

Phonon frequencies of paramagnetic chromium

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The phonon frequencies of paramagnetic chromium are calculated using the dielectric function which takes into account the local-field corrections. The Animalu-Harrison model pseudopotentials are used for the bare-ion potential and the results are compared with experimental values. The agreement is reasonable except in the transverse branches in the [110] direction. Some anomalies in the phonon dispersion relations are also found.

I. INTRODUCTION

The lattice-dynamical studies of simple metals¹⁻¹⁰ are based on the linear screening of the electron-ion interaction in which only the diagonal part of the dielectric matrix $\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$, where \vec{q} is the phonon wave vector, and \vec{G}, \vec{G}' are reciprocal-lattice vectors, is used to screen the pseudopotential. But in transition metals, the conduction electrons have both free-electron character (*s* or *p*) and localized character (*d*), which is evident from electronic-band-structure calculations.^{11,12} All the *d* subbands are also not completely filled. Therefore, the dielectric function does not reduce to a scalar, but it contains both diagonal and non-diagonal contributions and the latter become responsible for the local-field corrections.

Sinha¹³ proposed a factorization ansatz for the polarizability of insulators and semiconductors, and Hayashi and Shimizu¹⁴ have formulated a dielectric function for transition metals which takes into account local-field corrections, and have applied it to study the effective potential and induced charge density due to an impurity in ferromagnetic nickel. A similar formal theory of dielectric screening for normal insulators and transition-metal compounds was also studied by Sham.¹⁵

Hanke^{16,17} calculated the phonon frequencies of paramagnetic nickel and palladium using the non-

interacting-band model¹⁸ for the dielectric screening, but he neglected the interband parts of the dielectric matrix which were found to be relatively small. In the preceding paper¹⁹ (hereafter referred to as Paper I), we explicitly calculated the dielectric matrix for paramagnetic chromium using the formulation of our earlier paper^{19a} (hereafter referred to as II). We found that in this case, the nondiagonal part is comparable with the diagonal part for large values of the wave vector. Therefore, in this paper we plan to investigate the phonon spectrum of paramagnetic chromium taking into account the complete dielectric function. The scheme of the paper is as follows: The inversion of the dielectric matrix and the expression for the dynamical matrix are given in Secs. II and III, respectively. The calculations and results are presented in Sec. IV and discussed in Sec. V.

II. INVERSION OF THE DIELECTRIC MATRIX

The dielectric matrix in the random-phase approximation can be written as

$$\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}') = \delta_{\vec{G}\vec{G}'} - v(\vec{q} + \vec{G})\chi^0(\vec{q} + \vec{G}, \vec{q} + \vec{G}') \quad (1)$$

Here, $v(\vec{q} + \vec{G})$ is the effective electron-electron interaction potential, and $\chi^0(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$ is the generalized susceptibility matrix given by

$$\chi^0(\vec{q} + \vec{G}, \vec{q} + \vec{G}') = \sum_{\vec{k}, \vec{k}'} \sum_{\substack{l, m \\ l', m'}} \left(\frac{n_{l, m}(\vec{k}) - n_{l', m'}(\vec{k}')}{E_{l, m}(\vec{k}) - E_{l', m'}(\vec{k}')} \right) \langle \psi_{l, m}(\vec{k}) | e^{-i(\vec{q} + \vec{G}) \cdot \vec{r}} | \psi_{l', m'}(\vec{k}') \rangle \langle \psi_{l', m'}(\vec{k}') | e^{i(\vec{q} + \vec{G}') \cdot \vec{r}} | \psi_{l, m}(\vec{k}) \rangle, \quad (2)$$

where \vec{k} and \vec{k}' are Bloch wave vectors, and $\vec{k}' = \vec{k} + \vec{q}$ lies in the first Brillouin zone. *l* and *m* are orbital and magnetic quantum numbers and also act as band indices. $n_{l, m}(\vec{k})$ is the Fermi

occupation probability function. $\psi_{l, m}(\vec{k})$ is the wave function for the Bloch state \vec{k} with energy $E_{l, m}(\vec{k})$. The spin index σ is omitted for the paramagnetic phase and is included in $n_{l, m}(\vec{k})$. We call the factor

in parentheses in Eq. (2) the band structure part, and the remaining term involving the matrix elements, the overlap part of the dielectric matrix.

In our isotropic-band model for chromium, we found that the s band and three d subbands are partially filled. All the intraband and interband transitions between the electrons in the s and d subbands (as described in Paper I) will take place to adjust themselves to the thermal motion of the ions, and therefore, the dielectric matrix will consist of both diagonal and nondiagonal parts, the latter being a consequence of the localized nature of the d electrons. One way to have complete inversion of such a dielectric matrix is to apply the factorization ansatz developed by Sinha *et al.*^{20,21} for insulators and semiconductors and, later on, extended to metals (unpublished work) where intraband transitions also take part in screening. The main philosophy of the factorization ansatz is to separate the band structure and overlap parts of the intraband and interband contributions. This reduces the infinite-dimensional dielectric matrix into a finite-dimensional one, and therefore, inversion becomes possible.

