CHAPTER 3

LATTICE DYNAMICS OF PARAMAGNETIC TRANSITION METALS: APPLICATION TO BCC METALS, CHROMIUM AND VANADIUM

In the second chapter, we formulated the microscopic theory for the dielectric screening in the transition metals and applied it to calculate the diagonal and the nondiagonal parts of the dielectric matrix for the two bcc transition metals, paramagnetic chromium and vanadium. The phonon spectrum of a crystal is intimately related to the nature of the dielectric screening and provides a sensitive test for the model used for the screening. The so-called microscopic dielectric approach permits the complete solution of the lattice dynamical problem, within the harmonic approximation, once the charge on the nucleus and a properly defined inverse dielectric matrix \( \epsilon^{-1}(q+G, q+G') \), are known \(^{37,39}\). In this chapter, we present a completely general approach to the lattice dynamics of the transition metals and use it to calculate the phonon frequencies and the other related properties. The plan of this chapter is as follows: The inversion of the dielectric matrix and the evaluation of the dynamical matrix are given in section 3.1. In section 3.2, the results for the phonon frequencies are presented. A simplified estimation for the energy wavenumber characteristic function, the form factor, and the binding energy is also presented in section 3.2, where the local field corrections are neglected. The results are concluded in section 3.3.

3.1 THEORY

3.1.1. Inversion of the Dielectric Matrix.

In the chapter 2, we have seen that in the non-interacting
The dielectric matrix can be written as:

\[
\begin{align*}
\epsilon(qG, q'G') &= \epsilon_{ss}(qG, q'G') \delta_{GG'} - \epsilon_{sd}(qG, q'G') \\
&\quad - \epsilon_{ds}(qG, q'G') - \epsilon_{dd}(qG, q'G') \\
&= \epsilon_0(qG) - \epsilon_{\text{intra}}(qG, q'G') - \epsilon_{\text{inter}}(qG, q'G')
\end{align*}
\]

(3.1a)

(3.1b)

Here \(\epsilon_{ss}, \epsilon_{dd}, \epsilon_{ds}\) and \(\epsilon_{sd}\) have the same meaning as discussed in the chapter. \(\epsilon_0(qG)\) is the purely diagonal part of the dielectric matrix and is a dominating term for the free electron metals. The second term in Eq. (3.1b) represents the intraband contribution which contains both the diagonal and the nondiagonal parts. The third term represents the total interband contribution which again contains both the diagonal and the nondiagonal parts. It is evident from the Eq. (3.1) that the dielectric function becomes an infinite dimensional matrix for a transition metal and the inverse of the dielectric matrix becomes impossible. Therefore, one has to resort to some approximate method to invert the dielectric matrix. Phillips separated the total diagonal and the nondiagonal parts of the dielectric matrix and set up a bond charge model which was used by Martin to study the lattice dynamical properties of intrinsic semiconductors. Sinha et al. used the factorization ansatz to invert the infinite dimensional dielectric matrix. The main philosophy of the factorization ansatz is that the band structure and the overlap parts are in the separable form. This reduces the infinite dimensional dielectric matrix into a finite dimensional dielectric matrix and the inversion becomes possible. These authors used the ansatz...
to study the phonon frequencies of germanium and silicon. Here we also follow the approach of Sinha et al.\textsuperscript{40}

Now our main aim is to obtain the generalized dynamical matrix for a lattice with basis using the inverse of the complete dielectric matrix. Therefore, we write the dielectric matrix in a form which also includes the position of the basis atoms in the unit cell.

In our scheme the purely diagonal part of the dielectric matrix includes the contribution arising from the s-s transitions and is written as:

\[
\varepsilon_0 (q + G) = [1 - \varepsilon_{ss} (q + G, q + G')] \delta_{qq'} .
\] (3.2)

The intraband part \(\varepsilon_{\text{intra}} (q + G, q + G')\), which arises due to the d-d intraband transitions only, can also be written in the separable form including the overlapping between the d-wavefunctions on the different lattice sites. The overlap integral can be written as:

\[
\langle \psi \downarrow_m (k) | e^{-i(k + G + G').\mathbf{r}} | \psi \downarrow_m (k') \rangle = \delta \delta_{kk'} \delta_{GG'} .
\] (3.3)

Here \(\mathbf{r}_t\) represents the position of the \(t\)th atom in the unit cell.

Using the Eq. (3.3) in the Eq. (2.11), the polarizability function due to the d-d intraband (\(m = m'\)) transitions is given as:

\[
\chi_{\text{intra}} (q + G, q + G') = \sum_k \sum_{m} \sum_{tt'} \frac{n_{\text{dm}} (k) - n_{\text{dm}} (k + G)}{e_{\text{dm}} (k) - e_{\text{dm}} (k + G)}

\times e^{-i(k + G).\mathbf{r}_t} e^{i(k + G').\mathbf{r}_{t'}}

\times \int \phi_{\text{dm}}^*(\mathbf{r}) e^{-i(q + G).\mathbf{r}} \phi_{\text{dm}} (\mathbf{r} + \mathbf{r}_t) d\mathbf{r} \int \phi_{\text{dm}}^*(\mathbf{r} + \mathbf{r}_t') e^{i(q + G').\mathbf{r}} \phi_{\text{dm}} (\mathbf{r}') d\mathbf{r}' .
\] (3.4)
where

\[ f_{t' t}(q) = \sum_k \frac{n_{dm}(k) - n_{dm}(k+q)}{E_{dm}(k) - E_{dm}(k+q)} \exp[-i(k+q) \cdot (r_t - r_{t'})], \quad (3.6) \]

and

\[ \triangle_{dm, dm}(q+q') = e^{-i(q+q') \cdot r} \int \varphi_{dm}(r)^* \varphi_{dm}(r') \exp[-i(q+q') \cdot (r-t)] dr. \tag{3.7} \]

Here \( f_{t' t}(q) \) represents the band structure part and \( \triangle_{dm, dm}(q+q') \) represents the overlap part of the intraband contribution to the susceptibility function. Therefore, the intraband contribution to the dielectric matrix is given as:

\[ \epsilon_{dd}(q+q', q'') = v(q+q') \sum_m \sum_{t' t} \triangle_{dm, dm}(q+q') f_{t' t}(q) \triangle_{dm, dm}(q+q'). \tag{3.8} \]

The Eq. (3.8) represents the intraband contribution to the dielectric matrix in a separable form which is a consequence of the tight-binding wavefunctions used for the d-electrons. If we completely neglect the overlapping at the different lattice sites then the Eq. (3.8) reduces exactly to the Eq. (2.24) given for the intraband contribution in the Chapter 2.

In order to include the hybridization among all the five \( m \) components of the d-wavefunction we take the simple average giving equal weightage to each \( m \) value. Such an averaging leads to

\[ \triangle_{dm, dm}(q+q') = \Lambda_t(q+q'), \tag{3.9} \]

where

\[ \Lambda_t(q+q') = \Lambda(q+q') e^{-i(q+q') \cdot r_t}, \tag{3.10} \]
and

\[ A (q, G) = \int_0^\infty J_0 (2 |q| |r|) r^2 \, dr. \tag{3.11} \]

Here \( J_0 (2 |q| |r|) \) is the spherical Bessel function of zeroth order. Using the Eq. (3.9) in the Eq. (3.8), we can write

\[ \varepsilon_{\text{intra}} (q, G, q', G') = v (q, G) \sum_{tt'} A_q (q, G) f_{tt'} (q) k_{tt'} (q, G, G'), \tag{3.12} \]

where

\[ f_{tt'} (q) = - \left( \frac{N \Omega}{2 \pi^2} \right) \sum_i m_{di} k_{di} \left[ 1 - \frac{4 k_{di}^2 - q^2}{4 k_{di}^2} \right] \exp \left[ -i \mathbf{q} \cdot (\mathbf{r}_t - \mathbf{r}_{t'}) \right]. \tag{3.13} \]

The \( m \) dependence is left only in the band structure part through the masses \( m_{di} \) and the Fermi momenta \( k_{di} \) of the \( d \)-sub bands.

