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(ricevuto il 25 Agosto 1988)

Summary. — A semi-first principle (SFM) model using the concept of a rigid-shell moving relative to its nucleus to simulate the response of the d-electrons has been proposed for studying lattice dynamics of transition metals which belong to the h.c.p. structure. The long-range interaction between ion-ion as well as shell-shell via conduction electrons is described using the screened potential and the short-range interaction is described using two-body and three-body unpaired forces between cores as well as shells. Elastic constants, phonon dispersion curves and thermal properties, e.g. lattice specific heat, Debye characteristic temperature of three prominent transition metals (Zr, Hf, Tt) have been calculated and compared with the experimental results.

PACS 63.10 — General theory.

1. — Introduction.

The methods of soft X-ray spectroscopy have established that in the crystals of transition metals, the ns, np and (n − 1)d electron states of the free atom broaden into overlapping bands so that the electrons concerned are in the hybrid (spd) states. All these metals exhibit a large electronic specific heat. Recent work on the phonon dispersion relations from the momentum and energy changes in the inelastic scattering of the slow neutrons has, however, stimulated fresh interest in the study of these metals.

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The first-principle pseudopotential theory (\textsuperscript{(1)}) was found to be incapable to the transition metals among which the noble metals are included as the last members of the series. The failure, of course, arises from the \textit{d}-states. They are not sufficiently tightly bound (nor sufficiently localized) so that we may validly treat them as the same in the metals as in the free atom. At the same time they retain enough of their atomic character that, if they are treated as conduction-band states, the pseudowave function is not smooth, the pseudopotential is very large and perturbation theory is inapplicable. Harrison (\textsuperscript{(2)}) therefore reformulated the pseudopotential theory which met a little success. Recently, Fielek (\textsuperscript{(3)}) developed an altogether different approach for studying the lattice dynamic properties of cubic transition noble metals. This model has proved worthy of explaining the experimental phonon frequencies of cubic transition metals satisfactorily. This model, however, suffers from inherent shortcoming regarding equilibrium of crystal lattice. The derivative of the screened Coulomb interaction energy is not zero as it is for short-range term. This necessitates an external force to be applied to maintain the system of ions and electrons into equilibrium. It may be concluded that no suitable theoretical model has so far been proposed for studying the lattice dynamics of transition metals belonging to h.c.p. structure. The motivation behind the present study is therefore to propose a semi-first-principle theoretical model (SFM) for studying the lattice dynamics of h.c.p. transition metals.

2. The model.

In the case of transition metal the atoms in a solid are assumed to be composed of three entities: i) the conduction electrons which are spread throughout the solid, ii) a shell of outermost \textit{d}-electrons, and iii) the ion core, which consists of nucleus plus the remaining core electrons which are taken to move rigidly with the nucleus. From the first principles within the harmonic approximation, the vibrational energy of the system of atoms can be written as

\begin{equation}
\hat{\varphi} = \tilde{\varphi}^{\text{c-c}} + \tilde{\varphi}^{\text{d-d}} + \tilde{\varphi}^{\text{c-d}} - \frac{\varepsilon - 1}{\varepsilon} \tilde{\varphi}^{\text{c-c}} + \tilde{\varphi}^{\text{d-d}},
\end{equation}

where \(\tilde{\varphi}^{\text{c-c}}\) is the second-order change in the potential energy with respect to the displacement of ion core and due to the interaction between the ion cores. \(\tilde{\varphi}^{\text{d-d}}\) is the second-order change in the potential energy between \textit{d}-electron shells. \(\tilde{\varphi}^{\text{c-d}}\)

and \( \hat{\phi}^{e-e} \) are second-order changes arising from the interaction between the conduction electrons and the ion core and the shell of \( d \)-electrons, respectively. \( \varepsilon \) is the dielectric function arising from the interaction between the conduction electrons. Similarly \( \hat{\phi}^{e-d} \) is the change in the potential arising from the interaction between the ion core and its shell of \( d \)-electrons.

Since ion cores are well localized, the interaction between them can be taken as Coulomb interaction between the point charges. The interaction between conduction electrons and the ion core and the \( d \)-electrons can be considered as an interaction of the conduction electrons with the respective potentials arising from the ion core and \( d \)-electrons.

The potential energy terms in eq. (1) are dependent on the product of the displacements of the ion cores and \( d \)-electron charge distributions. It may therefore be written as

\[
\hat{\phi} = \hat{\phi}^{e-e}(U(l, c) U(l', c')) - \frac{\hat{\phi}^{e-e}(U(l, c) U(l', c'))}{\varepsilon} + \frac{\hat{\phi}^{e-d}(U(l, d) U(l', d'))}{\varepsilon} + \frac{\hat{\phi}^{e-d}(U(l, d) U(l', d'))}{\varepsilon}.
\]

The first three terms are the analogous to the potential energy terms for the simple metals. Let us replace these terms by \( \hat{\phi}_1 \). The next three terms are due to the shell of the \( d \)-electrons. These may be replaced by \( \hat{\phi}_2 \). Thus

\[
\hat{\phi} = \hat{\phi}_1(U(l, c) U(l', c')) + \hat{\phi}_2(U(l, d) U(l', d')) + \hat{\phi}^{e-d}(U(l, c) U(l', d')).
\]

\[ U(l, c) \] and \( U(l', c') \) are the displacements of the cores designated by \( c \) and \( c' \) situated within \( l \)-th and \( l' \)-th unit cells. Likewise \( U(l, d) \) and \( U(l', d') \) are the similar terms representing displacements for corresponding shells. The potential energy \( \hat{\phi}_1 \) obviously consists of i) core-core, and ii) core and conduction electrons interactions. The former gives rise to short-range forces whereas the latter gives rise to long-range forces. Likewise, \( \hat{\phi}_2 \) may also be regarded to consist of similar terms.

