and other physical parameters for Pd, Pt and V, are given in Tables I and II.

TABLE I. Physical parameters for Pd, Pt, and V in atomic units.

	Pd	Pt	V
Lattice parameter *a*	7.353	7.4161	5.7225
Volume of the unit cell, Ω_0	99.3879	101.9673	93.6973
Radius of the Brillouin zone, k_B	0.8414	0.8343	0.8581

TABLE II. Effective masses and Fermi momenta for s and d subbands.

	Pd		Pt		V	
	k_{Fs}	m_s	k_{Fs}	m_s	k_{Fs}	m_s
	0.4920	0.5731	0.4878	0.5764	0.6812	1.3256
i	k_{Fdi}	m_{di}	k_{Fdi}	m_{di}	k_{Fdi}	m_{di}
1	0.8414	−16.3057	0.8343	−20.0444	0.8581	63.1870
2	0.8414	−38.2075	0.8343	−52.0587	0.7943	22.7084
3	0.7811	3.2048	0.7745	2.3832	0.5078	9.1482
4	0.8414	−5.5552	0.8343	−5.0849	0.0	−10.0302
5	0.8414	12.7824	0.8343	9.1542	0.0	−10.6696

According to Figs. 1–3 the conduction electrons can readjust themselves, in response to the ionic motion, through all sorts of intraband and interband transitions. The various contributions to the dielectric matrix are obtained by removing the spin index σ and multiplying Eqs. (5), (7), (8), (11), (12), and (15)–(18) of paper I by a factor of 2 for spin degeneracy. In order to include the hybridization between the different magnetic quantum numbers m of a particular d subband we take the simple average of the contributions corresponding to different m values of that d subband. Such an averaging is done by us in our previous paper II and also by Hanke[15] and Brown.[16] The radial wave functions for Pd and Pt are taken from Herman and Skillman's[17] calculations and that for V from Clementi.[18] All the three radial wave functions are expressed in the analytical form given in paper II by the least-square-fit method. The parameters a_i and α_i of the radial wave functions are given in Table III.

As in the case of Ni and Cr the anisotropy of the dielectric matrices for Pd, Pt, and V are also found to be small and, therefore, the calculations of the dielectric matrices are carried out for the field wave vector $\vec{q}$ along the [001] direction only. The polarizability function exhibits the expected behavior in Pd, Pt, and V. The intraband contribution to the polarizability function dominates over the interband contribution at small values of the wave vector but at large values of the wave vector the reverse is the case. The interband part is comparatively larger in Pt than that in Pd.

III. PHONON FREQUENCIES

From the isotropic d-band models (Figs. 1 and 2) it is evident that the four d subbands are completely filled in both Pd and Pt. Therefore, the ion cores are limited to $4d^8$ and $5d^8$ configurations for Pd and Pt, respectively. A similar separation between the core and the conduction electrons is also done by Hanke[15] for Pd. From the isotropic band model shown in Fig. 3 it is found that only one d subband is filled, therefore, the core is limited up to the $3d^2$ configuration in case of V. The phonon frequencies for all the metals are calculated exactly in the same manner as is discussed in paper IV. In the present calculations the overlapping between the ions is neglected. The contribution due to the ion-ion Coulomb interaction is taken from the calculations of Animalu.[19] In the evaluation of the ion-electron-ion part the functions $B(\vec{q}+\vec{G})$ and $F(\vec{q})$, defined in paper IV, are represented for Pd in the following analytical form:

$$B(\vec{q}+\vec{G})=\begin{cases}\lambda|\vec{q}+\vec{G}|^2\exp(-\mu|\vec{q}+\vec{G}|+\delta|\vec{q}+\vec{G}|^2) & \text{for } |\vec{q}+\vec{G}|\leqslant 2.1,\\ A_1'\exp(-|\vec{q}+\vec{G}|^{1/2}) & \text{for } |\vec{q}+\vec{G}|>2.1,\end{cases} \tag{1}$$

TABLE III. Parameters of the radial wave functions of Pd, Pt, and V.