The interband part of the dielectric matrix \( \varepsilon_{\text{inter}} (q, G, G') \) consists of three contributions. The first contribution comes from the \( d-d \) transitions between the different \( d \)-sub bands, i.e., \( \varepsilon_{dd} (q, G, G') \) for \( m \neq m' \). This contribution is again in a separable form. The other two contributions due to the \( d-s \) and the \( s-d \) transitions are not in the separable form because of the nonorthogonality of the \( s \)-and the \( d \)-wavefunctions as pointed out in the second chapter. It is too difficult to use the orthogonal wavefunctions for the \( s \)-and the \( d \)-electrons as it demands heavy computational efforts. Therefore, to make the calculations tractable we resort to the factorization ansatz due to Sinha et al. The interband contribution, i.e., the sum of \( \varepsilon_{dd} \) for \( m \neq m' \), \( \varepsilon_{ds} \) and \( \varepsilon_{sd} \), represents the total interband contribution, i.e., the sum of \( \varepsilon_{dd} \) for \( m \neq m' \), \( \varepsilon_{ds} \) and \( \varepsilon_{sd} \), in some simple functional form which also includes the positions of the basis atoms in the unit cell, as:

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Here $F(q)$ and $B(q+G)$ are the functions representing the band structure and the overlap part of the interband contribution to the dielectric matrix and $r_s$ are the positions of the basis atoms in the unit cell. These functions will be determined with the help of the detailed calculations of the total interband part.

Substituting the Eqs. (3.12) and (3.14) in Eq. (3.1b) we can write the dielectric matrix as:

$$
\varepsilon(q+G, q'+G') = \varepsilon_0(q+G) \delta_{G+G'} - \nu(q+G) \sum_{tt'} A^*(q+G) \frac{f_{tt'}(q)}{f_G(q+G')} A_t(q+G),
$$

Using the orthogonality relations for the dielectric matrix

$$
\sum_{G''} \varepsilon(q+G, q''+G'') \varepsilon^{-1}(q+G'', q'+G'') = \delta_{G+G'},
$$

and making some mathematical manipulations, which are lengthy but straightforward, we obtain the inverse of the dielectric matrix as:

$$
\varepsilon^{-1}(q+G, q'+G') = \varepsilon^{-1}_0(q+G) \left[ \delta_{G+G'} - \nu(q+G) \varepsilon^{-1}_0(q+G) \right]
$$

where

$$
L^{*}_s(q) = \sum_{t' t}\frac{L^{*}_{st}(q)}{L^{*}_{tt}(q)} A^{*}_{st}(q) A_{t't}(q) T_{tt'}(q).
$$
Here the sum is over all the reciprocal lattice vectors of the lattice.

The detailed mathematical calculations of the Eq. (3.19) are given in Appendix E.

With the help of the Eq. (3.19) we can easily write the density response function

\[ \chi(G+G',\Omega+\Omega') = \left[ -\delta_{G+G',0} \epsilon_{G+G',0} \right] / \nu(G+G') \]

\[ = -\nu^{-1}(G+G') \left[ 1-\epsilon_{G+G',0}^{-1} \right] \delta_{G+G',0} \]
The electron density response function splits up into two parts, a purely diagonal part analogous to that of the free electron metals and a part which corresponds to a set of monopole and dipole distributions produced by the polarization of the d-electrons. The first term in square brackets corresponds to a set of monopole distributions centred at the sites \( \mathbf{r}_t \) with the effective form factors \( \tilde{A}_t(q+G)/\epsilon_0(q+G) \). \( \upsilon_{t\ell}(q) \) can be regarded as the coupling coefficient between the monopole distributions centred at the sites \( \mathbf{r}_t \) and \( \mathbf{r}_t' \), which interact via the screened electron-electron interaction potential \( v(q+G)/\epsilon(q+G) \). The second term in the square brackets corresponds to a set of dipole distributions centred at the sites \( \mathbf{r}_s \) with the effective form factor \( \tilde{B}_s(q+G)/\epsilon_0(q+G) \). \( \upsilon_{s\ell}(q) \) is the coupling coefficient between the dipole distributions centred at \( \mathbf{r}_s \) and \( \mathbf{r}_s' \), which again interact via the screened electron-electron interaction potential. The rest of the two terms in the square brackets give the cross contributions between the dipole and the monopole distributions and \( \upsilon_{st}(q) \) can be regarded as the coupling coefficient between the dipole and the monopole distributions.

The physical meaning of the functions \( \epsilon(q+G, q'+G') \) and \( \chi(q+G, q'+G') \) becomes transparent only in certain limiting cases. For instance, if we neglect the d-electron contribution the Eq. (3.28)
reduces to the simple metal like limit and the dielectric function becomes
a scalar and the conventional screening theory is retrieved. If we put
\( \varepsilon_0 (\mathbf{q} + \mathbf{G}) = 1 \) and omit the intraband transitions, the Eq. (3.28) gives
the dipolar model of screening for the ideal insulators. If we switch
off the interband transitions, the Eq. (3.19) reduces exactly to the
same expression as given by Hanke and Bilz\(^1\) and Hanke\(^3\). For a transi-
tion metal, the physical model that results from the Eq. (3.28) consists
of both the monopolar and the dipolar distributions associated with
the d-electrons and is similar to that of screened Breathing shell
model\(^6\).

3.1.2 Dynamical Matrix.

Let us consider a crystal composed of infinite number of unit
cells each of which is bounded by a parallelepiped having three non-
coplanar vectors \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_3 \). In a metallic crystal the ions are
embedded in a uniform or nonuniform background of conduction electrons.
The ionic positions are the same as those of lattice points and the
conduction electrons follow the Bloch waves. We denote the position vector
of the \( l \) th unit cell, relative to an origin located at some ion as:

\[
x (l) = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3,
\]

(3.29)

where \( l_1, l_2, l_3 \) are any integers, positive, negative or zero, which
we refer collectively as \( l \). If there are \( r_1 \) ions in a unit cell the
locations of the \( r_1 \) ions in the unit cell are given by the vectors
\( x (j) \), where \( j \) distinguishes the different ions in the unit cell and
takes the values \( 1, 2, \ldots r_1 \). Thus, in general the position of the \( j \)th
ion in the 1\textsuperscript{th} unit cell is given as:
\[ x_{(lj)} = x_{(l)} + x_{(j)}. \] (3.30)

Let the displacement of the \( j \textsuperscript{th} \) ion in the 1\textsuperscript{th} unit cell, due to thermal fluctuations, from its equilibrium position be \( y_{(lj)} \), so that the displaced position
\[ \tilde{x}_{(lj)} = x_{(lj)} + y_{(lj)}. \] (3.31)

As a result of the thermal fluctuations the total Hamiltonian of the lattice is written as:
\[ H = \frac{1}{2} \sum_{lj} M_j \tilde{u}_{(lj)}^2 + V(R), \] (3.32)
where \( M_j \) is the mass of the \( j \textsuperscript{th} \) ion, \( \tilde{u}_{(lj)} \) is the \( \alpha \)-cartesian component of \( y_{(lj)} \), \( \alpha = x,y,z \). The first term in Eq.(3.32)
represents the kinetic energy of the ions and the second term represents the potential energy of the ions which is assumed to be some function of the instantaneous positions of the ions.

