THE RICE INSTITUTE

PRELIMINARY INVESTIGATION OF THE NORMAL VIBRATIONS
OF WHITE TIN

by
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Introduction

This paper has as its object the preliminary work required for a proposed investigation of the vibrational spectra of \( \beta \)-tin.

The main body of the paper is divided into three sections. The first is an outline of the theory of normal vibrations. The second is the application of the theory to tetragonal white tin. The third is a summary of results.

In its most modern form, the theory is to be found in a paper of Born and Be"gbie\(^1\). Applications of the theory to various solids are to be found in papers of Kellermann\(^2\), Smith\(^3\) and Curien\(^4\). Other papers of particular interest include those of Blackman\(^5\), Montroll\(^6\), Houston\(^7\) and Kroll\(^8\). The series of papers by Blackman deserve special study since his work provided the first quantitative measure of the defect in the Debeye continuum theory. Houston's paper proposed a method of approximating the frequency distribution. The interesting work of Montroll and of Kroll treat the problem by taking the specific heat as a given function and solving an integral equation for the frequency distribution.
1. Theory of Normal Vibrations

In order to avoid the difficulty of boundary conditions for a finite crystal, the theory is developed for an infinite crystal. The Born-v.Karman periodic boundary conditions will be used.

A unit cell of the lattice is described by three vectors \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_3 \). The position of the vertex particle in any other unit cell is then given by

\[
\mathbf{r}^\ell = \mathbf{r}^\ell + \mathbf{a}_1 \ell_1 + \mathbf{a}_2 \ell_2 + \mathbf{a}_3 \ell_3 \quad (\ell^i = \text{an integer}) \tag{1.1}
\]

If there are \( S \) particles per unit cell with masses \( m_k (k = 1, \ldots, S) \) and \( \mathbf{r}^k \) is the position of the \( k \)-th particle relative to the vertex then

\[
\mathbf{r}^k (\ell) = \mathbf{r}^\ell + \mathbf{r}^k \tag{1.2}
\]

defines the equilibrium position of particle \( (\ell) \).

Consider small but otherwise arbitrary displacements \( \mathbf{u}^k (\ell) \) of the particles from equilibrium. The potential energy \( \Phi \) of the deformed lattice can be expanded in powers of the rectangular components of \( \mathbf{u}^k (\ell) \). The constant term can be removed by suitable choice of the zero of potential energy while the linear terms vanish in equilibrium. Therefore, to second order terms,

\[
\Phi = \frac{1}{2} \sum_{\ell, \ell'} \Phi_{\ell \ell'} \mathbf{u}^\ell (\ell) \mathbf{u}^{\ell'} (\ell') \tag{1.3}
\]

where

\[
\Phi_{\ell \ell'} (\ell, \ell') = \frac{\partial^2 \Phi}{\partial \mathbf{r}_\ell (\ell) \partial \mathbf{r}_{\ell'} (\ell')}
\]

(1.4)

and \((\ell, \ell') = 1, 2, 3\). These second derivatives in equilibrium depend only on the difference of cell indices \( \ell \) and \( \ell' \) and
satisfy the condition
\[ \Phi_{\alpha\beta}(k-k') = \pm \Phi_{\beta\alpha}(k-k'). \]
In particular, if \( k' = (0,0,0) \), then
\[ \Phi_{\alpha\beta}(k) = \pm \Phi_{\beta\alpha}(k). \] (1.5)

The equation of motion of a typical particle is, then,
\[ M_k \ddot{u}_k(l) + \sum_{k',\beta} \Phi_{\alpha\beta}(k-k') u_{\beta}(l') = 0. \] (1.6)

If the substitutions
\[ \bar{u}(l) = \sqrt{m_k} u(l) \] (1.7)
and
\[ \bar{D}_{\alpha\beta}(k-k') = -\frac{1}{\sqrt{m_km_{k'}}} \Phi_{\alpha\beta}(k-k') \] (1.8)
are made, the result is
\[ \bar{\ddot{u}}_k(l) + \sum_{k',\beta} \bar{D}_{\alpha\beta}(k-k') \bar{u}_{\beta}(l') = 0. \] (1.9)

A solution of this equation for an independent normal vibration is the plane wave
\[ u(l) = \bar{u}(k)e^{-i\omega t} + i\bar{\theta} \cdot \bar{r}. \] (1.10)

Substituting in (1.9) gives
\[ \omega^2 u(l) - \sum_{k',\beta} \bar{D}_{\alpha\beta}(k-k') \bar{u}_{\beta}(l') = 0 \] (1.11)
where
\[ \bar{D}_{\alpha\beta}(k-k') = \sum_{k'} \bar{D}_{\alpha\beta}(k-k') e^{-i\bar{\theta} \cdot \bar{r}}. \] (1.12)

The set of 35 homogeneous equations (1.11) has for a given value of \( \bar{\theta} \) a non-trivial solution if and only if the determinant
\[ |D(\bar{\theta}) - \omega^2 I| = 0 \] (1.13)
where \( I \) is a \( 35 \times 35 \) unit determinant.