Within the Born-Oppenheimer and harmonic approximations the ionic motion is determined by the Schrödinger equation

\[
(T(R) + \hat{\phi}(R)) \psi(R) = E \psi(R),
\]

\( T \) is the kinetic energy of the cores and shells of \( d \)-electrons. The phonon frequencies \( \omega^2(q) \) can be obtained as a solution of the secular determinant

\[
|D(q) - \omega^2 I| = 0,
\]
where \( I \) is the unit matrix. \( D \) is a \((6 \times 6)\) dynamical matrix defined by
\[
D = R - S^{-1} - K.
\]

\( R \) and \( S \) both are again \((6 \times 6)\) dynamical matrices belonging to core-core and shell-shell interactions. \( K \) describes the interaction between the core and its shell of \( d \)-electrons. \( S^{-1} \) is the inverse matrix of \( S \). Thus
\[
R = \begin{pmatrix}
R(q, cc) & R(q, cc') \\
R^*(q, cc') & R(q, cc)
\end{pmatrix}, \quad S = \begin{pmatrix}
S(q, dd) & S(q, dd') \\
S^*(q, dd') & S(q, dd)
\end{pmatrix}
\]

and
\[
K = k^2 \delta_{\alpha\beta},
\]
\( \delta_{\alpha\beta} = 1 \) when \( \alpha = \beta \) and zero when \( \alpha \neq \beta \).

In view of expression (3) the elements of dynamical matrices corresponding to core-core and shell-shell interactions are given by
\[
R_{\alpha\beta}(q, cc') = \frac{1}{M} \left[ \sum_{l, c, c'} \frac{\partial^2 \phi_{1}}{\partial U_{l}(c) \partial U_{l'}(c')} \right] \exp[-i(q \cdot R_c)]_{c = c'},
\]
\[
S_{\alpha\beta}(q, dd') = \frac{1}{m} \left[ \sum_{l, d, d'} \frac{\partial^2 \phi_{2}}{\partial U_{l}(d) \partial U_{l'}(d')} \right] \exp[-i(q \cdot R_c)]_{d = d'},
\]
\[
S_{\alpha\beta}(q, dd) = \frac{1}{m} \left[ \sum_{l, d, d} \frac{\partial^2 \phi_{2}}{\partial U_{l}(d) \partial U_{l}(d)} \right] \exp[-i(q \cdot R_c)]_{d = d'}
\]

\( R_c \) is the equilibrium separation between \((l, c)\)-th and \((l', c')\)-th ions such that \( R_c = (R^0_c - R^0_c) \). Similarly
\[
R_{\alpha\beta}(q, cc') = \frac{1}{M} \left[ \sum_{l, c, c'} \frac{\partial^2 \phi_{1}}{\partial U_{l}(c) \partial U_{l'}(c')} \right] \exp[-i(q \cdot R_c)]_{c = c'},
\]
\[
S_{\alpha\beta}(q, dd') = \frac{1}{m} \left[ \sum_{l, d, d'} \frac{\partial^2 \phi_{2}}{\partial U_{l}(d) \partial U_{l'}(d')} \right] \exp[-i(q \cdot R_c)]_{d = d'},
\]
\[
S_{\alpha\beta}(q, dd) = \frac{1}{m} \left[ \sum_{l, d, d} \frac{\partial^2 \phi_{2}}{\partial U_{l}(d) \partial U_{l}(d)} \right] \exp[-i(q \cdot R_c)]_{d = d'}
\]
where $\alpha, \beta = 1, 2$, $M$ and $m$ are masses of core and shell, respectively, $|_0$ denotes that the derivatives of potential energies have been evaluated when lattice is in equilibrium.

3. - Matrix elements corresponding to core-core interaction.

The potential energy $\hat{\phi}_i$ in eq. (3) obviously consists of 1) core-core and 2) core-conduction electron interactions. The former has the character of short-range interaction whereas the latter is described by long-range interaction. Thus

(11) \[ \hat{\phi}_i = \hat{\phi}_i^{\tau\tau} + \hat{\phi}_i^{\tau r}. \]

Each core of the h.c.p. lattice has six nearest neighbours at a distance $\sqrt{c^2/4 + a^2/3}$, lying on $Z = \pm c/2$ planes, six second neighbours at a distance $a$ in the basal plane and other six third neighbours at a distance $(c^2/4 + 4a^2/3)^{1/2}$ lying on the $Z = \pm c/2$. The reference core in the basal plane is supposed to interact with next nearest neighbours through noncentral interaction having the character of general tensor force whereas the cores of nonbasal planes are considered to interact with the reference core through radial as well as tangential forces.