If we treat the s electrons in the free-electron approximation and the d electrons in the tight-binding approximation (as done in Paper II), then the intraband part due to the s electrons reduces to the Lindhard function, and the intraband part of d electrons in the partially filled d subbands reduces to a separable form,

$$\begin{aligned} \epsilon_{dd-\text{intra}}(\vec{q}+\vec{G}, \vec{q}+\vec{G}') \\ = -v(\vec{q}+\vec{G}) \sum_m \Delta_{d_m, d_m}(\vec{q}+\vec{G}) \bar{f}(\vec{q}) \Delta_{d_m, d_m}^*(\vec{q}+\vec{G}'), \end{aligned} \quad (3)$$

where

$$\begin{aligned} \bar{f}(\vec{q}) = \frac{-N\Omega_0}{2\pi^2 e^2} m_{d_m} k_{Fd_m} \\ \times \left(1 + \frac{4k_{Fd_m}^2 - |\vec{q}|^2}{4k_{Fd_m} |\vec{q}|} \ln \left| \frac{2k_{Fd_m} + |\vec{q}|}{2k_{Fd_m} - |\vec{q}|} \right| \right). \end{aligned} \quad (4)$$

$\Delta_{d_m, d_m}(\vec{q}+\vec{G})$ are the same functions as defined in Paper II. k_{Fd_m} and m_{d_m} are the Fermi momentum and the effective mass for the electrons in the m th parabolic d subband. Ω_0 is the atomic volume, e is the electronic charge, and N is the number of unit cells in the crystal. It has been pointed out in Paper I that in the isotropic- d -band model, the m component of d wave functions mutually hybridize, and therefore, the assignment of a magnetic quantum number m to a particular d subband does not remain valid. Therefore, we number the d subbands from 1 to 5 in ascending

order of energy. We calculate the contribution from each d subband for all the five m components and average them with equal weight. Such an average has also been done by Hanke¹⁷ and Brown.²² Therefore,

$$\Delta_{d_i, d_i}(\vec{q}+\vec{G}) = I_0(\vec{q}+\vec{G}), \quad (5)$$

where

$$I_0(\vec{q}+\vec{G}) = \int_0^\infty \mathcal{J}_0(|\vec{q}+\vec{G}|r) R_{3d}^2(r) dr. \quad (6)$$

Here $R_{3d}(r)$ is the $3d$ radial wave function for paramagnetic chromium and has the same analytical expression as in Paper II, and $\mathcal{J}_0(|\vec{q}+\vec{G}|r)$ is the spherical Bessel function of zero order. The subscript i denotes the labeling of d subbands. Therefore, the intraband contribution can be written

$$\begin{aligned} \epsilon_{dd-\text{intra}}(\vec{q}+\vec{G}, \vec{q}+\vec{G}') \\ = -v(\vec{q}+\vec{G}) A(\vec{q}+\vec{G}) f(\vec{q}) A^*(\vec{q}+\vec{G}'), \end{aligned} \quad (7)$$

where

$$A(\vec{q}+\vec{G}) = I_0(\vec{q}+\vec{G}) \quad (8)$$

and

$$\begin{aligned} f(\vec{q}) = \frac{-N\Omega_0}{2\pi^2 e^2} \sum_i m_{d_i} k_{Fd_i} \\ \times \left(1 + \frac{4k_{Fd_i}^2 - |\vec{q}|^2}{4k_{Fd_i} |\vec{q}|} \ln \left| \frac{2k_{Fd_i} + |\vec{q}|}{2k_{Fd_i} - |\vec{q}|} \right| \right). \end{aligned} \quad (9)$$

The interband part contains three contributions due to (i) transitions between different d subbands, (ii) transitions from d subbands to the s band, and (iii) transitions from the s band to partially filled d subbands. In our formulation contribution (i) is in separable form, but the other two are not because of the nonorthogonality of s and d wave functions. If we follow Sinha's factorization ansatz and represent the total interband part in some simple separable functional form, we can write

$$\begin{aligned} \epsilon_{\text{total-inter}}(\vec{q}+\vec{G}, \vec{q}+\vec{G}') \\ = -v(\vec{q}+\vec{G}) B(\vec{q}+\vec{G}) F(\vec{q}) B^*(\vec{q}+\vec{G}'). \end{aligned} \quad (10)$$