A complete solution of the problem would involve solving
for the roots of (1.13) for all permissible values of the wave vector \( \vec{q} \). The frequency spectrum could then be determined. In practice, it is feasible to solve only for a relatively few wave numbers.

The labor is further reduced by two methods. The first is to assume that interactions involving only, say, first and second neighbors are appreciable. The second is to make use of the symmetry of the lattice to establish equalities among the various constants \( \Phi_{\alpha \beta} \).

Simply because the structure is periodic, it can be shown that

\[
\sum_{\vec{c}', \vec{k}'} \Phi_{\alpha \beta} (\vec{c}', \vec{k}') = 0 \tag{1.14}
\]

and that

\[
\sum_{\vec{k}} \Phi_{\alpha \beta} (\vec{c}, \vec{k}') \chi_\lambda = \sum_{\vec{k}} \Phi_{\lambda \beta} (\vec{c}, \vec{k}') \chi (\vec{c}) \tag{1.15}
\]

These two equations express, respectively, invariance to rigid translations and to rotations. Further, a given kind of lattice will belong to a particular point group. If \( T \) is the matrix representation of one of the operations of the point group, then

\[
\vec{F}(\vec{c}, \vec{k}) = T \vec{F}(\vec{c}, \vec{k}) \tag{1.16}
\]

and

\[
D(\vec{c}, \vec{k}') = T D(\vec{c}, \vec{k}') T. \tag{1.17}
\]

The change of indices in (1.17) is gotten from (1.16).

The possible wave vectors \( \vec{q} \) are determined by the cyclic lattice condition. The vectors of the reciprocal lattice are given by

\[
\vec{c}_i = \frac{\vec{a}_i \times \vec{a}_j \times \vec{a}_k}{\vec{a}_i \cdot \vec{a}_j \times \vec{a}_k}
\]

Cyclic permutation gives \( \vec{c}_2 \) and \( \vec{c}_3 \). The wave vector \( \vec{q} \) is
then given by

\[
\mathbf{q} = 2\pi \left[ \mathbf{g}_1 \mathbf{r}_1 + \mathbf{g}_2 \mathbf{r}_2 + \mathbf{g}_3 \mathbf{r}_3 \right]
\]

If the "grand" unit cell is chosen so that its sides are \( N_a, N_b, \) and \( N_c, \) the periodic boundary conditions require that

\[
e^{i\mathbf{q} \cdot \mathbf{r}} = e^{i\mathbf{q} \cdot \mathbf{r} + \mathbf{N}}.
\]

It follows that

\[
\delta_i = \frac{\xi_i}{N}, \quad \delta_j = \frac{\xi_j}{N}, \quad \delta_k = \frac{\xi_k}{N},
\]

where \( \xi_i, \xi_j, \) and \( \xi_k, \) are integers.

Since the quantities \( \mathbf{q}_{ij} \) are restoring forces per unit relative displacement, they must be expressible in terms of Voigt's constants. The relations are established in the following manner.

Letting

\[
\mathbf{V}(\mathbf{k}) = \mathbf{W}(\mathbf{k}) e^{-i\omega t + i\mathbf{g} \cdot \mathbf{r}}
\]

in (1.6) results in

\[
\omega^2 W_\alpha(\mathbf{k}) = \sum_{\mathbf{k}', \mathbf{p}} C_{\alpha\beta}(\mathbf{k}) W_\beta(\mathbf{k}')
\]

where

\[
C_{\alpha\beta}(\mathbf{k}) = \sum_{\mathbf{k}} D_{\alpha\beta}(\mathbf{k}) e^{-i\mathbf{g} \cdot \mathbf{r}}(\mathbf{k}).
\]