The potential energy includes the direct ion-ion interaction, the exchange overlap interaction between the ions and the ion-electron-ion interaction i.e., an interaction between the ions via the electrons. In the adiabatic approximation the potential can be written as:
\[ V(R) = \sum_{lj} U(R^l - R^j) + E_n(R), \] (3.33)
where \( R^l \) denotes the ionic positions and \( E_n(R) \) is the total energy of the conduction electrons and parameterically depends upon the instantaneous positions of the ions.
For small displacements of the ions, the potential energy of
the system may be expanded in a Taylor's series in powers of the
displacement, retaining powers up to the second order in \( u(l_j) \), i.e.
in the harmonic approximation, we write

\[
V = V_0 + \left( \frac{1}{2} \right) \sum_{l_j a l' j' \beta} V(l_j, l' j') u(l_j) u(l' j').
\]

The subscript zero indicates that the derivatives are to be evaluated
for the equilibrium configuration. \( V_0 \) is just the static potential
energy of the crystal. The linear term is absent since the resultant
force vanishes in the equilibrium configuration. Therefore, the
Hamiltonian of the crystal in the harmonic approximation is

\[
H = V_0 + \left( \frac{1}{2} \right) \sum_{l_j a l' j' \beta} V(l_j, l' j') u(l_j) u(l' j').
\]

The equation of motion of the lattice follows immediately:

\[
M_{\alpha} \ddot{u}_{\alpha}(l_j) = -\delta V/\delta u_{\alpha}(l_j) = -\sum_{l' j' \beta} V_{\alpha \beta}(l_j, l' j') u_{\beta}(l' j'),
\]

where

\[
V_{\alpha \beta}(l_j, l' j') = \frac{\delta^2 V}{\delta u_{\alpha}(l_j) \delta u_{\beta}(l' j')}.
\]

The coefficients \( V_{\alpha \beta}(l_j, l' j') \), which are the second derivatives
of the potential energy in the equilibrium configuration, are the
elements of the force tensor and in general called the force constants.
\( V_{\alpha \beta}(l_j, l' j') \) represents, to a first approximation, the negative of
the force exerted in the \( \alpha \)-direction on the ion \((l_j)\) when the ion 
\((l'_j')\) is displaced a unit distance in the \( \beta \)-direction, all other ions 
being kept at their equilibrium positions. \( V_{\alpha \beta}(l_j, l'_j') \) satisfy the 
following symmetry conditions

\[
V_{\alpha \beta}(l_j, l'_j') = V_{\beta \alpha}(l'_j', l_j) = V_{\alpha \beta}(l-l'_j, j, 0, 0') \quad (3.38)
\]

If the whole of the lattice is subjected to uniform translation, the 
Eq. (3.36) gives the following condition on the force constants

\[
\sum_{l'_j'} V_{\alpha \beta}(l_j, l'_j') = 0. \quad (3.39)
\]

The equation of motion given by Eq. (3.36) is an infinite 
set of simultaneous linear differential equations but their solution 
is simplified by the periodicity of the lattice. We use the running 
wave solution of the Eq. (3.36) in the form

\[
u_{\alpha}(l_j) = (\omega_j)^{-\frac{1}{2}} u_{\alpha}(j) \exp \left[-i(\omega t + \mathbf{r} \cdot \mathbf{q})/\lambda\right] \quad (3.40)
\]

The magnitude of the phonon wavevector \( \mathbf{q} \) is \( 2\pi/\lambda \), \( \lambda \) being the 
wavelength of the lattice wave. \( u_{\alpha}(j) \) is independent of \( l \). Substituting 
Eq. (3.40) in Eq. (3.36), we get

\[
\omega_j^2 u_{\alpha}(j) = \sum_{j''} D_{\alpha \beta}(j, j'') u_{\beta}(j''), \quad (3.41)
\]

where \( D_{\alpha \beta}(j, j'') \) are the elements of the dynamical matrix and are given 
as:

\[
D_{\alpha \beta}(j, j'') = (\omega_j)^{\frac{1}{2}} \sum_{l_j} V_{\alpha \beta}(l_j, l'_j') \exp \left[-i\mathbf{r} \cdot \mathbf{q}(l_j - l'_j')\right]. \quad (3.42)
\]

Thus, the infinite set of simultaneous equations given by Eq. (3.36) is
reduced to a set of \(3r_1\) linear homogeneous equations and this simplification is a consequence of the periodicity of the lattice. The nontrivial solutions of Eq. (3.41) are obtained by equating the determinant of the coefficients to zero, i.e.,

\[
\begin{vmatrix}
D_{\alpha\beta}(g,ij') - \omega^2 \delta_{\alpha\beta} \delta_{ij'}
\end{vmatrix} = 0.
\] (3.43)

It is an equation of \(3r_1\)th degree in \(\omega^2\) and the \(3r_1\) solutions for each value of \(g\) will be denoted by \(\omega_p^2(g)\) where \(p = 1, 2, \ldots, 3r_1\). These \(3r_1\) values of \(\omega_p^2(g)\) for each value of \(g\) can be regarded as the branches of the multivalued function \(\omega(g)\), then the relation

\[
\omega = \omega_p(g),
\] (3.44)

is known as the dispersion relation. For each value of \(\omega_p(g)\) there exists a polarization vector \(e(gp,j)\) whose components are the solutions of the set of Eqs. (3.41) which can now be written as:

\[
\omega_p^2(g) \ e_\alpha(gp,j) = \sum_{ij'} D_{\alpha\beta}(g,ij') \ e_\beta(gp,j').
\] (3.45)

The polarization vectors satisfy the following orthogonality and the closure relations

\[
\sum_{j} e_\alpha^*(g, p, j) \ e_\alpha(g, p', j) = \delta_{pp'} , 
\] (3.46)

and

\[
\sum_{p} e_\alpha^*(g, p, j) \ e_\beta(g, p', j') = \delta_{\alpha\beta} \delta_{jj'} .
\] (3.47)

The different allowed values of \(g\) are determined by the Born-von-Kármán cyclic boundary conditions imposed on \(u(lj)\) and are equal to the number of unit cells in the crystal.
In Toya's self-consistent field method, the elements of the dynamical matrix $D_{\alpha\beta}(q,jj')$, in the adiabatic approximation, for a metallic crystal can be written as the sum of three contributions

$$D_{\alpha\beta}(q,jj') = D_{\alpha\beta}^C(q,jj') + D_{\alpha\beta}^R(q,jj') + D_{\alpha\beta}^E(q,jj'). \quad (3.43)$$

$D_{\alpha\beta}^C(q,jj')$, $D_{\alpha\beta}^R(q,jj')$ and $D_{\alpha\beta}^E(q,jj')$ arise from the Coulomb interaction between the ions, exchange overlap interaction between the ions and from the ion-electron-ion interactions, respectively. A similar separation has also been done by Pick, Cohen and Martin in a more appealing and unified form by introducing the inverse of the microscopic dielectric function. For a system of non-interacting electrons and nuclei these authors write

$$D_{\alpha\beta}(q,jj') = \bar{D}_{\alpha\beta}(q,jj') - \delta_{jj'} \sum_{j'} \bar{D}_{\alpha\beta}(0,jj'), \quad (3.49)$$

where

$$\bar{D}_{\alpha\beta}(q,jj') = \frac{4\pi Z_j Z_{j'}}{V(i_{j,j'})} \sum_{G \neq 0} \frac{(G+G')}{|2\pi G|^2} \epsilon^{-1}(G+G,G+G')$$

$$\times \exp \{ i(G \cdot \bar{x}(j) - G' \cdot \bar{x}(j')) \}. \quad (3.50)$$

$Z_j$ and $Z_{j'}$ are the charges on the $j$th and $j'$th ions at the positions $\bar{x}(j)$ and $\bar{x}(j')$, respectively. Substituting the value of $\epsilon^{-1}(G+G,G+G')$ from Eq. (3.19), the three contributions mentioned in Eq. (3.43) are separated.