Here $F(\vec{q})$ and $B(\vec{q}+\vec{G})$ are the functions representing the band-structure and overlap-integral parts of the total interband part of the dielectric function. These functions can be obtained by actual calculations of the total interband part. Therefore, the total dielectric function can be written as

$$\begin{aligned} \epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}') &= \epsilon_0(\vec{q} + \vec{G})\delta_{\vec{G}\vec{G}'} \\ &+ \epsilon_{dd-\text{intra}}(\vec{q} + \vec{G}, \vec{q} + \vec{G}') \\ &+ \epsilon_{\text{total-inter}}(\vec{q} + \vec{G}, \vec{q} + \vec{G}'). \end{aligned} \quad (11)$$

Here the first term arises from purely diagonal contributions which include the free-electron part of the intraband contribution. The second and third terms in Eq. (11) include both the diagonal and the nondiagonal terms. Using Eqs. (7) and

(10) in Eq. (11), the total dielectric matrix can be written

$$\begin{aligned} \epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}') &= \epsilon_0(\vec{q} + \vec{G})\delta_{\vec{G}\vec{G}'} \\ &- \nu(\vec{q} + \vec{G})A(\vec{q} + \vec{G})f(\vec{q})A^*(\vec{q} + \vec{G}') \\ &- \nu(\vec{q} + \vec{G})B(\vec{q} + \vec{G})F(\vec{q})B^*(\vec{q} + \vec{G}'). \end{aligned} \quad (12)$$

After some mathematical manipulation, the inverse of the dielectric matrix can be written

$$\begin{aligned} \epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}') &= \frac{1}{\epsilon_0(\vec{q} + \vec{G}')} \left(\delta_{\vec{G}\vec{G}'} - \frac{\nu(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} [A(\vec{q} + \vec{G})L^*(\vec{q})B^*(\vec{q} + \vec{G}') + B(\vec{q} + \vec{G})L(\vec{q})A^*(\vec{q} + \vec{G}')] \right. \\ &\quad \left. - B(\vec{q} + \vec{G})S(\vec{q})B^*(\vec{q} + \vec{G}') - A(\vec{q} + \vec{G})T(\vec{q})A^*(\vec{q} + \vec{G}') \right), \end{aligned} \quad (13)$$

where

$$L(\vec{q}) = -E(\vec{q})X^*(\vec{q})T(\vec{q}) = -S(\vec{q})X^*(\vec{q})C(\vec{q}), \quad (14)$$

$$\begin{aligned} S(\vec{q}) &= [F^{-1}(\vec{q}) - V(\vec{q}) - X^*(\vec{q})C(\vec{q})X(\vec{q})]^{-1} \\ &= E(\vec{q})X^*(\vec{q})T(\vec{q})X(\vec{q})E(\vec{q}) + E(\vec{q}), \end{aligned} \quad (15)$$

$$\begin{aligned} T(\vec{q}) &= [f^{-1}(\vec{q}) - U(\vec{q}) - X(\vec{q})E(\vec{q})X^*(\vec{q})]^{-1} \\ &= C(\vec{q})X(\vec{q})S(\vec{q})X^*(\vec{q})C(\vec{q}) + C(\vec{q}), \end{aligned} \quad (16)$$

$$V(\vec{q}) = \sum_{\vec{G}} B^*(\vec{q} + \vec{G}) \frac{\nu(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} B(\vec{q} + \vec{G}), \quad (17)$$

$$X(\vec{q}) = \sum_{\vec{G}} A^*(\vec{q} + \vec{G}) \frac{\nu(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} B(\vec{q} + \vec{G}), \quad (18)$$

$$U(\vec{q}) = \sum_{\vec{G}} A^*(\vec{q} + \vec{G}) \frac{\nu(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} A(\vec{q} + \vec{G}), \quad (19)$$

$$E(\vec{q}) = [F^{-1}(\vec{q}) - V(\vec{q})]^{-1}, \quad (20)$$

and

$$C(\vec{q}) = [f^{-1}(\vec{q}) - U(\vec{q})]^{-1}. \quad (21)$$

The proof for Eq. (13) is lengthy but straightforward, therefore, it is not given here.

The density response matrix is defined

$$\chi(\vec{q} + \vec{G}, \vec{q} + \vec{G}') = \frac{-\delta_{\vec{G}\vec{G}'} + \epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')}{\nu(\vec{q} + \vec{G})}. \quad (22)$$