Equation (1.20) may be compactly expressed as

\[
\mathbf{N} \mathbf{W}(\mathbf{k}) = C(\mathbf{g}) \mathbf{W}(\mathbf{k})
\]

where \( \mathbf{N} \) is a 3\( \times \)3 unit matrix multiplied by \( \omega^2 \). \( \mathbf{N}, \mathbf{W} \), and \( C \) may each be expanded in a power series in the components of \( \mathbf{g} \). To second order terms, the expansion of \( C \) is

\[
\mathbf{C}_{\alpha\beta}(\mathbf{g}) = \sum_{\mathbf{k}} D_{\alpha\beta}(\mathbf{k})
\]

\[
\mathbf{C}_{\alpha\beta}(\mathbf{g}) = \mathbf{C}_{\alpha\beta}(\mathbf{g}) + \mathbf{C}_{\alpha\beta}(\mathbf{g})
\]

(5)
Let the expansions of $\mathcal{J}$ and $W$ be expressed by the notation $\mathcal{J}$, $\mathcal{W}$, etc. Substitution into (1.22) and equating of the coefficients of like powers of $\mathcal{J}$ results in the equations

$$\dot{\mathcal{J}} \dot{W} = \dot{\mathcal{J}} \mathcal{W}$$

$$\ddot{\mathcal{J}} \dot{W} + \ddot{\mathcal{J}} \mathcal{W} = \dot{\mathcal{J}} \mathcal{W} + \dot{\mathcal{J}} \dot{W} + \ddot{\mathcal{J}} \dot{W}.$$

A considerable amount of matrix algebra results in the following approximations to the equations of motion:

$$\sum_{\kappa, \lambda} \left\{ \dot{C}_{\kappa \lambda} (\mathcal{J}) \mathcal{W}_{\kappa} (\mathcal{J}) + \sqrt{m_k \lambda} \dot{C}_{\kappa \lambda} (\mathcal{J}) \mathcal{W}_{\lambda} \right\} = 0 \tag{1.24}$$

$$\left( \sum_{\kappa} m_{\kappa} \right) \mathcal{J} \mathcal{W}_{\kappa} = \sum_{\kappa, \lambda} \left\{ \sqrt{m_k \lambda} \dot{C}_{\kappa \lambda} (\mathcal{J}) \mathcal{W}_{\kappa} (\mathcal{J}) + \sqrt{m_k \lambda} \dot{C}_{\kappa \lambda} (\mathcal{J}) \mathcal{W}_{\lambda} \right\} \tag{1.25}$$

where $\mathcal{W}_{\kappa}$ are three arbitrary constants and trivial solutions of the zeroth approximation.

Eliminating $\dot{W}_{\kappa} (\mathcal{J})$ between (1.24) and (1.25) results in

$$\rho \omega^2 \mathcal{W}_{\kappa} = \sum_{\kappa} D'_{\kappa \lambda} (\mathcal{J}) \mathcal{W}_{\lambda} \quad (\rho = \text{density}) \tag{1.26}$$

where $D'_{\kappa \lambda}$ is a function of the quantities $\Phi_{\kappa \lambda}$. Now (1.26) is nothing but the equations for amplitudes from elasticity theory. The coefficients of (1.26) contain the $\Phi_{\kappa \lambda}$ while the coefficients of the elasticity equations contain Voigt's constants. Comparison of the two sets of equations leads to the relation between the $\Phi_{\kappa \lambda}$ and $C_{ij}$ which may conveniently expressed as
The procedure, then, is to evaluate (1.24) and (1.25) for the lattice under consideration; establish (1.26) and (1.27); compare with (1.27) and write down the relations between the $C_j$ and the $\Phi_{\alpha\beta}$ by equating corresponding elements of the two matrices.
2. Application to \( \beta \)-tin

The white tin crystal is built up of tin atoms lying on two equal interpenetrating face-centered tetragonal lattices relatively displaced one-quarter of the way along a body diagonal. The structure is thus quite similar to diamond. (The notation of Smith\(^3\) is used insofar as possible.)

The following diagram will serve to define the lattice parameters and the unit cell and set up a coordinate system.

The vectors of the two particle unit cell are given in terms of rectangular components by

\[
\vec{a}_1 = (0, a, 0), \quad \vec{a}_2 = (a, 0, 0), \quad \vec{a}_3 = (a, a, 0)
\]

where \( 2a = 3.24 \text{ Å} \) and \( 2c = 3.17 \text{ Å} \). The coordinates of the two particles are \((0,0,0)\) and \((\frac{a}{2}, \frac{a}{2}, \frac{c}{2})\). Atoms lying on the same lattice as \( O \) are labelled \( k=1 \), while those lying on the same lattice as \( O' \) are labelled \( k=2 \).
It proves possible here to replace the labelling by simply $\ell$. Table 1 gives the coordinates of first neighbors, their label $\ell$ and the integers $(\ell', \ell^2, \ell^3)$. Table 2 gives the rectangular components of $\vec{F}(\ell)$ for first neighbors.