Let the displacements of the reference core and its neighbour from their normal positions be $U_0$ and $U_{jmn}$. The total potential energy $\hat{\phi}_i^{\tau\tau}[R_c]$, when expanded in a Taylor series, gives

(12) \[ \hat{\phi}_i^{\tau\tau} = \sum_{j=1}^3 \left\{ \frac{1}{R_c} \left( \frac{d\hat{\phi}_i^{\tau\tau}}{dR_c} \right)_{R_c=R_j} \left( R_{jmn} \cdot (U_{jmn} - U_0) + \frac{1}{2} |U_{jmn} - U_0|^2 \right) + \right. \]

\[ + \left. \frac{1}{2} \frac{1}{R_c} \left[ \frac{d}{dR_c} \left( \frac{1}{R_c} \left( \frac{d\hat{\phi}_i^{\tau\tau}}{dR_c} \right) \right) \right]_{R_c=R_j} \left( R_{jmn} \cdot (U_{jmn} - U_0) \right)^2 \right\}, \]

where $j = 1$ for first neighbour and 3 for third neighbour. $R_{jmn}$ represents the position coordinates of neighbouring atoms in equilibrium. The higher terms in the expansion of Taylor series have been neglected. $l mn$ represent the direction cosine of the line joining the reference core and nearest neighbour. In this case the first derivative of the potential energy $(d\hat{\phi}_i^{\tau\tau}/dR_c)_{R_c=R_j}$ is not equal to zero. This is because our potential energy $\hat{\phi}(|R_c|)$ does not represent the entire potential determining the equilibrium distance $R_c$.

Let $\beta_c$ and $A_{2c}$ correspond to the expression

(13) \[ \left( \frac{1}{R_c} \frac{d\hat{\phi}_i}{dR_c} \right)_{R_c=R_j} \quad \text{and} \quad \left( \frac{1}{R_c} \frac{d}{dR_c} \left( \frac{1}{R_c} \frac{d\hat{\phi}_i}{dR_c} \right) \right)_{R_c=R_j} \]
for second neighbour and let $\gamma_3$ and $A_3$ be the similar quantities for third neighbour.

$\alpha_1$ and $\alpha_2$ are the force constants which adequately cover core-core tensor interaction for the second neighbour. The expressions for matrix elements are given in the appendix.

The matrix elements corresponding to the long-range part of the potential energy $\varepsilon_1$ have been obtained using the screened Coulomb potential.

In the case of transition metals conduction electrons screen the potential field of core as well as shells of $d$-electrons (\(^1\)). Obviously the strength of the screening is partitioned through a parameter $P$ into two parts. For core-core interaction the screened Coulomb potential (\(^2\)) is of the form

$$\varepsilon_1^{cc}(R_c) = \frac{1 - P}{R_c} \exp[-\lambda R_c],$$

where $\lambda$ is the screening parameter such that

$$\lambda = \sigma r_o^{1/2} K_F.$$

$\sigma$ takes the value 0.353 in Bohm-Pines theory (\(^3\)) and 0.814 in Thomas-Fermi theory (\(^4\)). $r_o$ is the interelectron spacing and $K_F$ is the Fermi wave vector.

The elements of dynamical matrix for the long-range part are as follows:

\[ R_{ij}^{cc}(q, cc) = (1 - P) A_p \left[ \sum_\omega \frac{(q + h)_i (q + h)_j G^2(x_\omega)}{|q + h|^2 + \lambda^2 f(t_i)} - \sum_{k=1}^n \frac{\hbar h_{\omega k} (1 + \cos (\hbar \cdot r_{12}))}{|q + h|^2 + \lambda^2 f(t_i)} G^2(x_\omega) \right]. \tag{15} \]

\[ R_{ij}^{cc}(q, cc') = (1 - P) A_p \left[ \sum_\omega \frac{(q + h)_i (q + h)_j}{|q + h|^2 + \lambda^2 f(t_i)} \exp [i (q + h) \cdot r_{12}] \right]. \tag{16} \]

$r_{12}$ is the vector distance between two cores in the unit cell. Here $A_p$ is a parameter which depends upon the structure of the lattice. Its value is obtained in the long wavelength limit ($q \to 0$). For h.c.p. structure $A_p$ is $(\sqrt{3}/4) a^2 c K_n \lambda^2$ where $K_n$ is the bulk modulus of the electron gas and $(\sqrt{3}/4) a^2 c$ is the atomic volume. The summation in eqs. (15) and (16) extends over the reciprocal lattice

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vector $\mathbf{h}$. The expressions for functions $f(t)$ and $G(x)$ as appearing in the matrix elements are as follows:

$$f(t) = 0.5 + \frac{1 - t^2}{4t} \ln \left| \frac{1 + t}{1 - t} \right|$$

with

$$t_1 = |\mathbf{q} + \mathbf{h}|/2K_F \quad \text{and} \quad t_2 = |\mathbf{h}|/2K_F$$

and

$$G(x) = 3(\sin x - x \cos x)/x^5$$

and

$$x_1 = |\mathbf{q} + \mathbf{h}| \cdot r_e, \quad x_2 = |\mathbf{h}| \cdot r_e.$$ 

4. - Matrix elements corresponding to shell-shell interaction.