$D_{\alpha\beta}^C(q,jj')$ is evaluated with the help of Ewald's $\Theta$-function transformation and the explicit expression is given as:

$$\bar{D}_{\alpha\beta}^C(q,jj') = \frac{4\pi Z_j Z_{j'}}{V(i_{j,j'})} \sum_{G \neq 0} \frac{(G+G')}{|2\pi G|^2} \epsilon^{-1}(G+G,G+G') \exp(-|G'|^2/4 \eta)$$
\[ X \exp \left( i \mathbf{G} \cdot \mathbf{x}(j,j') \right) - \frac{Z_i^2 Z_j e^2}{\sqrt{(i,j,j')}} \sum_k \left\{ \frac{\left[ \mathbf{X}(1,j,j') \right]_\alpha \left[ \mathbf{X}(1,j,j') \right]_\beta}{\left| \mathbf{X}(1,j,j') \right|^5} \right\} \]

\[ X \left[ \text{erf} \left( \eta \left| \mathbf{X}(1,j,j') \right| \right) + \left( \frac{4 \eta^3}{\pi} \frac{\left| \mathbf{X}(1,j,j') \right|^3}{\left| \mathbf{X}(1,j,j') \right|} \right) + \frac{6 \eta \left| \mathbf{X}(1,j,j') \right|}{\sqrt{\pi}} \right] \]

\[ \exp \left( -\eta^2 \left| \mathbf{X}(1,j,j') \right|^2 \right) - \frac{2 \eta \left| \mathbf{X}(1,j,j') \right|}{\sqrt{\pi}} \exp \left( -\eta^2 \left| \mathbf{X}(1,j,j') \right|^2 \right) \]

\[ \exp \left[ -i \mathbf{G} \cdot \mathbf{x}(1,j,j') \right]. \]

Here \( \text{erf} (x) = \frac{1}{2} \left( \frac{1}{\pi} \right)^{\frac{3}{2}} \int_{-\infty}^{x} e^{-\xi^2} d\xi, \)

\[ (3.51) \]

\[ (3.52) \]

and \( \mathbf{X}(1,j,j') = \mathbf{X}(j) - \mathbf{X}(j') - \mathbf{X}(1), \)

\[ (3.53) \]

\( \delta^2 (\omega,j,j') \) is neglected in the present calculations because the core size is small as compared to the atomic sphere radius for the transition metals.

The last contribution to the dynamical matrix which arises due to the interaction of the ions via the electrons can be written as

\[ \mathbf{D}^{\mathbf{E}}_{\alpha\beta}(\omega,j,j') = \sum_{\mathbf{G}} \left( \mathbf{W}(\mathbf{G}) \right)_\alpha \left( \mathbf{W}(\mathbf{G}) \right)_\beta \chi_{j,j}(\mathbf{G}+\mathbf{G}^\prime) \chi_{j,j}(\mathbf{G}+\mathbf{G}^\prime) \exp \left[ i \left( \mathbf{G} \cdot \mathbf{x}(j) - \mathbf{G} \cdot \mathbf{x}(j') \right) \right]. \]

\[ (3.54) \]

Here \( \mathbf{W}(\mathbf{G}) \) is the bare ion potential ascribed to the \( j \)th ion in the unit cell. Putting the value of the density response function \( \chi_{j,j}(\mathbf{G}+\mathbf{G}^\prime) \) from Eq. (3.23), we get

\[ \mathbf{D}^{\mathbf{E}}_{\alpha\beta}(\omega,j,j') = -\sum_{\mathbf{G}} \left( \mathbf{W}(\mathbf{G}) \right)_\alpha \left( \mathbf{W}(\mathbf{G}) \right)_\beta \left[ \frac{1}{1 - \mathbf{W}(\mathbf{G})} \right] \mathbf{W}(\mathbf{G}) \chi_{j,j}(\mathbf{G}+\mathbf{G}^\prime). \]

\[ (3.55) \]
\[ \chi e^{i \mathbf{Q} \cdot \mathbf{x}} (j^t) + \sum_{tt'} \mathbf{W}^t_{tt}(\mathbf{q}) T_{tt'}(\mathbf{q}) \mathbf{W}_t^{t'}(\mathbf{q}) + \sum_{ss'} \mathbf{Y}^{j^t}_{ss}(\mathbf{q}) \]

\[ \chi_s s_{ss'}(\mathbf{q}) \mathbf{Y}^{\alpha}_{ss'}(\mathbf{q}) - \sum_{ts} \mathbf{W}^t_{\alpha}(\mathbf{q}) L_{\alpha}^{s}(\mathbf{q}) \mathbf{Y}^{j^t}_{\alpha}(\mathbf{q}) - \sum_{ts} \mathbf{Y}^{j^t}_{\alpha}(\mathbf{q}) L_{\alpha}(\mathbf{q}) \]

\[ \chi_s s_{ss'}(\mathbf{q}) \mathbf{W}^{j^t}_{\beta}(\mathbf{q}), \quad (3.55) \]

where

\[ \mathbf{W}^{j^t}_{\alpha}(\mathbf{q}) = \sum_{G} (s \mathbf{q} \mathbf{G}) \mathbf{A}_\alpha (s \mathbf{q} \mathbf{G}) \mathbf{W}_\alpha (s \mathbf{q} \mathbf{G}) e^{-1} (s \mathbf{q} \mathbf{G}) e^{i \mathbf{q} \cdot \mathbf{x}(j)), \quad (3.56) \]

and

\[ \mathbf{Y}^{j^t}_{\alpha}(\mathbf{q}) = \sum_{G} (s \mathbf{q} \mathbf{G}) \mathbf{B}_\alpha (s \mathbf{q} \mathbf{G}) \mathbf{W}_\alpha (s \mathbf{q} \mathbf{G}) e^{-1} (s \mathbf{q} \mathbf{G}) e^{i \mathbf{q} \cdot \mathbf{x}(j)) . \quad (3.57) \]

Here \( \mathbf{W}^{j^t}_{\alpha}(\mathbf{q}) \) is the coupling coefficient between the ions on the sublattice \( j \) and the monopole distributions on the sublattice \( t \) via the screened bare ion potential \( \mathbf{W}_j (s \mathbf{q} \mathbf{G}) / \varepsilon_0 (s \mathbf{q} \mathbf{G}) \). Similarly \( \mathbf{Y}^{j^t}_{\alpha}(\mathbf{q}) \) is the coupling coefficient between the ions on the sublattice \( j \) and the dipole distributions on the sublattice \( s \) via the screened bare ion potential. Here it is to be noted that the dipoles and the monopoles are not the point dipoles and monopoles. The first term in Eq. (3.55) represents the simple metal-like electron-ion contribution. The second and the third terms represent the contributions due to monopole-monopole and dipole-dipole interactions, respectively. The last two terms represent the contributions due to the monopole-dipole and the dipole-monopole interactions. In Eq. (3.55), all the terms except the simple metal-like term contain the bond bending or noncentral forces because these contributions couple the two ions together via the polarization produced on the third ion.