Using Eq. (13) in Eq. (22), it simplifies as

$$\begin{aligned} \chi(\vec{q} + \vec{G}, \vec{q} + \vec{G}') &= -\frac{1}{\nu(\vec{q} + \vec{G})} \left(1 - \frac{1}{\epsilon_0(\vec{q} + \vec{G})} \right) \delta_{\vec{G}\vec{G}'} + \left(\frac{B(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} S(\vec{q}) \frac{B^*(\vec{q} + \vec{G}')}{\epsilon_0(\vec{q} + \vec{G}')} + \frac{A(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} T(\vec{q}) \frac{A^*(\vec{q} + \vec{G}')}{\epsilon_0(\vec{q} + \vec{G}')} \right. \\ &\quad \left. - \frac{A(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} L^*(\vec{q}) \frac{B^*(\vec{q} + \vec{G}')}{\epsilon_0(\vec{q} + \vec{G}')} - \frac{B(\vec{q} + \vec{G})}{\epsilon_0(\vec{q} + \vec{G})} L(\vec{q}) \frac{A^*(\vec{q} + \vec{G}')}{\epsilon_0(\vec{q} + \vec{G}')} \right). \end{aligned} \quad (23)$$

Thus the electron density response splits up into two parts. The first is a purely diagonal part analogous to that in the case of simple metals. The second part is due to the polarization of d electrons and corresponds to a set of dipole and monopole distributions centered on the atomic sites. The dipoles and monopoles interact via the screened electron-electron potential $\nu(\vec{q} + \vec{G})/\epsilon_0(\vec{q} + \vec{G})$ rather than the bare electron-electron potential $\nu(\vec{q} + \vec{G})$. Therefore, the dipoles and monopoles have effective form factors $B(\vec{q} + \vec{G})/\epsilon_0(\vec{q} + \vec{G})$ and $A(\vec{q} + \vec{G})/\epsilon_0(\vec{q} + \vec{G})$, respectively. Looking into Eqs. (17) and (19), we can regard

$V(\vec{q})$ and $U(\vec{q})$ as the coupling coefficients between dipolar and monopolar distributions which interact via the screened electron-electron interaction $\nu(\vec{q} + \vec{G})/\epsilon_0(\vec{q} + \vec{G})$. Therefore, if the factorization ansatz scheme is extended to d -band metals where intraband and interband transitions are important, the novel feature of monopole and dipole distributions is introduced in the theory. However, it is to be noted that these are not point dipoles and monopoles.

If we switch off the interband transitions [i.e., $B(\vec{q} + \vec{G}) = 0$ and $F(\vec{q}) = 0$] Eq. (13) reduces to

$$\epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}') = \frac{1}{\epsilon_0(\vec{q}+\vec{G})} \left(\delta_{\vec{G}\vec{G}'} + \frac{v(\vec{q}+\vec{G})}{\epsilon_0(\vec{q}+\vec{G})} \times \frac{A(\vec{q}+\vec{G})A^*(\vec{q}+\vec{G}')}{f^{-1}(\vec{q}) - \sum_{\vec{G}} \frac{A(\vec{q}+\vec{G})}{|\vec{q}+\vec{G}|^2} v(\vec{q}+\vec{G})/\epsilon_0(\vec{q}+\vec{G})} \right), \quad (24)$$

which is exactly the same expression as that used by Hanke.¹⁷ If we consider the case of simple metals, the terms in large parentheses in Eq. (23) vanish and the density response function becomes scalar. For insulators $\epsilon_0(\vec{q}+\vec{G})=1$ and intraband transitions are also absent. Therefore, we get the dipolar model of screening for ideal insulators. In the case of transition metals, the screening matrix $\epsilon(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$ consists of both the intraband and interband parts, and therefore, all the terms in Eq. (23) are retained, which yields a model similar to the breathing-shell model for insulators.

III. LATTICE DYNAMICS

If the adiabatic and harmonic approximations are valid, the phonon frequencies $\omega_j(\vec{q})$ for wave vector \vec{q} and polarization branch j , in the case of a monoatomic lattice are given by the solution of the determinantal equation,

$$\det |D_{\alpha\beta}(\vec{q}) - M \omega_j^2(\vec{q}) \delta_{\alpha\beta}| = 0, \quad (25)$$

where $D_{\alpha\beta}(\vec{q})$ are the elements of the dynamical matrix, M is the mass of the ion, and α, β are the Cartesian components. For a system of non-interacting electrons and nuclei,^{15,23,24} the dynamical matrix can be written

$$D_{\alpha\beta}(\vec{q}) = \bar{D}_{\alpha\beta}(\vec{q}) - \mathcal{D}_{\alpha\beta}(0), \quad (26)$$

where

$$\begin{aligned} \bar{D}_{\alpha\beta}(\vec{q}) &= \frac{4\pi Z^2 e^2}{\Omega_0} \sum_{\vec{G}, \vec{G}'} \frac{(\vec{q}+\vec{G})_{\alpha}(\vec{q}+\vec{G}')_{\beta}}{|\vec{q}+\vec{G}'|^2} \epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}') \\ &= \frac{4\pi Z^2 e^2}{\Omega_0} \sum_{\vec{G}, \vec{G}'} \frac{(\vec{q}+\vec{G})_{\alpha}(\vec{q}+\vec{G}')_{\beta}}{|\vec{q}+\vec{G}'|^2} \epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}') \end{aligned} \quad (27)$$