The potential energy $\hat{\phi}_d$ describes

1) $d$-shell--$d$-shell interaction, and

2) $d$-shell--conduction electron interaction.

The former has the nature of short-range interaction and is considered through the tensor-type force. Constants $s_{1d}$ and $s_{2d}$ are restricted up to the first neighbour only. The matrix elements are given in the appendix. The long-range part is described through a screened Coulomb potential for the shell of $d$-electrons. This potential is of the form $(P/R_d) \exp[-\lambda R_d]$. $P$ adjusts the strength of the screening produced by conduction electrons on the shell of $d$-electrons.

The matrix elements corresponding to the long-range part for $d$-shell--$d$-shell interaction are as follows:

$$S_{d+}^{d+}(\mathbf{q}, dd) = PA_p a_{d+}(\mathbf{q}), \quad d = d', \quad (17)$$

$$S_{d+}^{d+}(\mathbf{q}, dd') = PA_p b_{d+}(\mathbf{q}), \quad d \neq d'. \quad (18)$$

5. - Elastic constants.

In the long wavelength limit ($q \to 0$), the waves are effectively propagating as in a continuous medium. The secular determinant (*) as given by eq. (5) is

compared with elasticity determinants in the long wavelength limit and the following expressions for elastic constants have been obtained:

\[ C_{11} = \frac{1}{2 \sqrt{3} c} \left[ \frac{(9x_{1e} + 9x_{1s} + 3X_{3c} + 12X_{3s}) + (4\beta_{2e} + 16\gamma_{3s}) -}{2(\beta_{2e} + \gamma_{3e}) + (X_{3c} + X_{3s})} \right] + 2K_e, \]

\[ C_{12} = \frac{1}{2 \sqrt{3} c} \left[ \frac{1}{3} (9x_{1e} + 9x_{1s} + 3X_{2c} + 12X_{3s}) - (4\beta_{2c} + 16\gamma_{3s}) +}{2(\beta_{2c} + \gamma_{3e}) + (X_{2c} + X_{3s})} \right] + 2K_e, \]

\[ C_{13} = \frac{\sqrt{3}}{2} \frac{c}{a^2} [(X_{2c} + X_{3s}) - 2(\beta_{2c} + \gamma_{3e})] + 2K_e, \]

\[ C_{44} = \frac{\sqrt{3}}{2} \frac{c}{a^2} [(X_{2c} + X_{3s}) + 2(\beta_{2c} + \gamma_{3e})], \]

\[ C_{44} = \frac{1}{\sqrt{3} c} \left[ \frac{3}{2} n^2X_{2e} + \frac{9}{16} n^2X_{3e} + 3(\beta_{2e} + \gamma_{3e}) \right], \]

\[ C_{33} = \frac{1}{\sqrt{3} c} \frac{c}{a^2} \left[ \frac{9}{4} n^2X_{3c} + \frac{9}{16} n^2X_{3s} + 3(\beta_{2e} + \gamma_{3e}) \right] + 2K_e, \]

where

\[ X_{2e} = \frac{A_{2e}}{1 + \frac{3}{4} n^2}, \quad X_{3c} = \frac{A_{3c}}{1 + \frac{3}{16} n^2}, \quad n = \frac{c}{a}. \]

**Cauchy discrepancy.** – In this model Cauchy discrepancy is defined by

\[ C_{13} - C_{44} = 2K_e - 2 \sqrt{3} \frac{c}{a^2} (\beta_{2e} + \gamma_{3e}). \]

The condition of lattice equilibrium may be determined by the minimization of \( \phi \) with respect to the lattice parameters \( a \) and \( c \), that is by the condition (\(^\ast\))

\[ \left( \frac{\delta \phi}{\delta a} \right)_c = 0 \quad \text{and} \quad \left( \frac{\delta \phi}{\delta c} \right)_a = 0. \]

Assuming the electron pressure $P^E$ to be isotropic, we can conclude that

$$\left( \frac{\partial^2 P^E}{\partial \Omega} \right)_c = \left( \frac{\partial^2 P^E}{\partial \Omega} \right)_a = P^E \quad \text{(say)}. $$

The pressure $P^c$ exerted by core and $d$-shell is given by

$$\left( \frac{\partial^2 P}{\partial \Omega} \right)_c = P^c, \quad (P^c)_c + P^E = 0 \quad \text{and} \quad (P^c)_a + P^E = 0, $$

or

$$\beta_{2c} + 4 \gamma_{3c} + \frac{\sqrt{3}}{2} c P^E = 0,$$

and

$$\beta_{2c} + \gamma_{2c} + \frac{a^2}{\sqrt{3} c} P^E = 0.$$

The pressure exerted by the electron gas is assumed to be $P^E = (6/5) K_e$. Thus the following equilibrium conditions are obtained:

$$\beta_{2c} + 4 \gamma_{2c} + \frac{\sqrt{3}}{2} c \cdot \frac{6}{5} K_e = 0 \quad \text{(28)}$$

and

$$\beta_{2c} + \gamma_{2c} + \frac{a^2}{\sqrt{3} c} \cdot \frac{6}{5} K_e = 0 \quad \text{(29)}.$$