	Palladium		Platinum		Vanadium	
i	a_i	α_i	a_i	α_i	a_i	α_i
1	−631.3905	12.1103	16 316.8060	16.3363	5.168 07	3.024 85
2	451.7826	19.4000	−13 460.9170	15.4451	38.698 51	9.971 04
3	1037.2056	11.2508	−78.1036	5.2590	31.225 14	4.791 90
4	−15.7052	2.8666	26.5629	3.0783	2.396 39	2.075 60
5	⋯	⋯	⋯	⋯	0.093 45	1.172 00

and

$$F(\vec{q}) = -B_1' N m_s k_{Fs} \left(1 + \frac{4k_{Fs}^2 - q^2}{4k_{Fs}q} \ln\left|\frac{2k_{Fs}+q}{2k_{Fs}-q}\right|\right). \quad (2)$$

Here N is the total number of atoms in the crystal. m_s and k_{Fs} are the effective mass and the Fermi momentum for the s electrons. The function $F(\vec{q})$ for Pt has the same form as for Pd but the function $B(\vec{q}+\vec{G})$ is represented in the following analytical form:

$$B(\vec{q}+\vec{G}) = \begin{cases} 39.72|\vec{q}+\vec{G}|^2 \exp(1.6337|\vec{q}+\vec{G}|^2) & \text{for } |\vec{q}+\vec{G}| \leqslant 0.6, \\ \lambda|\vec{q}+\vec{G}|^2 \exp(-\mu|\vec{q}+\vec{G}| + \delta|\vec{q}+\vec{G}|^2) & \text{for } 0.6 < |\vec{q}+\vec{G}| \leqslant 1.7, \\ A_1' \exp(-|\vec{q}+\vec{G}|^{1/2}) & \text{for } |\vec{q}+\vec{G}| > 1.7. \end{cases}$$

The analytical forms of $F(\vec{q})$ and $B(\vec{q}+\vec{G})$ for V are the same as that for Pd except that the first part of Eq. (1) is valid for $|\vec{q}+\vec{G}| \leqslant 4.8$ and the second part for $|\vec{q}+\vec{G}| > 4.8$. The parameters λ, μ, δ, A_1', and B_1' are obtained by fitting the actual interband contribution by least-square-fit method within an accuracy of ±10% and are tabulated in Table IV. The exchange and correlation corrections due to Singwi *et al.*[20] are applied to the free-electron part of the dielectric function, where s electrons are itinerant but for d electrons we apply Lindgren and Schwarz[21] exchange correction exactly in the same way as applied in paper IV. Lindgren and Schwarz have calculated the modified Slater coefficient α only for $3d$ shell. Therefore, it is not possible to interpolate the values of α for $4d$ and $5d$ shells from those of $3d$ shell only. Because the trend of α for d shells cannot be predicted by just seeing the trend of α in case of s or p shells, since s or p shells are entirely of a different nature. So in view of the above uncertainty and in the absence of the detailed calculations of α we take the value of α for Pd and Pt to be the same as for Ni as they belong to the same group.

In the present calculations we use the Animalu[22] transition-metal model potential (TMMP), which includes s-d hybridization. This hybridization, represented by parameter A_2, is taken to be the same as taken by Animalu. The parameter α_{eff} is taken to be zero. As found by Animalu, the parameters A_0 and A_1 are renormalized by matching the phonon frequencies in the longitudinal branch in the [100] direction at the symmetry point X for Pd and Pt and at H for V. These parameters are given in Table V. The phonon frequencies for Pd, Pt, and V are shown in Figs. 4–6, respectively, and compared with the experimental results due to Miller and Brockhouse[23] for Pd, due to Dutton *et al.*[24] for Pt, and due to Colella *et al.*[25] for V. The agreement with the experimental values is good in the longitudinal branches, while the calculated phonon frequencies are lower than experimental values in the transverse branches by about 12% in Pd and about 19% in Pt. The interesting feature of the experimental phonon dispersion curves of Pd and Pt is that an anomaly is found in the [110] T_1 branch which is responsible for the existence of the long-range forces[23,24,26] in these metals. In the calculated phonon frequencies similar anomalous behavior has been found but it may not be attributed to the Kohn anomaly, because in the present calculations the spherical Fermi surface is used which does not exhibit nesting of Fermi surfaces. In our calculations the change in slope of the T_1 [110] branch occurs at $q = 0.3$ and 0.4 for Pd and Pt, respectively. The agreement between the calculated and the experimental values for V is reasonable except in the longitudinal branch in the [100] direction and the transverse branch T_1 in the [110] direction.