The Eq. (3.55) gives a general expression for the dynamical matrix and is similar to that of the screened Breathing shell model. Here \( \varepsilon_0 \) and \( \varepsilon_s \) may be anything not necessarily the ion positions.
If one takes $\mathbf{r}_t$ and $\mathbf{r}_s$ as the ion positions, the formalism becomes equivalent to a generalized shell model. In covalent crystals $\mathbf{r}_t$ and $\mathbf{r}_s$ may be chosen at the centres of the covalent bonds and the intraband transitions are omitted. This gives a model similar to that of bond charge model. If one neglects the polarization produced by the $d$-electrons, one gets the dynamical matrix similar to that for simple metals. If one switches off only the interband transitions one gets exactly the same expression for the dynamical matrix as given by Hanke and Bilz" and Hanke" where only the $s-s$ and $d-d$ intraband transitions are taken into account.

3.2 CALCULATIONS AND RESULTS.

In the section 3.1 we developed a formalism for the dynamical matrix for a lattice with a basis. In this section we first apply the above formalism to study the phonon frequencies for bcc paramagnetic chromium and vanadium which constitute a monoatomic lattice. In this case we take $\mathbf{r}_t = \mathbf{r}_t', \mathbf{r}_s = \mathbf{r}_s'$ and $\mathbf{x}(j) = \mathbf{x}(j')$ and situate them at the origin. This reduces the Coulomb and the ion-electron-ion parts of the dynamical matrix as:

$$\mathbf{F}^G_{\alpha\beta}(q) = (4\pi Z^2 e^2 / \hbar \lambda) \sum_{G} \frac{\alpha(\mathbf{q}+\mathbf{G})\beta(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2} \exp \left(-\frac{|\mathbf{q}+\mathbf{G}|^2}{4\eta^2}\right)$$

$$- (\frac{e^2}{\hbar \lambda}) \sum_{1} \left[ \frac{[\mathbf{x}(1)]_{\alpha}[\mathbf{x}(1)]_{\beta}}{|\mathbf{x}(1)|^5} \right] \left[ 3 \text{erf} \left( \eta \right) \right]$$

$$+ (\pi)^{1/2} \left( 4\eta^3 |\mathbf{x}(1)|^3 + 6\eta |\mathbf{x}(1)| \right) \exp \left(-\eta^2 |\mathbf{x}(1)|^2\right)$$

67
\[
\delta a_\beta \left| x(1) \right| \left( \text{erf} \left( \frac{\eta \left| x(1) \right|}{\sqrt{\pi} \sigma} \right) + 2n(\pi)^{-\frac{1}{2}} |x(1)| \exp(- \eta^2 |x(1)|^2) \right) \exp \left[ -i \frac{q}{\sigma} \cdot x(1) \right],
\]

and
\[
E_{\alpha \beta}(q) = - \sum_{G} \frac{(g+G) \cdot (g+G)}{v(g+G)} \left[ 1 - \varepsilon_{\alpha}^{-1}(g+G) \right] \left[ \mathcal{W}(g+G) \right]^{2}
\]

\[
+ \delta_{\alpha}(q) \left( T(q) \cdot \delta_{\beta}(q) + Y_{\alpha}(q) \right) S(q) Y_{\beta}(q)
- \delta_{\alpha}(q) \left( Y_{\alpha}(q) \gamma_{\beta}(q) - Y_{\alpha}(q) \right) L(q) \gamma_{\beta}(q),
\]

where
\[
\mathcal{W}_{\alpha}(q) = \sum_{G} \left( g+G \right) \mathcal{A}(g+G) \varepsilon_{\alpha}^{-1}(g+G),
\]

\[
Y_{\alpha}(q) = \sum_{G} \left( g+G \right) \mathcal{B}(g+G) \varepsilon_{\alpha}^{-1}(g+G).
\]

The other quantities involved in Eqs. (3.59), (3.60) and (3.61) are the same as defined in section 3.1 except that the subscripts and the superscripts \( t, s \) and \( j \) are dropped.

### 3.2.1 Phonon Frequencies of Paramagnetic Chromium

For the calculation of the phonon frequencies, the separation between the core and the conduction electrons is necessary. In the isotropic band model for paramagnetic chromium shown in the Fig. 2.4, it is found that the two d-sub bands are completely filled, therefore we assume that the core is limited to (3d)\(^4\) and there are two conduction electrons per atom. In Toya's\(^{12}\) self-consistent field method, the phonon frequencies along the three principal symmetry directions can be written as:

\[
\omega^2 = \omega_c^2 + \omega_r^2 + \omega_e^2,
\]

68
where $\omega_c^{a_1}$ and $\omega_c$ are the frequencies due to the direct ion-ion interaction, core-core exchange overlap and ion-electron-ion interactions, respectively. We have taken $\omega_c$ from the values tabulated by Animalu for bcc metals along the three principal symmetry directions $[100]$, $[110]$ and $[111]$ in units of plasma frequency, $\omega_{pl} = (\frac{\pi^2 e^2}{\hbar m})^{1/2}$. $\omega_c$ is completely neglected because of the small core size. Now main interest is to calculate ion-electron-ion contribution to the phonon frequencies.

The functions $B(q,G)$ and $F_{ss}(q)$ were introduced in Eqs. (3.15) and (3.16) to represent the total interband part of the dielectric matrix in a separable form. These are the same as $B(q,G)$ and $F(q)$ for the monoatomic lattice. We represent them as:

$$B(q+G) = a_1|q+G|^2 \exp\left[-\alpha_2|q+G|^2+\alpha_3|G|^2\right]$$

for $|G|^2 \leq p_1$,

$$= a_4 \exp\left[-\alpha_5|G|^2\right] \quad \text{for} \quad |q+G| > p_1, \quad (3.63)$$

and

$$F(q) = -\alpha_6 q s R \left[ \frac{\omega_{RS}^2 - q^2}{4k q} \ln \left( \frac{2k q + q}{2k q - q} \right) \right]. \quad (3.64)$$

The parameters $a_1, a_2, a_3, a_4, a_5, a_6$ and $p_1$ are obtained by fitting the actual total interband part of the dielectric matrix for paramagnetic chromium by the least square fit method with the accuracy of $\pm 10\%$. These parameters are tabulated in Table 3.1. The above functional form gives the correct behaviour of the susceptibility due to the interband part, i.e., it reduces to zero at $|G|^2 = 0$ and again
becomes zero for large values of $|\eta + G|$

It was found by Prakash and Joshi\textsuperscript{30} that, if the bare ion potential calculated with the help of Hartree-Fock-Slater self-consistent scheme is used, the phonon frequencies become imaginary. This difficulty primarily originates from the fact, that the s- and d-wavefunctions which have been used to evaluate the dielectric matrix are neither mutually orthogonal nor orthogonal to the core wavefunctions. An explicit orthogonalization of all these functions is a difficult task and would involve $k$-dependent coefficients of wavefunctions in their combinations.