Eliminating $K_e$ from eqs. (28) and (29) we get

$$\beta_{2c} + 4 \gamma_{2c} = \frac{3}{2} n^2 (\beta_{2c} + \gamma_{2c}).$$

This is the equilibrium condition of Collins\(^{(4)}\) for vanishing internal stress. Equations (25) and (28) give

$$C_{13} - C_{44} = 4.4 K_e \quad \text{(31)}.$$

It is evident that three-body unpaired as well as volume-dependent long-range forces contribute to Cauchy discrepancy.

Recently, it has been pointed out by Bertoni et al.,\(^{(5)}\) that second-order perturbation theory is inadequate to explain the measured frequencies and the


sequence of the phonon modes along [11\bar{2}0] for some of the h.c.p. metals at K points.

By the group-theoretical study of the lattice dynamics of h.c.p. solids, it can be shown quite generally that at this point there are three modes with eigenvectors polarized in the basal plane, whose frequencies are given in terms of the dynamical matrix by

\[ \omega_k = \left( [R_{11}(q, cc) - S_{11}^1(q, dd) K] + 2 \text{Re} [R_{11}(q, cc) - S_{11}^1(q, dd) K] - \text{Im} [R_{12}(q, cc) - S_{12}^1(q, dd) K] \right), \]

\[ \omega_k^2 = \left( [R_{11}(q, cc) - S_{11}^1(q, dd) K] - 2 \text{Re} [R_{11}(q, cc') - S_{11}^1(q, dd') K] - \text{Im} [R_{12}(q, cc) - S_{12}^1(q, dd) K] \right), \]

\[ \omega_k^3 = \left( [R_{11}(q, cc) - S_{11}^1(q, dd) K] + \text{Im} [R_{12}(q, cc) - S_{12}^1(q, dd) K] \right). \]

Here Re stands for real part and Im stands for imaginary part.

\( \omega_k \) is a doubly degenerate eigenvalue and the other frequencies are not degenerate. If the dynamical properties depend only on pairwise central forces \( \text{Im} [R_{12}(q, cc) - S_{12}^1(q, dd) K] = 0 \) and \( \omega_k = \frac{1}{2} (\omega_k^1 + \omega_k^2) \), so that the degenerate eigenvalue falls between \( \omega_k \) and \( \omega_k^3 \). It is clear that any deviation of the experimental data from this sequence of eigenvalues gives a measure of the importance of many ion forces. Brovman and Kagan (2) have shown that corrections in the dynamical matrix arising from higher- and second-order scattering of conduction electrons by a local pseudopotential give rise to tensor forces. In the present model such forces appear in the first neighbour through the equation

\[ \text{Im} [R_{12}(q, cc)] = 2x_2 [S_{21} - 2S_1 C_2]. \]

Terms like \( S_{21}, S_1 \) and \( C_2 \) have been explained in the appendix.

The present model leads to the conclusion that unpaired three-body forces are of short-range type and such forces play an important role in the study of lattice dynamics of h.c.p. metals.

6. – Numerical computation.

The numerical value for the bulk modulus \( K \) is obtained from eq. (31). The remaining force constants have been calculated with the aid of experimental elastic constants and frequencies along [01\bar{1}0] and [11\bar{2}0] symmetry directions at zone boundaries. The input data for fixing force constants are given in table I, while the evaluated force constants are given in table II.

### Table I. – Input data for evaluating force constants.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Lattice constants (Å)</th>
<th>Elastic constants ($10^{11}$ dyn/cm²)</th>
<th>$\tau_\lambda$ (Å)</th>
<th>$k_F$ (Å⁻¹)</th>
<th>$M$ (a.m.u.)</th>
<th>Experimental frequencies</th>
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<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$c$</td>
<td>$C_{11}$</td>
<td>$C_{12}$</td>
<td>$C_{13}$</td>
<td>$C_{22}$</td>
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<tr>
<td>Zirconium</td>
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<td>5.15</td>
<td>14.34</td>
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<td>16.49</td>
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<td>1.45</td>
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<td>20.44</td>
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<td>Titanium</td>
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<td>4.68</td>
<td>17.61</td>
<td>8.69</td>
<td>6.83</td>
<td>19.05</td>
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</table>