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<table>
<thead>
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<th>\ell</th>
<th>\ell'</th>
<th>\ell^2</th>
<th>\ell^3</th>
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<tbody>
<tr>
<td>0</td>
<td>-a/2</td>
<td>a/2</td>
<td>0</td>
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<tr>
<td>a/2</td>
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<td>0</td>
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The atoms $O$ and $O'$ each have eight next-nearest neighbors lying on the same face-centered tetragonal lattice. Tables 3, 4, and 5 give the analogous information for next-nearest particles as 1 and 2 give for nearest particles.

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<table>
<thead>
<tr>
<th>\ell</th>
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(5)
\[ \begin{array}{cccccccc}
& 5 & 6 & 7 & 8 & 11 & 12 & 13 & 14 \\
\mathbf{e} & \frac{5}{1} & \frac{6}{12} & \frac{7}{13} & \frac{8}{14} & \frac{7}{5} & \frac{12}{6} & \frac{13}{7} & \frac{7}{8} \\
\mathbf{e}' & 1 & 0 & 0 & 1 & -1 & 0 & 0 & -1 \\
\mathbf{e}^2 & 0 & -1 & 1 & 0 & 0 & 1 & -1 & 0 \\
\mathbf{e}^3 & 0 & 1 & 0 & -1 & 0 & -1 & 0 & 1 \\
\end{array} \]

\[ \begin{align*}
X^x & \quad 5 \quad 6 \quad 7 \quad 8 \quad 11 \quad 12 \quad 13 \quad 14 \\
X_{1}(\frac{e}{zz}) & \quad 0 \quad 0 \quad -a \quad a \quad 0 \quad 0 \quad a \quad -a \\
X_{2}(\frac{e}{zz}) & \quad -a \quad -a \quad 0 \quad 0 \quad a \quad a \quad 0 \quad 0 \\
X_{3}(\frac{e}{zz}) & \quad -c \quad c \quad -c \quad -c \quad c \quad c \quad -c \quad c \\
X_{4}(\frac{e}{zz}) & \quad -c \quad c \quad -c \quad -c \quad c \quad c \quad -c \quad c \\
\end{align*} \]

\[ X_{4}(\frac{e}{zz}) = -X_{1}(\frac{e}{zz}) \]

\( \beta \)-tin belongs to the point group \( D_{4h} \). The matrices which represent operations of this group are

\[ \begin{align*}
T^{1} & = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & T_{e}^{1} & = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} & T_{e} & = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix} \\
T_{4} & = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & T_{4} & = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix} & T_{e} & = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & T_{e} & = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \\
T_{7} & = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix} & T_{7} & = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & T_{e} & = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & -1 \end{pmatrix} & T_{e} & = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \\
T_{8} & = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} & T_{8} & = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 1 \end{pmatrix} & T_{e} & = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 1 \end{pmatrix}
\end{align*} \]

(2.2)

(10)
Obviously, some of the matrices can be expressed as products of others.

Denoting by \( D(\varepsilon) \) the \( 3 \times 3 \) matrix whose elements are the interactions between particles connected by \( F(\varepsilon) \), the relations (1.5), (1.16) and (1.17) will now be used to set up equalities between the interaction constants.

First, (1.5) is equivalent to the statement

\[
\tilde{D}(\varepsilon) = D(\varepsilon)
\]

But, from (1.16)

\[
D(\varepsilon) = T, D(\varepsilon) T^T
\]

which, by actual multiplication, shows that

\[
D(\varepsilon) = D(\varepsilon)
\]

Therefore

\[
\tilde{D}(\varepsilon) = D(\varepsilon)
\]

and all matrices are symmetric.