and Z is the ionicity. Thus we find that the dynamical matrix is completely determined by the inverse dielectric matrix $\epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$. Eq. (27) can be written

$$\begin{aligned} \bar{D}_{\alpha\beta}(\vec{q}) &= \frac{4\pi Z^2 e^2}{\Omega_0} \sum_{\vec{G}} \frac{(\vec{q}+\vec{G})_{\alpha}(\vec{q}+\vec{G})_{\beta}}{|\vec{q}+\vec{G}|^2} \\ &+ N \sum_{\vec{G}, \vec{G}'} (\vec{q}+\vec{G})_{\alpha} W(\vec{q}+\vec{G}) \chi(\vec{q}+\vec{G}, \vec{q}+\vec{G}') \\ &\times W(\vec{q}+\vec{G}')(\vec{q}+\vec{G}')_{\beta}, \end{aligned} \quad (28)$$

where the Fourier transform of the electron-ion potential

$$W(\vec{q}+\vec{G}) = -4\pi Z e^2 / N \Omega_0 |\vec{q}+\vec{G}|^2. \quad (29)$$

Substituting the value of the inverse dielectric matrix from Eq. (13) into Eq. (27), the dynamical matrix is written

$$\begin{aligned} \bar{D}_{\alpha\beta}(\vec{q}) &= \frac{4\pi Z^2 e^2}{\Omega_0} \sum_{\vec{G}} \frac{(\vec{q}+\vec{G})_{\alpha}(\vec{q}+\vec{G})_{\beta}}{|\vec{q}+\vec{G}|^2} + \frac{4\pi Z^2 e^2}{\Omega_0} \sum_{\vec{G}} \frac{(\vec{q}+\vec{G})_{\alpha}(\vec{q}+\vec{G})_{\beta}}{|\vec{q}+\vec{G}|^2} \left(\frac{1}{\epsilon_0(\vec{q}+\vec{G})} - 1 \right) \\ &+ N \left(\sum_{\vec{G}} (\vec{q}+\vec{G})_{\alpha} B(\vec{q}+\vec{G}) \frac{W(\vec{q}+\vec{G})}{\epsilon_0(\vec{q}+\vec{G})} \right) S(\vec{q}) \left(\sum_{\vec{G}'} (\vec{q}+\vec{G}')_{\beta} B^*(\vec{q}+\vec{G}') \frac{W(\vec{q}+\vec{G}')}{\epsilon_0(\vec{q}+\vec{G}')} \right) \\ &+ N \left(\sum_{\vec{G}} (\vec{q}+\vec{G})_{\alpha} A(\vec{q}+\vec{G}) \frac{W(\vec{q}+\vec{G})}{\epsilon_0(\vec{q}+\vec{G})} \right) T(\vec{q}) \left(\sum_{\vec{G}'} (\vec{q}+\vec{G}')_{\beta} A^*(\vec{q}+\vec{G}') \frac{W(\vec{q}+\vec{G}')}{\epsilon_0(\vec{q}+\vec{G}')} \right) \\ &- N \left(\sum_{\vec{G}} (\vec{q}+\vec{G})_{\alpha} B(\vec{q}+\vec{G}) \frac{W(\vec{q}+\vec{G})}{\epsilon_0(\vec{q}+\vec{G})} \right) L(\vec{q}) \left(\sum_{\vec{G}'} (\vec{q}+\vec{G}')_{\beta} A^*(\vec{q}+\vec{G}') \frac{W(\vec{q}+\vec{G}')}{\epsilon_0(\vec{q}+\vec{G}')} \right) \\ &- N \left(\sum_{\vec{G}} (\vec{q}+\vec{G})_{\alpha} A(\vec{q}+\vec{G}) \frac{W(\vec{q}+\vec{G})}{\epsilon_0(\vec{q}+\vec{G})} \right) L^*(\vec{q}) \left(\sum_{\vec{G}'} (\vec{q}+\vec{G}')_{\beta} B^*(\vec{q}+\vec{G}') \frac{W(\vec{q}+\vec{G}')}{\epsilon_0(\vec{q}+\vec{G}')} \right). \end{aligned} \quad (30)$$

In this derivation, the overlapping between nearest neighbors is completely neglected. This is justified in transition metals like chromium.²⁵ The first term in the above equation denotes the usual ion-ion Coulomb interaction contribution to the dynamical matrix. The second term represents the simple-metal-like electron-ion contribution

where only the scalar screening appears. The third and the fourth terms represent the contribution to the dynamical matrix due to dipole-dipole and monopole-monopole interactions, respectively. The last two terms are contributions due to dipole-monopole and monopole-dipole interactions. As a particular case, if we switch off the interband

transitions, we get for the dynamical matrix the same expression that was given by Hanke¹⁷ in which only intraband transitions are taken into account.