We, therefore, introduce these corrections by replacing the bare ion potential by a local pseudopotential. We have chosen for simplicity the Harrison simple metal model potential, whose Fourier transform is given as:

$$W(q) = - \left(4\pi Z e^2/\Omega q^2\right) + \beta_c \frac{1}{\left[1 + (qr_c)^2\right]}. \tag{3.65}$$

The first term in Eq. (3.65) represents the Coulomb potential due to the charge $Ze$ while the second term represents the repulsive part of the potential, $\beta_c$ is the strength of this repulsion. The parameter $r_c$ is introduced to bring the desired decay of $W(q)$ for large $q$. The parameters $\beta_c$ and $r_c$ are adjusted to achieve the rapid convergence in the sum over the reciprocal lattice vectors and to obtain an agreement of the calculated and experimental phonon frequencies. This model potential is a good approximation for the s-like electrons. Hanks\textsuperscript{32} pointed out that the potential seen by the d-electrons should be purely Coulombic because of the tight-binding wave-functions used for
the d-electrons. However, in principle the d-electrons are not completely localized and the potential seen by the d-electrons deviates from the central field as pointed out by Animalu in his calculations of TMF. The noncentral forces for the d-electrons are also included in the Harrison transition metal pseudopotential and this gives rise to the hybridization term distinguishing the simple metals and the d-band metals. However, the noncentral potentials for the s- and d-electrons may be of different nature, but in view of the computational difficulties and parameterized nature of the model potential, we use the same potential for the s- and the d-electrons in our calculations of the phonon frequencies.

It is established that the exchange and correlation interactions among the conduction electrons are very important in the calculation of the phonon frequencies. A rigorous calculation of these corrections for d-electrons is too difficult. Therefore, we include these corrections in a phenomenological manner by replacing the Coulomb interaction between the electrons by an effective electron-electron interaction given by Eq. (2.12), where the function \( f_{\text{xc}}(q+\delta) \) stands for the exchange and correlation corrections. We have taken \( f_{\text{xc}}(q+\delta) \) for the s-electrons due to Singwi et al.\(^{71}\).

\[
f_{\text{xc}}(q) = A_p \left[ 1 - \exp \left( - B_p \left( q/\kappa_p \right)^2 \right) \right], \tag{3.66}
\]

where the parameters \( A_p \) and \( B_p \) are taken with the consideration of the inter-electronic distance of the s-electrons.

The exchange and correlation corrections given in Eq. (3.66) are not applied to the d-electrons because it is valid for the free
electrons while the d-electrons are partially localized\textsuperscript{100}. For d-electrons we follow Horiarty\textsuperscript{46} and use the Lindgren\textsuperscript{74} exchange correction in the modified Slater exchange form for which
\[
\xi_{xc}(q) = \frac{5a'}{16k_{F}^{2}}q^{2} \quad \text{for} \quad 5a'q^{2} < 16k_{F}^{2}
\]
\[
= 0 \quad \text{for} \quad 5a'q^{2} \geq 16k_{F}^{2} .
\] (3.67)

Here \(a'\) is a parameter for 3d shell of chromium taken from the calculations of Lindgren et al.\textsuperscript{74} and \(k_{F}^{2}\) is the average Fermi momentum of all the active d-sub bands. The Eq. (3.67) also includes core-conduction exchange while the correlations for the d-electrons are completely neglected which are not yet established. The core-conduction exchange for the s-electrons is also neglected which is assumed to be very small.\textsuperscript{25}

In the interband part of the dielectric matrix we find that the major contribution arises from \(\varepsilon_{dd}\) for \(m \neq n\) and \(\varepsilon_{ds}\) parts where the d-electrons are mobile. Therefore, we use \(f_{xc}(q)\) given by Eq. (3.67) for the interband part also.

Using Eq. (3.65) in Eq. (3.59), the phonon frequencies of paramagnetic chromium are calculated along the three principal symmetry directions \([100]\), \([110]\) and \([111]\). It has been found that the sum converges for 369 reciprocal lattice vectors. The parameters \(\beta_{c}\) and \(r_{c}\) are obtained by matching the phonon frequencies in the longitudinal branch in the \([110]\) direction at the symmetry point \(N\) and at \(q = (0, 0.1, 0.0, 0.0)\) in reduced units. The parameters \(\beta_{c}\) and \(r_{c}\) are found to be 7.5 and 0.25, respectively. The calculations are extended along
all the three principal symmetry directions and these results are shown in Fig. 3.1 by the dashed lines.

Animalu\textsuperscript{55} generated transition metal model potential by examining the spectroscopic data for large number of 3d, 4d and 5d series elements in the periodic table (the Fourier transform of the Animalu TMP is given in Appendix F). In this model potential, the parameter $A_2 \approx (E_g^2 - E_d^2)^{-1}$ is strongly dependent on the energy and gives s-d hybridization and provides an evidence for the resonance model of the transition metal d-bands in the framework of pseudopotential\textsuperscript{45}. We also calculated the phonon frequencies of paramagnetic chromium using the Animalu TMP in conjunction with our dielectric function. Because here the ionic charge is $Z = 2$ (according to our isotropic band model) for paramagnetic chromium and we are using a different dielectric function, therefore, parameters are renormalized to get an agreement of the phonon frequencies with the experimental values. A similar renormalization was also done by Animalu in conjunction with the free electron dielectric function. In our calculations the dielectric function is definitely an improved one. In this calculation we have taken the contribution due to the s-d hybridization, represented by parameter $A_2$, to be the same as taken by Animalu\textsuperscript{55} and varied $A_0$, $A_1$ and $R_m$ so that $A_0$ is as near to $Z/R_m$ as possible as discussed by Animalu and Heine\textsuperscript{101}. The electronic charge is taken to be unity (atomic units) and not the effective electron charge because the orthogonalization of the core and the conduction electron wavefunctions is not explicitly included in our calculations of the dielectric matrix. The parameters are obtained by
matching the phonon frequencies in the longitudinal branch of [110] direction at the two points mentioned in the case of the Harrison model potential. These parameters are tabulated in Table 3.2. The phonon frequencies obtained by using the Animalu TMP are also shown in the Fig. 3.1 by the solid lines. The theoretical results are compared with the experimental values of the phonon frequencies taken from Muhlestein et al. The overall agreement with the experimental values is reasonable except for the transverse branches in the [110] direction.

In the present calculations of paramagnetic chromium it is found that in the longitudinal branches, the maximum contribution of the local field corrections is 15% which in any case cannot be neglected. But in transverse branches the contribution is very small. It is because in fcc and bcc crystals the diagonal contribution cancels the non-diagonal contribution in the transverse branches, therefore, the transverse branches are not renormalized by the d-type contribution to the dynamical matrix. But in the longitudinal branches the diagonal and the non-diagonal contributions sum up to a maximum of 15% and therefore the local field corrections contribute most in the direction of propagation.

There are various anomalies in the phonon spectra of paramagnetic chromium. The Fermi surface of chromium shows electron and hole pockets and electron and hole surfaces near some symmetry points and the existence of these has been established by the de Haas van Alphen studies on pure chromium. The anomalies may occur either at the extremal portions of the Fermi surface (Kohn anomalies) or at wave-
vectors which separate the nesting portions of the Fermi surface of a crystal. Anomalies like softening of the longitudinal branches appear in our calculations as shown in the Fig. 3.1 which are also found experimentally. In the longitudinal branches in the [100] direction the softening occurs at \( q = 0.7158 \) (atomic units) which is equal to the Fermi momentum of s-band and the d-sub band which contributes maximum towards the dielectric matrix. The softening of the longitudinal branch in the [111] direction occurs at \( q = 0.4387 \) (atomic units). The softening of the longitudinal branches appears in our calculation approximately at the same value of the wavevector \( q \) at which it is experimentally found. A dip in the longitudinal branch in the [111] direction, is also observed at \( q = 0.6928 \) which in our calculations is more pronounced and is found at \( q = 0.8082 \).