Using (1.5) again, it is seen that

\[
(11)
\]
\[ D(i) = T_z D(i) T_z^* . \]

Setting
\[ D(i) = -\frac{1}{\mu} \begin{pmatrix} D_n(i) & D_{nz}(i) & D_{n3}(i) \\ D_{nz}(i) & D_{zz}(i) & D_{z3}(i) \\ D_{n3}(i) & D_{z3}(i) & D_{33}(i) \end{pmatrix} \]

and carrying out the multiplication, it is found that
\[ D_n(i) = D_{zz}(i), \quad D_{n3}(i) = D_{z3}(i). \]

Therefore, \( D(i) \) may be expressed as
\[ D(i) = D(\gamma) = -\frac{1}{\mu} \begin{pmatrix} \alpha & \gamma & \delta \\ \gamma & \alpha & \delta \\ \delta & \delta & \beta \end{pmatrix} \]

The same type of analysis shows that \( D(s) \) may be expressed as
\[ D(s) = D(\bar{s}) = -\frac{1}{\mu} \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \mu & 0 \\ 0 & 0 & \nu \end{pmatrix} \]

Using (1.16) and (1.17) each of the other matrices may be expressed similarly. The final results are collected below.

\[ D(\tilde{z}) = D(\tilde{\bar{z}}) = -\frac{1}{\mu} \begin{pmatrix} \alpha & \gamma & -\delta \\ \gamma & \alpha & -\delta \\ -\delta & -\delta & \beta \end{pmatrix} \]

\[ D(\tilde{s}) = D(\tilde{\bar{s}}) = -\frac{1}{\mu} \begin{pmatrix} \alpha & -\gamma & \delta \\ -\gamma & \alpha & -\delta \\ \delta & -\delta & \beta \end{pmatrix} \]

(12)
\[ D(4) = D(4) = -\frac{1}{m} \begin{pmatrix} \alpha & -\gamma & -\delta \\ -\gamma & \alpha & \delta \\ -\delta & -\delta & \beta \end{pmatrix} \]

\[ D(6) = D(6) = -\frac{1}{m} \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \mu & -\nu \\ 0 & -\nu & \tau \end{pmatrix} \]

\[ D(12) = D(12) = -\frac{1}{m} \begin{pmatrix} \mu & 0 & \nu \\ 0 & \lambda & 0 \\ \nu & 0 & \tau \end{pmatrix} \]

\[ D(8) = D(8) = -\frac{1}{m} \begin{pmatrix} \mu & 0 & -\nu \\ 0 & \lambda & 0 \\ -\nu & 0 & \tau \end{pmatrix} \]

\[ D(14) = D(14) = -\frac{1}{m} \begin{pmatrix} \lambda & -\gamma & -\delta \\ -\gamma & \lambda & \delta \\ -\delta & -\delta & \beta \end{pmatrix} \]

\[ D(11) = D(\bar{1}1) = D(5) \]

\[ D(9), D(10), D(15) \text{ and } D(16) \] refer to third-nearest neighbors which are here neglected.

(1.26) and (1.27) may now be obtained for this lattice and the resulting expression compared with the general expression (1.27). The substitutions and eliminations involved are quite straightforward but extremely laborious. Only the result will be given here. It turns out that \( D'(q) \) is expressed as

\[ (15) \]
\[
\begin{align*}
D_{11}(q) &= \frac{1}{\kappa \alpha} (\alpha + 4\mu) \quad \frac{1}{\kappa \alpha} (\alpha + 4\lambda - \frac{s^2}{\alpha}) \quad \frac{\beta}{\kappa \alpha^2} (\alpha + 4\lambda + 4\mu - \frac{\nu^2}{\alpha}) \quad 0 \quad 0 \quad 0 \\
D_{22}(q) &= \frac{1}{\kappa \alpha} (\beta + 4\nu - \frac{s^2}{\alpha}) \quad \frac{1}{\kappa \alpha} (\beta + 4\nu - \frac{s^2}{\alpha}) \quad \frac{\beta}{\kappa \alpha^2} (\beta + 4\nu - \frac{\nu^2}{\alpha}) \quad 0 \quad 0 \quad 0 \\
D_{33}(q) &= \frac{1}{\kappa \alpha} (\beta + 4\nu - \frac{s^2}{\alpha}) \quad \frac{1}{\kappa \alpha} (\beta + 4\nu - \frac{s^2}{\alpha}) \quad \frac{\beta}{\kappa \alpha^2} (\beta + 4\nu - \frac{\nu^2}{\alpha}) \quad 0 \quad 0 \quad 0 \\
D_{12}(q) &= 0 \quad 0 \quad 0 \quad 0 \quad \frac{\beta}{\kappa \alpha} (\nu - \frac{s^2}{\alpha}) \quad 0 \quad 0 \\
D_{13}(q) &= 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad \frac{\beta}{\kappa \alpha} (\nu - \frac{s^2}{\alpha}) \quad 0 \\
D_{23}(q) &= 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad \frac{\beta}{\kappa \alpha} (\nu - \frac{s^2}{\alpha})
\end{align*}
\]
It follows immediately by comparison with (1.27) that