IV. CALCULATIONS AND RESULTS

For the calculation of phonon frequencies, it is necessary to separate the core from the conduction electrons. In the isotropic-energy-band calculations, it is found that the two d subbands are completely filled (Paper I); therefore, we assume that the core is limited to the $3d^4$ configuration and that there are two conduction electrons per atom. In Toya's⁵ self-consistent-field method, the solution of Eq. (25) along the principal symmetry directions can be

$$\omega^2 = \omega_c^2 + \omega_r^2 + \omega_e^2, \quad (31)$$

where ω_c , ω_r , and ω_e are the frequencies due to direct ion-ion interaction, core-core overlap, and ion-electron interactions, respectively. We have taken for ω_c the values, tabulated by Animalu²⁶ for bcc metals, along the principal symmetry directions [100], [110], and [111], in units of the plasma frequency ω_p . Animalu²⁵ pointed out, by calculating the ratio of the core radius to the atomic-sphere radius, that the core-core overlap for transition metals is very small, and therefore, we assume ω_r to be negligible for paramagnetic chromium. Now our main interest is to calculate the ion-electron-ion contribution to phonon frequencies.

In Eq. (30), all the terms except the first contribute towards the ion-electron-ion part of phonon frequencies. In Paper II, the purely diagonal part in the free-electron approximation is given

$$\begin{aligned} \epsilon_0(\vec{q} + \vec{G}) &= 1 + v(\vec{q} + \vec{G}) \frac{Nm_s k_{Fs} \Omega_0}{2\pi^2 \hbar^2} \\ &\times \left(1 + \frac{4k_{Fs}^2 - |\vec{q} + \vec{G}|^2}{4k_{Fs} |\vec{q} + \vec{G}|} \ln \left| \frac{2k_{Fs} + |\vec{q} + \vec{G}|}{2k_{Fs} - |\vec{q} + \vec{G}|} \right| \right), \end{aligned} \quad (32)$$

where

$$v(\vec{q} + \vec{G}) = \frac{4\pi e^2}{N\Omega_0 |\vec{q} + \vec{G}|^2} [1 - f_{xc}(\vec{q} + \vec{G})]. \quad (33)$$

Here k_{Fs} and m_s are the Fermi momentum and the effective mass for the s electrons, respectively. The exchange and correlation corrections are taken into account through the factor $f_{xc}(\vec{q} + \vec{G})$ in the expression for the electron-electron interaction given by Eq. (33). We have taken for the s electrons the $f_{xc}(\vec{q} + \vec{G})$ given by Singwi *et al.*,²⁷

$$f_{xc}(\vec{q} + \vec{G}) = A \left[1 - \exp\left(\frac{-B|\vec{q} + \vec{G}|^2}{k_{Fs}^2}\right) \right], \quad (34)$$

where the parameters A and B depend upon the inter-electronic distance of s electrons.

The intraband contribution to the dielectric function due to d electrons is represented by Eq. (7) which is evidently in separable form in our model formalism. The exchange and correlation corrections given in Eq. (34) are not applied to d electrons because they are valid for free electrons, while the d electrons are partially localized.²⁸ For d electrons we follow Moriarty²⁹ and use the Lindgren³⁰ exchange correction in the modified Slater exchange form for which

$$f_{xc}(\vec{q} + \vec{G}) = \begin{cases} \frac{5\alpha_1 |\vec{q} + \vec{G}|^2}{16k_{Fd}^2}, & \text{for } 5\alpha_1 |\vec{q} + \vec{G}|^2 < 16k_{Fd}^2 \\ 0, & \text{for } 5\alpha_1 |\vec{q} + \vec{G}|^2 \geq 16k_{Fd}^2 \end{cases}. \quad (35)$$

Here α_1 is a parameter for the $3d$ electrons of chromium tabulated by Lindgren *et al.*,³⁰ and k_{Fd} is the average Fermi momentum for the partially filled d subbands. Equation (35) also includes the core-conduction exchange, while the correlations for d electrons which are yet not established, are completely neglected. The core-conduction exchange for s electrons which is very small is also neglected. In the interband part of the dielectric function, we find that the major contribution arises from d - d and d - s parts where d electrons are mobile. Therefore, we use the $f_{xc}(\vec{q} + \vec{G})$ given by Eq. (35) for the interband part also, where k_{Fd} is taken as the average of the Fermi momenta of all the active d subbands.