### Table II. – Numerical values of the force constants.

<table>
<thead>
<tr>
<th>Elements</th>
<th>$x_{1s}$</th>
<th>$x_{2s}$</th>
<th>$x_{1s}$</th>
<th>$x_{2s}$</th>
<th>$\beta_{2s}$</th>
<th>$\gamma_{3s}$</th>
<th>$X_{2s}$</th>
<th>$X_{3s}$</th>
<th>$K$</th>
<th>$K_s$($10^{11}$ dyn/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($10^3$ dyn/cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zirconium</td>
<td>2.52</td>
<td>0.021</td>
<td>0.049</td>
<td>0.546</td>
<td>-1.721</td>
<td>0.582</td>
<td>9.802</td>
<td>-0.179</td>
<td>-2.418</td>
<td>0.075</td>
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<tr>
<td>Hafnium</td>
<td>21.900</td>
<td>12.58</td>
<td>0.209</td>
<td>0.306</td>
<td>-7.446</td>
<td>7.272</td>
<td>11.987</td>
<td>2.281</td>
<td>-0.446</td>
<td>0.125</td>
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<tr>
<td>Titanium</td>
<td>26.230</td>
<td>1.170</td>
<td>1.601</td>
<td>2.650</td>
<td>1.281</td>
<td>-1.733</td>
<td>10.237</td>
<td>1.655</td>
<td>-3.110</td>
<td>0.398</td>
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</table>
These force constants have been used to compute phonon dispersion relations along three symmetry directions [0001], [01\overline{1}0] and [11\overline{2}0].

The specific heat $C_v$ has been computed by dividing the frequency spectra in steps of $\Delta \nu = 0.1 \cdot 10^{12} \text{ s}^{-1}$ and the corresponding Debye characteristic temperatures have been plotted as functions of temperature. The specific-heat calculations have been limited only to 10 K because the mesh of the points becomes too coarse to give dependable results below this temperature.

7. - Result and discussion.

i) Zirconium. - The axial ration $c/a$ for Zr is 1.593 which is smaller than for ideal packing for which $c/a$ is 1.633. The elastic constants of Zr have been measured by Fisher and Renken (\cite{Fisher1964}) whereas the phonon dispersion relations were obtained by Stassis et al. (\cite{Stassis1978}), who fitted their experimental data on the basis of a 17-parameter modified axially symmetric (MAS) model. The calculated

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Fig. 1. - Phonon dispersion relations for zirconium along symmetry directions. Experimental points (\(\bullet\), \(\triangle\)) have been shown for comparison.


phonon dispersion relations for zirconium along symmetry directions as obtained from the present work have been plotted in fig. 1, where we have also shown the experimental points for comparison. There exists a very good agreement for all the modes except for $\Gamma A_1$, $\Gamma O_1$ and $L O$ modes along [0110] direction where maximum discrepancy is $\sim 5\%$.

The earliest measurements of the specific heat of Zr are those of Todd (19) in the temperature range $(53 \div 290)$ K and Skinner and Johnston (20) in the range $(14 \div 300)$ K. The agreement between the two sets of observations was attributed to different purities of the specimens. The low-temperature specific heat measurements are due to Estermann et al. (21) and Walcott (22). The earlier workers reported the value of $\gamma_e$ (electronic specific heat coefficient) to be $6.92 \cdot 10^{-4}$ cal/g atom degree$^2$, while Walcott (23) found $\gamma_e$ to be $7.25 \cdot 10^{-4}$ cal/g atom degree$^2$. Burk et al. (24) obtained a value $6.92 \cdot 10^{-4}$ cal/g atom degree$^2$ for $\gamma_e$ from their work on specific-heat measurements.

Results on Debye characteristic temperature as obtained from calculated specific-heat data have been plotted in fig. 2. Calculated results compare well with the experimental data except at low temperatures.

![Figure 2](image)

Fig. 2. – ($\theta_D \sim T$) graph for zirconium. Experimental points • (Burk et al.) and ○ (Walcott) have been shown for comparison. —— theoretical.

ii) Hafnium. – Stassis et al. (25) made use of inelastic-scattering technique for measuring phonon dispersion relations of hafnium in the temperature range $(295 \div 1300)$ K. Theoretical studies on the lattice dynamics of hafnium have been

(22) N. M. WALCOTT: Philos. Mag., 2, 1249 (1957).
reported by Rajput and Kushwaha. The calculated results based on the present model have been plotted and compared with the experimental data in fig. 3. There exists good agreement between theoretical and experimental results except for the TA branch where the maximum discrepancy is 5%.

The specific heat of hafnium has been measured by several workers in different temperature ranges. Burk et al. measured the specific heat in the range (20 \( \pm \) 200) K. These workers have also computed the characteristic temperatures \( \theta_0 \), assuming the electronic specific heat coefficient to be \( 6.00 \times 10^{-4} \text{cal/g atom degree}^2 \). Kneip et al. carried out low-temperature measurements in the range 1.1 to 4.5 K and found values of \( \gamma_e \) and \( \theta_0 \) to be \( 5.16 \times 10^{-4} \text{cal/g atom K}^2 \) and 252 K, respectively.

![Phonon dispersion curves for hafnium](image)

Fig. 3. – Phonon dispersion curves for hafnium. Experimental points (○, △) have been shown for comparison.