\[ C_n = C_{zz} = \frac{1}{2C} (\alpha + 4\mu) \]
\[ C_{33} = \frac{C}{2a^2} (\beta + 8\nu) \]
\[ C_{44} = \frac{C}{2a^2} (\alpha + 4\lambda + 4\mu - \nu^2/\alpha) \]
\[ = \frac{1}{2C} (\beta + 4\nu - S^2/\alpha) = C_{xx} \]
\[ C_{66} = \frac{1}{2C} (\alpha + 4\lambda - S^2/\beta) \]

\[ \frac{1}{2} (C_{xx} + C_{44}) = \frac{1}{2} (C_{33} + C_{55}) = \frac{1}{2a} (S + 4\nu - \frac{S^2}{2a}) \]
\[ \frac{1}{2} (C_{12} + C_{66}) = \frac{1}{2C} (\nu - \frac{S^2}{2\beta}) \]

The values of the \( C_{ij} \) have been calculated by Arlmann\(^9\) from data given by Bridgmann\(^10\). They are

\[ C_n = 83.9 \times 10^{-6} \text{ c.g.s.} \quad C_{44} = 17.5 \]
\[ C_{12} = 48.7 \quad C_{33} = 96.6 \]
\[ C_{13} = 28.1 \quad C_{66} = 74. \]

Thus, there are seven independent relations among eight constants. Without further information it is impossible to get numerical values for the constants. Furthermore, a straightforward elimination leads to the result that

\[(\alpha - \nu)^2 < 0.\]

Since the constants are real, this result is a distinct contradiction. Possible explanations will be discussed in the conclusion.

It remains to evaluate the sums of (1.12) and substitute

(15)
in (1.13). Again the work is quite laborious and the results
only are given.

\[ D_n\left(\frac{\varphi}{n}\right) = \frac{2}{m} \left[ 2 \lambda + \lambda \left\{ \lambda - \cos z\pi \left( g_s - g_2 \right) \right\} + \mu \left\{ \lambda - 
\right. \]

\[ \cos z\pi g_2 \right\} \right]\]

\[ D_{21}\left(\frac{\varphi}{n}\right) = D_{21}\left(\frac{\varphi}{n}\right) = 0 \]

\[ D_{22}\left(\frac{\varphi}{n}\right) = D_{22}\left(\frac{\varphi}{n}\right) = \frac{2}{m} \left[ \lambda \left\{ \lambda - \cos z\pi g_2 \right\} - \cos z\pi g_2 \right]
\]

\[ D_{32}\left(\frac{\varphi}{n}\right) = D_{32}\left(\frac{\varphi}{n}\right) = \frac{2}{m} \left[ \lambda \left\{ \lambda - \cos z\pi g_2 \right\} - \cos z\pi g_2 \right]
\]

\[ D_{23}\left(\frac{\varphi}{n}\right) = D_{23}\left(\frac{\varphi}{n}\right) = \frac{2}{m} \left[ \lambda \left\{ \lambda - \cos z\pi g_2 \right\} - \cos z\pi g_2 \right]
\]

\[ D_{33}\left(\frac{\varphi}{n}\right) = D_{33}\left(\frac{\varphi}{n}\right) = \frac{2}{m} \left[ \lambda \left\{ \lambda - \cos z\pi g_2 \right\} - \cos z\pi g_2 \right]
\]

\[ D_{4}\left(\frac{\varphi}{n}\right) = D_{22}\left(\frac{\varphi}{n}\right) = -\frac{\lambda}{m} \left[ \lambda \left\{ 1 - e^{\frac{z \pi i g_2}{1}} + e^{\frac{z \pi i g_2}{2}} + e^{\frac{z \pi i g_2}{3}} \right\} \right]
\]

\[ D_{5}\left(\frac{\varphi}{n}\right) = D_{22}\left(\frac{\varphi}{n}\right) = -\frac{\lambda}{m} \left[ \lambda \left\{ 1 + e^{\frac{z \pi i g_2}{1}} - e^{\frac{z \pi i g_2}{2}} - e^{\frac{z \pi i g_2}{3}} \right\} \right]
\]