The functions $B(\vec{q} + \vec{G})$ and $F(\vec{q})$ in the expression for the total interband part are given by

$$B(\vec{q} + \vec{G}) = \begin{cases} \lambda |\vec{q} + \vec{G}|^2 \exp(-\mu |\vec{q} + \vec{G}| + \delta |\vec{q} + \vec{G}|^2), & \text{for } |\vec{q} + \vec{G}| \leq 5.0, \\ A'_1 \exp(-|\vec{q} + \vec{G}|^{1/2}), & \text{for } |\vec{q} + \vec{G}| > 5.0, \end{cases} \quad (36)$$

and

$$\begin{aligned} F(\vec{q}) &= NB'_1 m_s k_{Fs} \left(1 + \frac{4k_{Fs}^2 - |\vec{q}|^2}{4k_{Fs} |\vec{q}|} \ln \left| \frac{2k_{Fs} + |\vec{q}|}{2k_{Fs} - |\vec{q}|} \right| \right). \end{aligned} \quad (37)$$

The functional form of $F(\vec{q})$ is the same as for free electrons. λ , μ , δ , A'_1 , and B'_1 are parameters which have been calculated by fitting the actual total interband contribution (Paper I) in the above functional form by the least-squares method with an accuracy of 10%. The parameters are tabulated in Table I(a). The above functional form

TABLE I(a). Parameters for the interband part of the dielectric function.

λ	μ	δ	A_1'	B_1'
10.0	2.022 38	0.186 74	12.8613	5.0

gives the correct behavior of the susceptibility due to the interband contribution. It is zero at $|\vec{q} + \vec{G}| = 0$ and also becomes zero as $|\vec{q} + \vec{G}|$ becomes very large.

In the core region, the conduction-electron wave function has oscillatory behavior. The mutual orthogonality of the wave functions of the s and d conduction electrons and their orthogonality to the core states gives a repulsive contribution which largely cancels the attractive Coulomb potential in the core region. In the present scheme, the s and d wave functions are not orthogonal; therefore, the bare-ion potential calculated from first principles does not reproduce the real phonon frequencies.¹⁸ To overcome this difficulty, we replace the bare-electron-ion potential by a local pseudopotential. However, it has been shown by Sham⁶ that the structure of Eq. (28) is still preserved. We adopt the Harrison's local pseudopotential,

$$W(\vec{q} + \vec{G}) = \frac{4\pi Z e^2}{N\Omega_0 |\vec{q} + \vec{G}|^2} \left(-1 + \frac{|\vec{q} + \vec{G}|^2}{4\pi Z e^2} \frac{\beta'}{(1 + |\vec{q} + \vec{G}|^2 r_c^2)^2} \right). \quad (38)$$

Here the first term represents the Coulomb part due to the ionic charge, while the second term describes in a phenomenological way the repulsive part of the potential. The parameter β' gives the strength of the repulsive potential, and r_c is the decay radius in units of the Bohr radius. The parameters are determined by matching the phonon frequencies with the experimental values at two points.

Using Eq. (38), in Eq. (30) the phonon frequencies for 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 β' and r_c are obtained by matching the phonon frequencies in the longitudinal branch in the [110] direction at H and at $\vec{q} = (0.1, 0.1, 0.0)$ in reduced units. The parameters β' 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. 1 by dashed lines.

Recently, Animalu²⁵ devised a transition-metal model potential by examining the spectroscopic data for a large number of $3d$ -, $4d$ -, and $5d$ - series elements in the Periodic Table. In this model potential, the parameter $A_2 \approx (E - E_d)^{-1}$ is strongly dependent on the energy, gives s - d hybridization, and provides evidence for the resonance model of transition-metal d bands in the pseudopotential framework.³¹ We have also calculated the phonon frequencies of paramagnetic chromium using the Animalu model pseudopotential, in conjunction with our dielectric function. Because here the ionic charge $Z = 2$ (according to our isotropic