IV. DISCUSSION

In Pd, Pt, and V both the diagonal and the nondiagonal contributions to the polarizability functions are of the same order of magnitude. In the calculation of phonon frequencies it is found that the diagonal and the nondiagonal contributions sum up in the longitudinal branches to give a maximum con-

TABLE IV. Parameters for the interband part of the dielectric matrix.

	λ	μ	δ	A_1'	B_1'
Pd	1852.0	12.6954	4.1498	8.5262	3.0
Pt	692.8	6.6068	2.1026	43.3508	20.0
V	22.2	1.3368	0.0967	69.2744	0.15

TABLE V. Parameters of the Animalu TMMP. Here all the quantities are in atomic units except $|E_c|$ which is in rydbergs.

	A_0	A_1	A_2	R_m	Z	R_c	$\lvert E_c\rvert$
Pd	1.575	0.90	0.87	2.6	2.0	1.512	0.091
Pt	0.97	0.965	0.85	2.6	2.0	1.512	0.091
V	2.15	2.50	2.90	1.6	3.0	1.248	0.101

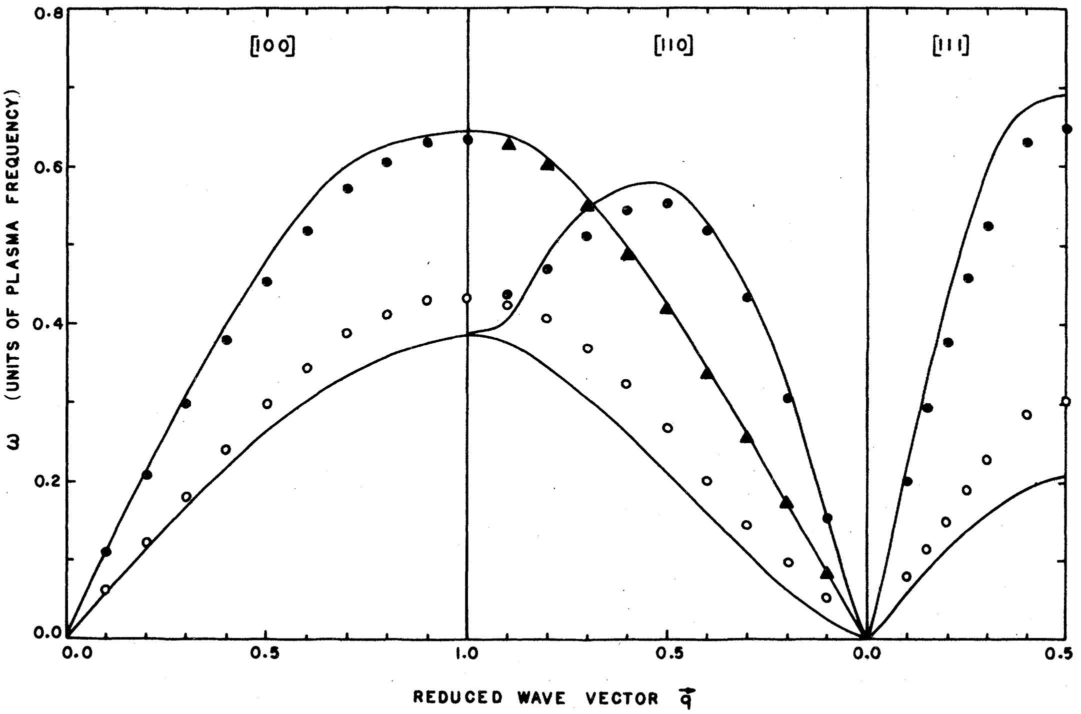

FIG. 4. Phonon frequencies of Pd. The solid and the open circles show the experimental values for the longitudinal and the transverse branches, respectively. The triangles show the transverse branch T_2 in the [110] direction. The solid lines represent the present calculations.