Gupta and Dayal (29) and Kushwaha and Rajput (30) have calculated the specific heat of hafnium. In the present work the lattice specific heat \( C \) has been calculated in the usual way. The results for the Debye characteristic temperature have been plotted in fig. 4. The experimental points of Burk et al. (2) have also been plotted for comparison. The electronic contribution has been evaluated by taking \( \gamma_e = 5.16 \cdot 10^{-4}\text{cal/g atom K}^2 \) from the low-temperature measurements of Kneip et al. (29). Our calculated results show a remarkable discrepancy at low temperatures. This is probably due to the contribution of anharmonic terms, which has been totally neglected in the harmonic approximation.

iii) **Titanium.** — Titanium is another metal with \( c/a \) ratio = 1.59. The measurements of temperature dependence of elastic constants of titanium have been performed by Fisher and Renken (28) in the temperature range (4 \( \div \) 1155) K. The inelastic neutron scattering technique has been used to study the lattice dynamics of h.c.p. titanium by Stassis et al. (27).

Among the early workers Kushwaha and Kumar (29) phenomenologically explained the dispersion relation of the titanium taking ionic and electron gas contributions to dynamical matrix. Bajpai (28) obtained an expression for electron interaction by averaging Bhatia’s expression for force at ionic centres over the whole Wigner-Seitz sphere and explained the dispersion curves along [0001] and [0110] directions. The present theoretical model explains the dispersion curves of titanium along all the symmetry directions as shown in fig. 5 with experimental results of Stassis et al. (27).

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Fig. 5. — Phonon dispersion curves for titanium. Experimental points (○, △) have been shown for comparison.

Among the early workers, Kelley (2) determined the atomic heat of titanium in the temperature region (51 ± 298) K. Friedberg et al. (3) determined the specific heat in the low-temperature range (1.8 ± 4.2) K. These authors reported $\gamma_s$ as $8.3 \times 10^{-4}$ cal/g atom degree$^2$. The atomic specific heat of titanium was also determined by Aven et al. (4) in the range (4 ± 15) K and by Kothen and Johnston (5) in the range (15 ± 305) K. From the results of their measurements Aven et al. (4) concluded the value of $\gamma_s$ to be $8.08 \times 10^{-4}$ cal/g atom degree$^2$.

and Debye temperature \((421 \pm 2)\) K. Walcott \((\text{Note} 5)\) from his low-temperature specific-heat measurements between 1.2 and 20 K assigned \(\gamma_e\) a value of \(8.3 \cdot 10^{-4}\) cal/g atom degree\(^2\) which is in good agreement with the values obtained by earlier workers. The latest measurements on the specific heat of titanium at moderate temperature are those of Stalinski and Bieganski \((\text{Note} 6)\). Kneip et al. \((\text{Note} 7)\) also carried out the specific-heat measurements in the low-temperature region \((1.1 \pm 4.5)\) K. They obtained \(\gamma_v\) and \(\theta_0\) to be \(8.01 \cdot 10^{-4}\) cal/g atom degree\(^2\) and \((4.30 \pm 60)\) K. However, Clausius and Franzosni \((\text{Note} 8)\) recommended \(\gamma_v = 14.1 \cdot 10^{-4}\) cal/g atom degree\(^2\). Using electron gas model the specific-heat calculation was done by Gupta and Dayal \((\text{Note} 9)\). There is satisfactory agreement between theoretical and experimental results with \(\gamma_v = 14.1 \cdot 10^{-4}\) cal/g atom degree\(^2\).

\[\text{Fig. 6.} \ (\theta_0/T) \text{ graph for titanium. Experimental points } \bigtriangleup (\gamma_v = 14.1), \bigcirc (\gamma_v = 8.01) \text{ have been shown for comparison. —— theoretical.}\]

It has been found that our results are in good agreement in the temperature range \((60 \pm 140)\) K for both values of \(\gamma_v\). However, \(\theta_0\) is 2.5% more than the experimental value as shown in fig. 6.

** * * * **

The authors express their sincere thanks to Dr. S. K. Mishra, D.B.S. College, Kanpur, and Dr. S. P. Singh, B.H.U., Varanasi, for several useful discussions. One of us (S. K. Srivastava) expresses his gratefulness to Prof. S. K. Handa for the encouragement during the progress of this work.

\((\text{Note} 5)\) N. M. Walcott: Philos. Mag., 2, 1556 (1957).
Matrix elements corresponding to core-core interaction:

\[ MR_{11}(q, cc) = z_{1t}[3 - (C_1 C_2 + 2 C_{21})] + 6(\beta_{2c} + \gamma_{2c}) + 3(X_{2e} + X_{3e}), \]

\[ MR_{22}(q, cc) = 3z_{1t}[1 - C_1 C_2] + 6(\beta_{2c} + \gamma_{2c}) + 3(X_{2e} + X_{3e}), \]

\[ MR_{23}(q, cc) = 6(\beta_{2c} + \gamma_{2c}) + \frac{9}{8} n^2(X_{2e} + X_{3e}), \]

\[ MR_{23}(q, cc) = R_{23} = R_{23} = R_{23} = 0, \]

\[ MR_{11}(q, cc') = -C_{23}[3 X_{2e} D_1 C_1 + 3 X_{3e} D_2 C_2] + \]
\[ + \gamma_{2e}(2 D_2 + 4 C_{21} D_2) + \beta_{2e}(2 D_1 + 4 C_1 D_1), \]