It is found in our calculations that the contribution due to the interband part is relatively small as compared with the intraband part. In the [110] and [111] directions the longitudinal branches show good agreement with the experimental values but in the [100] direction longitudinal branch is lower by 15% than the experimental values. The transverse branches along [100] and [111] directions are lower approximately by 18% but in the [110] direction the calculated phonon frequencies are too low as compared to the experimental values. From the Fig. 3.1 we also notice that both the model potentials give approximately the same values along all the polarization branches. This is because of the parameterized nature of the pseudopotential.

3.2.2 Phonon Frequencies of Vanadium.
It has been found in the isotropic band model of vanadium, shown in the Fig. 27, that one of the d-sub bands is completely filled. Therefore, in the present calculations the core is limited to $(3d)^2$ configuration and there are three conduction electrons per atom. We represent the total interband part in the separable form given in Eq. (3.14). The functional forms of $B(q+G)$ and $F(q)$ are the same as given by Eqs. (3.63) and (3.64). The parameters $a_1, a_2, a_3, a_4, a_5, a_6$ and $p_1$ are obtained by the least square fit of the actual interband part of the dielectric matrix within an accuracy of $10\%$. These parameters are also given in the Table 3.1. The exchange and the correlation corrections for the $s$- and the $d$-electrons are applied in the same manner as in the paramagnetic chromium.

Since the Animalu TIP is better based, therefore, we use only the Animalu TIP in the present calculations of the phonon frequencies. The s-d hybridization contribution, represented by the parameter $A_2$, is taken to be the same as given 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 H. These parameters are also given in the Table 3.2. The calculated phonon frequencies are compared, in Fig. 3.2, with the experimental data due to Collina et al. The agreement between the calculated and the experimental values is reasonable except in the longitudinal branch in the $[100]$ direction and the transverse branch $T_\perp$ in the $[110]$ direction.

In the experimental dispersion relations for vanadium it is observed that the transverse branch $T_\perp$ in the $[110]$ direction rises
with a large slope, approximately equal to that of the longitudinal branch, which is also found in our calculations. 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 observations. The longitudinal and the transverse branches in the [100] direction intersect in our calculations at $q = 0.1$ while in the experimental dispersion curves these intersect at $q = 0.75$. The initial slopes of the longitudinal and the transverse branches in the [100] direction are quite different, but the slopes of the two branches are found almost equal for $q > 0.3$ in our calculations, which is consistent with the observations of Collela et al.\textsuperscript{105} Such a behaviour is also found for $q > 0.2$ by Kashyap et al.\textsuperscript{106} In the longitudinal branch in the [111] direction, the anomalous behaviour is observed at $q = 0.31$, but it is not present in our calculations. The other anomalies in the branches in the [111] direction are also not found in our calculation.

In our calculations of the phonon frequencies, we also include the contribution due to the noncentral forces through the nondiagonal part of the dielectric matrix. This is consistent with the analysis of the interatomic force constants of vanadium based on the experimental phonon dispersion relations. The axially symmetric model\textsuperscript{107,108} does not fit the phonon frequencies. This is an indication of the pronounced asphericity of the charge distribution, which gives rise to noncentral forces. This has also been verified by the results of Weiss and Delmarco\textsuperscript{109} for the 3d orbital population in vanadium.

An overall agreement of the calculated and the experimental
phonon frequencies is reasonable in paramagnetic chromium but poor in vanadium. This is because of the fact that many approximations, as discussed in the chapter 2, are involved in the present calculations. One of the reasons why all the anomalies do not appear in our calculations of phonon frequencies for paramagnetic chromium and vanadium is that we have used the spherical Fermi surfaces for the s- and d-electrons which may not exhibit explicitly all the details of the Fermi surfaces of these metals. The results can further be improved by choosing orthogonalized set of s- and d-wavefunctions and including the band structure effects and the exchange correlation corrections self-consistently. But this is a prohibitively difficult task from the computational point of view. In the present scheme the electron phonon interaction is in a simple reproducible form which can be used to study the other physical properties of these metals.

3.2.3 Form Factor, Energy Wavenumber Characteristic Function and Binding Energy.

In the study of the phonon frequencies of the transition metals we have seen that both the diagonal and the nondiagonal parts of the dielectric matrix are explicitly involved. It is found that the noncentral forces, which are a consequence of the nondiagonal part of the dielectric matrix, also contribute appreciably. One gets tempted to calculate the form factor, the energy wavenumber characteristic function and the other related properties of these metals as they are extensively studied for the simple metals. In the present scheme, the form
factor and the energy wavenumber characteristic function may not be defined as in the simple metals because these quantities become matrices as the dielectric function is a matrix, while it is scalar for the simple metal. However, to have a simple metal-like look on a transition metal, we consider only the total diagonal part of the dielectric matrix which corresponds to the uniform distribution of the s- and the d-electrons and try to estimate the form factor, energy wavenumber characteristic function and the binding energy. A similar analysis was also done by Singh and Prakash\textsuperscript{54} and Moriarty\textsuperscript{46} for the noble metals and by Prakash\textsuperscript{56} and Singh et al.\textsuperscript{55} for nickel, and by Animalu\textsuperscript{55}.

The usual definition of the form factor for the simple metals is

\[ \mathcal{W}'(q+G) = \langle \mathbf{r} | \mathcal{W}(\mathbf{r}) | \mathbf{k} \rangle = (1/\Omega) \int \exp[-i(k+q+G) \cdot \mathbf{r}] \mathcal{W}_s(\mathbf{r}) \exp[i k \cdot \mathbf{r}] \, d\mathbf{r}, \quad (3.68) \]

where \( \mathcal{W}_s(\mathbf{r}) \) is the screened pseudopotential. In the simple metals where the screening function is a scalar, the form factor becomes

\[ \mathcal{W}'(q+G) = \langle \mathbf{r} | \mathcal{W}(\mathbf{r}) | \mathbf{k} \rangle / \varepsilon(q+G) \quad (3.69) \]

where \( \mathcal{W}(\mathbf{r}) \) is unscreened pseudopotential and \( \varepsilon(q+G) \) is the scalar dielectric function. In the present calculations we take \( \varepsilon(q+G) \) as the total diagonal part of the dielectric matrix. Therefore

\[ \varepsilon(q+G) = \varepsilon_0(q+G) - \varepsilon_{\text{intra}}(q+G) - \varepsilon_{\text{inter}}(q+G) \quad (3.70) \]

and the Eq. (3.69) for the form factor is preserved. We calculate the
form factor using only the Animalu TKHP for both the metals paramagnetic chromium and vanadium. These are shown in Fig. 3.3 by the solid and the dashed lines for paramagnetic chromium and vanadium, respectively. The form factor for paramagnetic chromium is larger in magnitude as compared with that of vanadium at small values of $|q+G|$ because the dielectric function for vanadium is larger in magnitude than that of paramagnetic chromium at small values of $|q+G|$. The form factors for both the metals show the oscillatory behaviour at large values of $|q+G|$. The form factor for vanadium is larger in magnitude for large values of $|q+G|$ and decays slowly as compared with that of chromium. The general behaviour of the form factors of both the metals is the same as that for simple metals. A hump is found in the low $|q+G|$ region which is consistent with the Harrison transition metal pseudopotential calculations for copper.  