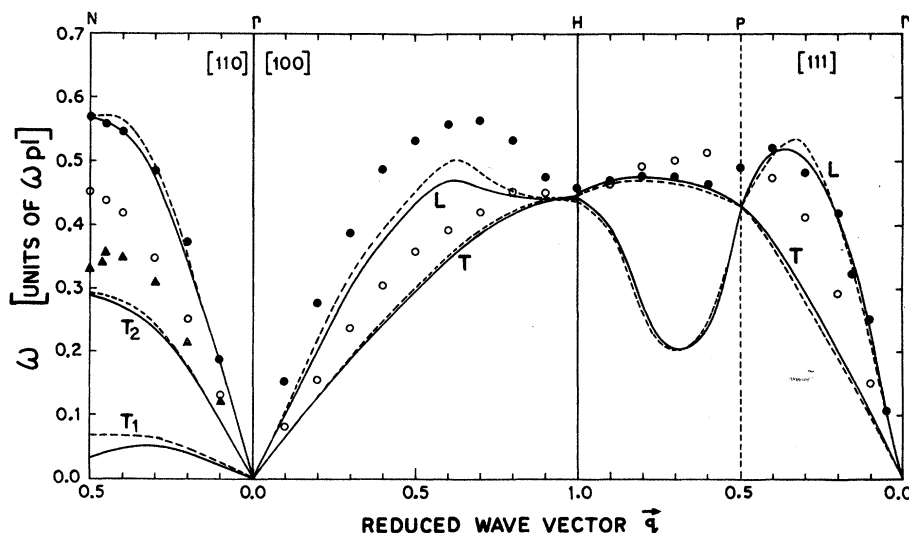


FIG. 1. Phonon frequencies of paramagnetic chromium along the three principal symmetry directions [100], [110], and [111]. The solid and the open circles show experimental values for the longitudinal and the transverse branches, respectively. The triangles show the T_1 branch in the [110] direction. The solid lines show the phonon frequencies due to the Animalu transition-metal model potential and the dashed lines show the phonon frequencies due to Harrison model potential.

model) for paramagnetic chromium, and we are using a different dielectric function, the Animalu potential parameters are renormalized to get agreement of the phonon frequencies with experimental values. In this calculation, we have taken the contribution due to s - d hybridization, represented by the parameters A_2 , to be the same as taken by Animalu,²⁵ 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.⁴ The electronic charge is taken to be unity (in atomic units) and not the effective electron charge because orthogonalization of the core- and conduction-electron wave functions is not explicitly included in our calculation. The parameters are obtained by matching the phonon frequencies in the longitudinal branch of the [110] direction at the two points mentioned in the case of the Harrison model potential. These parameters are tabulated in Table I(b). The phonon frequencies obtained by using the Animalu potential are also shown in Fig. 1 by solid lines. The theoretical results are compared with the experimental values of phonon frequencies taken from Muhlestein *et al.*³² The overall agreement with experimental values is reasonable except for the transverse branches in the [110] direction.

V. DISCUSSION

It was found in Paper I that the local-field corrections are important in the dielectric screening of paramagnetic chromium. Because lattice dynamics are intimately connected with the nature of screening, it is expected that the local-field corrections contribute appreciably towards the phonon spectrum. In the present calculations for chromium, it is found that in the longitudinal branches, the maximum contribution of these corrections is 15%, which cannot be neglected in any case. But in transverse branches the contribution is very small. This is because in fcc and bcc crystals the diagonal contribution cancels the nondiagonal contribution in transverse branches, and therefore, the transverse branches are not renormalized by the d -type contribution to the dynamical matrix. But in longitudinal branches, the diagonal and the nondiagonal contributions sum up to a maximum of 15%, and therefore, local-field corrections contribute most in the direction of propagation.

There are various anomalies^{32,33} in the phonon spectra of bcc transition metals. The Fermi surface of chromium³⁴ shows electron and hole pockets and electron and hole surfaces near some symmetry points, the existence of which has been established by de Hass–Van Alphen studies³⁵ on pure chromium. The anomalies may occur either

TABLE I(b). Parameters of the Animalu transition-metal model pseudopotential. All the parameters are in atomic units except $|E_c|$ which is in rydbergs.

A_0	A_1	A_2	R_m	Ω_0
1.6	1.08	1.40	1.70	80.6
Z	m^*	R_c	α_{eff}	$ E_c $
2.0	1.0	1.588	0.0	0.102

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 longitudinal branches (Kohn anomalies), which are also found experimentally, appear in our calculation as shown in Fig. 1. In the longitudinal branch in the [100] direction, the softening occurs at $q=0.7158$ (atomic units), which is equal to Fermi momentum of the s band and the d subband which contributes most to the dielectric matrix. The softening along the longitudinal branch in the [111] direction occurs at $q=0.4387$ (in atomic units). The softening of longitudinal branches appears in our calculation approximately at the same value of the wave vector \vec{q} at which it is experimentally observed. A dip, in the longitudinal branch in the [111] direction, is also observed at $q=0.6928$, but in our calculations it is more pronounced and is found at $q=0.8082$. One of the reasons why all the anomalies do not appear in our calculation is that we have used a spherical Fermi surface for s and d electrons which may not exhibit explicitly all the details of the Fermi surface.

It has been found in our calculations that the contribution due to the interband part is relatively small as compared to that of the intraband part. In the [110] and [111] directions, longitudinal branches show good agreement with experimental values but in the [100] direction the longitudinal branch is lower by 15% than the experimental values. The transverse branches along the [100] and [111] directions have lower values approximately by 18%, but in the [110] direction agreement is not good. From Fig. 1 we see that both model potentials give approximately the same values along all the polarization branches. This is because of the parametrized nature of the pseudopotentials.

We conclude our paper by saying that ours is the first attempt to apply a screened breathing-shell model to calculate the phonon frequencies of a bcc transition metal. The agreement between theoretical and experimental values can further be improved if we properly take into account the

local-field corrections and s - d hybridization, but this may lead to an enormous amount of computations.

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