\[ MR_{22}(q, cc') = -C_{23}[X_{2e}(2 D_2 + C_1 D_1) + X_{3e}(C_{21} D_2 + 2 D_1)] + \]
\[ + \gamma_{2e}(2 D_4 + 4 C_{21} D_2) + \beta_{2e}(2 D_1 + 4 C_1 D_1), \]

\[ MR_{23}(q, cc') = -C_{23}\left[ \frac{3}{2} D_2^2 X_{2e} + 3 D_2 C_1 D_1 X_{2e} + D_2 \left( \frac{3}{4} D_2^2 C_{21} + \frac{3}{2} D_1 \right) X_{3e} + \right. \]
\[ + \gamma_{2e}(2 D_4 + 4 C_{21} D_2) + \beta_{2e}(2 D_1 + 4 C_1 D_1), \]

\[ MR_{12}(q, cc') = C_{23}\sqrt{3} i[D_2^2 S_{21} X_{3e} - D_1 S_1 X_{2e}], \]

\[ MR_{13}(q, cc') = 3 n S_{23} \left( D_1 S_1 X_{2e} + \frac{1}{2} D_2 S_{21} X_{3e} \right), \]

\[ MR_{23}(q, cc') = i\sqrt{3} n S_{23} \left( (D_2^2 - C_1 D_1) X_{2e} + (C_{21} D_2^2 - D_1) \frac{X_{3e}}{2} \right). \]

Matrix elements correspond to d-shell electron–d-shell electron interaction:

\[ mS_{11}(q, dd) = z_{1t}[3 - (C_1 C_2 + 2 C_{21})], \]

\[ mS_{22}(q, dd) = 3z_{1t}[1 - C_1 C_2], \]

\[ mS_{23}(q, dd) = 0, \]

\[ mS_{23}(q, dd) = mS_{23}(q, dd) = m[S_{23}(q, dd) = mS_{23}(q, dd) = mS_{23}(q, dd) = 0] \]
and

\[ mS_{11}(q, dd') = mS_{22}(q, dd') = mS_{12}(q, dd') = mS_{23}(q, dd') = 0, \]

where

\[
C_1 = \cos \pi K_a a, \quad C_{21} = \cos 2\pi K_a a, \\
C_2 = \cos \pi K_a \sqrt{3}, \quad C_{23} = \cos \pi K_a c, \\
S_1 = \sin \pi K_a a, \quad S_{21} = \sin 2\pi K_a a, \\
S_2 = \sin \pi K_a \sqrt{3}, \quad S_3 = \sin \pi K_a c/2, \quad S_{23} = \sin \pi K_a c,
\]

\[ D_1 = \exp \left[ \pi iaK_y / \sqrt{3} \right], \quad D_2 = \exp \left[ -2\pi iaK_y / \sqrt{3} \right], \quad D_4 = \exp \left[ 4\pi iaK_y / \sqrt{3} \right], \]

\( q \) is a phonon wave vector such that \( q = 2\pi K \) with components \( q_x, q_y \) and \( q_z \) along \( x, y, \) and \( z \) directions, respectively. \( z_{2a} \) represents the tensor force constant corresponding to shell-shell interaction for second neighbour.

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**RIASSUNTO (*)**

Un modello a principio semi primo (SFM) che usa il concetto di uno strato rigido con movimento relativo al suo nucleo per simulare la risposta degli elettroni d è stato proposto per studiare la dinamica reticolare dei metalli di transizione che appartengono alla struttura h.c.p. Si descrive l'interazione a lungo raggio tra ione-ione e strato-strato via elettroni di conduzione usando il potenziale schermato e l'interazione a corto raggio è descritta usando forze spaziate a due e tre corpi tra i nuclei e gli strati. Sono state calcolate e confrontate con i risultati sperimentali le curve di dispersione dei fononi con costanti elastiche e le proprietà termiche, cioè calore specifico del reticolo, la temperatura caratteristica di Debye di tre importanti metalli di transizione (Zr, Hf, Ti).

(*) Traduzione a cura della Redazione.

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**Теория колебательных спектров переходных гексагональных с плотной упаковкой металлов.**

**Резюме (*)** — Для исследования динамики решетки переходных металлов, которые имеют гексагональную с плотной упаковкой структуру, предлагается модель, использующая концепцию жесткой оболочки, движущейся относительно ее ядра, чтобы смоделировать отклик \( d \)-электронов. Описывается динамоиздействующее взаимодействие между ионами, а также между оболочками через электроны проводимости, используя экранированный потенциал. Короткодействующее взаимодействие описывается с помощью двух-частичных и трех-частичных неспаренных сил между остовами и оболочками. Вычисляются уширение постоянные, фононные дисперсионные кривые и тепловые свойства, т.е. удельная теплоемкость решетки, характеристическая температура Дебая для трех переходных металлов (Zr, Hf, Ti). Полученные результаты сравниваются с экспериментальными данными.

(*) Переведено редакцией.