\[ D_{6}\left(\frac{\varphi}{n}\right) = D_{22}\left(\frac{\varphi}{n}\right) = -\frac{\lambda}{m} \left[ \lambda \left\{ 1 - e^{z \pi i g_2} + e^{z \pi i g_2} - e^{z \pi i g_2} \right\} \right]
\]

\[ D_{7}\left(\frac{\varphi}{n}\right) = D_{22}\left(\frac{\varphi}{n}\right) = -\frac{\lambda}{m} \left[ \lambda \left\{ 1 - e^{z \pi i g_2} + e^{z \pi i g_2} - e^{z \pi i g_2} \right\} \right]
\]

\[ D_{8}\left(\frac{\varphi}{n}\right) = D_{22}\left(\frac{\varphi}{n}\right) = -\frac{\lambda}{m} \left[ \lambda \left\{ 1 + e^{z \pi i g_2} + e^{z \pi i g_2} + e^{z \pi i g_2} \right\} \right]
\]

\[ D_{9}\left(\frac{\varphi}{n}\right) = D_{22}\left(\frac{\varphi}{n}\right) = -\frac{\lambda}{m} \left[ \lambda \left\{ 1 + e^{z \pi i g_2} + e^{z \pi i g_2} + e^{z \pi i g_2} \right\} \right]
\]

\[ D\left(\frac{\varphi}{n}\right) = D\left(\frac{\varphi}{n}\right) \quad D\left(\frac{\varphi}{n}\right) = D\left(\frac{\varphi}{n}\right) \]

(16)
The allowable values of $\overline{g}$ are determined by the Brillouin zone structure. Consider the vector

$$\overline{g} = \frac{2\pi}{a} \left[ g_x \overline{g} + g_y \overline{g} + g_z \overline{g} \right]$$

or

$$\overline{g} = \frac{2\pi}{a} \left[ \left( g_x + g_y + g_z \right), \left( g_x - g_y + g_z \right), \frac{a}{c} \left( g_x + g_y - g_z \right) \right]$$

or

$$\overline{g} = \frac{2\pi}{a} \left[ g_x, g_y, g_z \right]$$

in rectangular components. Solving for $g_x$, $g_y$ and $g_z$ gives

$$g_x = \frac{1}{2} \left[ g_y + \frac{a}{c} g_z \right]$$

$$g_y = \frac{1}{2} \left[ g_x + \frac{a}{c} g_z \right]$$

$$g_z = \frac{1}{2} \left[ g_x + g_y \right]$$

(2.6)

These values may be substituted into $D(\overline{g})$ and the symmetry of the zone structure utilized. The boundaries of the first zone are the planes

$$g_x = \pm \frac{a}{2}, \quad g_y = \pm \frac{a}{2}, \quad g_z = \pm \frac{a}{c}$$

(see diagram III) (2.7)

In general, numerical methods are required to evaluate the roots of (1.13). However, along special directions or at special points the determinant can be factored into determinants of lower order. The following definitions are made to facilitate illustrations. Let

$$A = D_n \left( \overline{g} \right)_n \quad B = D_{18} \left( \overline{g} \right)_{18} \quad C = D_{22} \left( \overline{g} \right)_{22}$$

$$D = D_{29} \left( \overline{g} \right)_{29} \quad E = D_{33} \left( \overline{g} \right)_{33} \quad F = D_n \left( \overline{g} \right)_{12}$$

$$G = D_{12} \left( \overline{g} \right)_{12} \quad H = D_{13} \left( \overline{g} \right)_{13} \quad J = D_{29} \left( \overline{g} \right)_{12}$$

$$K = D_{33} \left( \overline{g} \right)_{12}$$

(17)
In this notation, (1.13) is

\[
\begin{vmatrix}
A-\omega^2 & 0 & B & F & G & H \\
0 & C-\omega^2 & D & G & F & J \\
B & D & E-\omega^2 & H & J & K \\
F^* & G^* & H^* & A-\omega^2 & 0 & B \\
G^* & F^* & J^* & 0 & C-\omega^2 & D \\
H^* & J^* & K^* & B & D & E-\omega^2 \\
\end{vmatrix} = 0. \\
\text{(2.8)}
\]