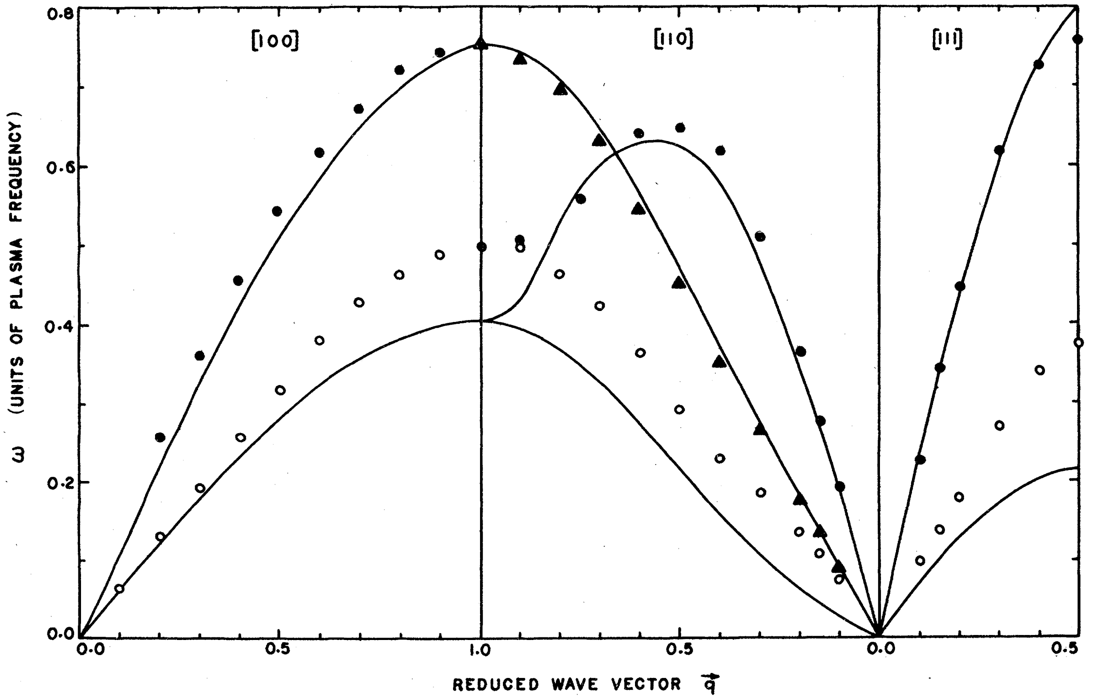

FIG. 5. Phonon frequencies of Pt. The description is the same as that of Fig. 4.