Again we define the energy wavenumber characteristic function $F(q+G)$, in analogy with the simple metals, as:

$$F(q+G) = - (2\pi Z^2 e^2 / \Omega |q+G|^2 ) F_N(q+G),$$

(3.71)

where normalized energy wavenumber characteristic function $F_N(q+G)$ is given as:

$$F_N(q+G) = [W(q+G)]^2 \left[ 1 - \epsilon^{-1}(q+G) \right],$$

(3.72)

where

$$W(q+G) = (\sum |q+G|^2 / 4 \pi Z e^2 ) W(q+G).$$

(3.73)

The results are calculated for both the metals chromium and vanadium using the Animalu TKHP and are shown in Fig. 3.4. It is
evident from the figure that the function $F_n(q+G)$ for both the metals
decays exponentially at small values of $|q+G|$ and shows oscillatory
behaviour at large values of $|q+G|$. The function $F_n(q+G)$ for vanadium
is larger in magnitude at large values of $|q+G|$ and decays slowly as
compared with that of paramagnetic chromium. The qualitative behaviour
of $F_n(q+G)$ is the same for both the metals.

We also made an attempt to estimate the binding energy of a
transition metal in a manner similar to that for the simple metals.
The cohesive energy per particle of the neutral atoms is given as

$$E_{\text{coh}} = E_T + E_{\text{BI}},$$

where $E_T$ is a, the first ionization energy for monovalent metals, second
ionization energy for divalent metals and so on, $E_{\text{BI}}$ is the binding
energy of the metal which is given as

$$E_{\text{BI}} = E_{\text{os}} + E_{\text{cl}} + E_o + E_x + E_C + E_1 + E_b$$

$$= - \left( \frac{2^2 e^2}{\alpha} / \frac{2(3\pi)}{4} \right) + (1/2) \sum_{i} \nu_{\text{cl}}(E_i)$$

$$+ \left( \frac{3}{5} \right) \frac{N}{\pi} - \left( \frac{3}{4} \right) \frac{N}{\pi} + \sum_{k} \epsilon_{k}^{2} E_{k}^{2}$$

The first term in Eq. (3.75) is the electrostatic energy of the ions, $\alpha$
is the Hakedung constant which is 1.79186 for bcc lattice. The second term
which represents the exchange overlap interaction between the ions is
neglected. The third term which is the average kinetic energy is
calculated using the valency two for the paramagnetic chromium and three for vanadium and the Fermi energy $E_F$ is taken from the detailed band structure calculations. The fourth term which is the exchange energy due to conduction electrons is calculated for the s- and d-electrons separately and then added up. Fifth term is the correlation energy which has been taken from the recent calculations of Vashishta and Singwi. This is also calculated for the s- and d-electrons separately and added up. Here $r_s$ is the interelectronic distance. However, the calculation of correlation energy is hardly justified for the d-electrons because of their tight-binding nature. The sixth term represents core-conduction exchange overlap energy and is calculated using the Animalu TIP, which also includes s-d hybridization. However, it has been found that this term represents the attractive interaction. If we use the Harrison model potential, this term represents a repulsive contribution. The last term represents the so-called band structure energy which is calculated by summing over 459 reciprocal lattice vectors excluding $G = 0$. All the contributions are calculated for both the paramagnetic chromium and vanadium and are tabulated in Table 3.3. The magnitude of the calculated binding energy is higher than the experimental value. The calculated binding energy for vanadium is much higher than the experimental value. However, our estimation of the binding energy is of very elementary nature. Our calculations for the exchange and the correlation energy are very crucial. Also numerous approximations have been included in the calculation of the band structure energy. The contribution to the binding due to the noncentral
forces is completely neglected. The exchange and correlation interactions between the s- and d-electrons and the core-core exchange overlap interaction contribution are also neglected.

3.3 CONCLUSIONS

In this chapter a general formalism is developed for the lattice dynamics of the transition metals using the non-interacting band model. The phonon frequencies for both the metals chromium and vanadium are in reasonable agreement with the experimental values except in a few branches. Some interesting features like anomalies in the phonon spectra are also found although we use a simplified model for the electronic band structure. The contribution of the noncentral forces is found appreciable and is consistent with the experimental results. The estimation of the form factor, energy wavenumber characteristic function and the binding energy is rather of the lowest order. Thus we conclude the chapter by saying that ours is the first attempt to apply a model similar to that of the screened breathing shell model for the calculation of the phonon spectra of the bcc transition metals where a multiband electronic band structure is taken into account.
TABLE 3.1 Parameters for the interband part of the dielectric function and exchange correlation corrections for paramagnetic chromium and vanadium.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Paramagnetic chromium</th>
<th>Vanadium</th>
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<tbody>
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<td>Vanadium</td>
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<tr>
<td>$A_0$</td>
<td>1.600</td>
<td>2.150</td>
</tr>
<tr>
<td>$a_1$</td>
<td>1.080</td>
<td>2.500</td>
</tr>
<tr>
<td>$a_2$</td>
<td>1.400</td>
<td>2.900</td>
</tr>
<tr>
<td>$R_m$</td>
<td>1.700</td>
<td>1.600</td>
</tr>
<tr>
<td>$Z$</td>
<td>2.000</td>
<td>3.000</td>
</tr>
<tr>
<td>$n^*$</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>$R_c$</td>
<td>1.588</td>
<td>1.248</td>
</tr>
<tr>
<td>$\alpha_{\text{eff}}$</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>$</td>
<td>E_c</td>
<td>$</td>
</tr>
</tbody>
</table>
TABLE 3.3  Binding energies of paramagnetic chromium and vanadium in ryd.

<table>
<thead>
<tr>
<th></th>
<th>Paramagnetic Chromium</th>
<th>Vanadium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{es}$</td>
<td>-2.6744</td>
<td>-5.7228</td>
</tr>
<tr>
<td>$E_0$</td>
<td>1.0800</td>
<td>1.3254</td>
</tr>
<tr>
<td>$E_X$</td>
<td>-0.6749</td>
<td>-1.0270</td>
</tr>
<tr>
<td>$E_c$</td>
<td>-0.2097</td>
<td>-0.3215</td>
</tr>
<tr>
<td>$E_{1}$</td>
<td>-0.1226</td>
<td>-0.0899</td>
</tr>
<tr>
<td>$E_{bs}$</td>
<td>-0.2577</td>
<td>-0.0499</td>
</tr>
<tr>
<td>$E_{BI}$ (THOM)</td>
<td>-2.8594</td>
<td>-5.8857</td>
</tr>
<tr>
<td>$E_{BI}$</td>
<td>-2.0110</td>
<td>-3.9265</td>
</tr>
</tbody>
</table>

The experimental binding energy is equal in magnitude to the cohesive energy of the ionized lattice plus the ionization energy of the free atom.
FIGURE CAPTIONS

Fig. 3.1 \( \omega(q) \) vs \( q \) for paramagnetic chromium along the three principal symmetry directions \([100]\), \([110]\) and \([111]\). The solid and the open circles show experimental values for the longitudinal and the transverse branches, respectively. The triangles show \( T_1 \) branch in the \([110]\) direction. The solid lines show phonon frequencies due to the Animalu THP and the dashed lines show phonon frequencies due to the Harrison model potential.

Fig. 3.2 \( \omega(q) \) vs \( q \) for vanadium. The solid lines show the calculated phonon frequencies. 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.

Fig. 3.3 \( \langle k + q \mid \psi_n^0(k) \mid k \rangle \) vs \( q \) for paramagnetic chromium and vanadium. The solid line represents the form factor for paramagnetic chromium and the dashed line shows the form factor for vanadium.

Fig. 3.4 \( F_n(q) \) vs \( |q| \). The solid line represents the normalized energy wavenumber characteristic function for paramagnetic chromium and the dashed line shows that for vanadium.
FIG. 3.2

\[ \omega \text{ (in units of plasma frequency)} \]

\[ \text{Reduced wave-vector } \bar{q} \]
\[ \langle k + q + G | W_S'(\alpha) | k \rangle \] (Ry)

FIG. 3.3