Along a body diagonal, \( q_1 = q_2 = q_3 \). It is easily verified that \( C=A \), \( D=B \) and \( J=H \) in this direction. Equation (2.8) then reduces to

\[
\begin{vmatrix}
A-\omega^2 & 0 & B & F & G & H \\
0 & A-\omega^2 & B & G & F & H \\
B & B & E-\omega^2 & H & H & K \\
F^* & G^* & H^* & A-\omega^2 & 0 & B \\
G^* & F^* & H^* & 0 & A-\omega^2 & B \\
H^* & H^* & K^* & B & B & E-\omega^2 \\
\end{vmatrix} = 0. \\
\]

This may be factored into the product of a fourth order determinant and the second order determinant

\[
\begin{vmatrix}
A-\omega^2 & F-G \\
F^* & A-\omega^2 \\
\end{vmatrix}
\]

Equating this determinant to zero leads to the result that

\[
\omega^2 = A \pm |F-G|. \\
\text{(2.9)}
\]
Substituting for $A$, $F$ and $G$ gives

$$\omega^2 = \frac{2}{m} \left[ 2\alpha + (\lambda + \mu)(1 - \cos 2\pi q_1) \right]$$

$$\pm \frac{1}{m} \left[ (\lambda - \mu) + (3\alpha + \beta) e^{2\pi i q_1} \right].$$

The roots of (2.9) for the positive sign determine one curve of the optical branch while the roots for the negative sign determine one curve of the acoustical branch. Setting $q_1 = 0$ gives the limiting values

$$\omega_1 = \sqrt{\frac{2\alpha}{m}}, \quad \omega_2 = 0.$$

Along a face diagonal, $q_1 = q_2$ and $q_3 = 0$. In this direction $H = J = B = E = 0$. Equation (2.8) now factors into three second order determinants one of which is, for example,

$$\begin{vmatrix}
E - \omega^2 & K \\
K^* & E - \omega^2
\end{vmatrix}.$$\

Equating this determinant to zero leads to the result that

$$\omega^2 = E \pm |K|.$$\

Substituting for $E$ and $K$ gives

$$\omega^2 = \frac{4}{m} \left[ \beta + 2\alpha(1 - \cos 2\pi q_1) \right] \pm \frac{2\beta}{m} \left[ 1 + e^{2\pi i q_1} \right].$$

The discussion concerning the roots in the previous example again applies. The limiting values are

$$\omega_1 = \sqrt{\frac{2\beta}{m}}, \quad \omega_2 = 0.$$\

An additional feature is the degeneracy of the two curves at $q_1 = \frac{1}{2}$ where

$$\omega_1 = \omega_2 = \sqrt{\frac{4\alpha}{m}} \left( \beta + 4\alpha \right).$$

(19)
First Zone of $\beta$-Tin
3. Conclusions

As previously mentioned, the equations (2.3) result in a relation that contradicts the fact that the atomic constants are real numbers. There are, at least, two possible explanations. The first is that the second-neighbor approximation is insufficient. The second is that the measured values of the $C_{ij}$ are in error.

In any event, there are eight atomic constants introduced by the theory with but seven equations relating them. Therefore, even if the above mentioned difficulty is resolved, an additional relation must be postulated before any calculations can be made. (It is well to point out here that if third-neighbors are introduced, equations (2.3) will contain additional constants.)

The few exact solutions for the frequencies exhibit degeneracies at various points including a double degeneracy in the optical branch at the origin of reciprocal space. Lack of numerical values for the atomic constants precludes any discussion of these special cases.
Let \( x_A \) be the coordinates of the lattice point \((\xi)\) in the chosen system. Consider another axis system, the initial system, which can be brought into coincidence with the chosen system by a symmetry operation. Let the coordinates of \((\xi)\) be \( x_\alpha \) in the initial system.

Then:
\[
x_\alpha = \sum T_{\alpha A} x_A
\]

where \( T_{\alpha A} \) is the matrix for the symmetry operation. Now if \( T_{\alpha A} \) is actually a symmetry operation, then the \( x_\alpha \) that located \((\xi)\) in the initial system should equal the \( x_\beta \) that locate another point \((\zeta)\) in the chosen system.

Thus:
\[
x_\beta (\zeta) = \sum T_{\alpha A} x_A(\xi)
\]

Where all coordinates mentioned refer to the chosen system.

If the chosen system is indicated by \( x_1, x_2, x_3 \) and the initial system by \( x_1', x_2', x_3' \), then

\[
T_{\alpha A} = \begin{vmatrix} x_1 & x_1' & x_1'' \\ x_2 & x_2' & x_2'' \\ x_3 & x_3' & x_3'' \end{vmatrix}
\]
Bibliography

2. Kellermann, Phil. Trans., A238, 513, 1940.
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