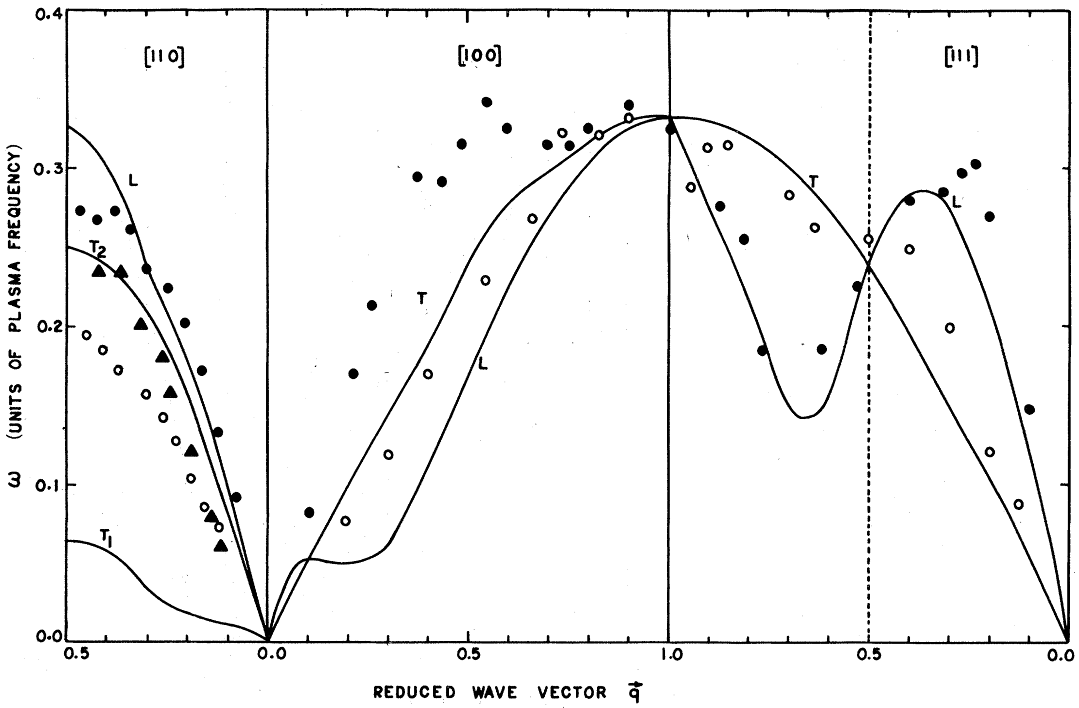

FIG. 6. Phonon frequencies of V. The description is the same as that of Fig. 4.

tribution of 22% for Pd, of about 26% for Pt, and 15% for V, which shows the importance of the local-field corrections in these metals. The transverse branches in all the metals do not get renormalized due to noncentral contributions, because the diagonal and the nondiagonal contributions cancel each other due to the symmetry of the crystal structure. The results for the transverse branches can further be improved especially in case of Pd and Pt by including a suitable ion-ion exchange overlap potential, because, the size of the ion-cores for Pd and Pt are sufficiently large. Moreover we have neglected the relativistic effects which are quite important in Pt.

It is, again, interesting to compare the results for Ni (papers I and III), Pd, and Pt because all lie in the same group of the Periodic Table and have ion cores of increasing order. The polarizability function goes on increasing in magnitude and in oscillatory nature and the convergence of the polarizability function also becomes poor as we go from Ni to Pt. This is consistent with the nature of the 3*d*, 4*d*, and 5*d* radial wave functions of Ni, Pd, and Pt, respectively. The phonon dispersion curves of Ni, Pd, and Pt resemble one another and differ only by a scale factor of approximately the inverse square root of their mass ratio. The disagreement in the transverse branches increases as we go from Ni to Pt, which is due to the increasing core size, and here the core-core overlap may be significant.

Both in the calculated and the experimental results[25,27] for the phonon frequencies of vanadium it is found that the transverse branch T_2 rises with a large slope approximately equal to that of the longitudinal branch. The change in slope of the longitudinal branch in the [110] direction is found at $q = 0.35$ in our calculations which is consistent with the experimental results. In our calculations we explicitly include the noncentral forces through the nondiagonal part of the dielectric matrix. The interatomic force constant analysis of the experimental phonon dispersion curves[25] shows the pronounced asphericity of the charge distribution which gives rise to the noncentral forces. This has also been verified by the results of Weiss and deMarco[28] for the 3*d* orbital population in vanadium. Oli and Animalu[29] have also calculated the phonon frequencies of V, in the resonance model, taking it to be pentavalent. But according to our noninteracting energy band model vanadium turns out to be trivalent because one *d* subband is completely filled and is treated in the ion core. Therefore, in evaluating the phonon frequencies we have used a different valency and the ion-core radius R_c (in accordance with valency 3) for vanadium rather than the values used by Oli and Animalu,[29] and in order to achieve good agreement with experiment we have renormalized the parameters A_0 and A_1. Although a direct quantitative comparison may not be made the qualitative features are the same in both calculations. We do not get Kohn anomalies in the phonon dispersion curves because we have used the spherical Fermi surface for both *s* and *d* electrons. In the present calculations the electron-phonon interaction has a simple reproducible form which can be used to study other physical properties.

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