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The equations of motion for a diatomic molecule of gallium are derived using the harmonic approximation. The interatomic forces are found analytically using the "6-exp" potential form, and the intermolecular force constants and secular determinant are evaluated numerically. An attempt to evaluate the normal mode frequencies is unsuccessful since no method for determining satisfactory potential parameters was developed.

APPROVAL SHEET

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LATTICE DYNAMICS IN A GALLIUM CRYSTAL USING THE "6-EXP" POTENTIAL

by

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INTRODUCTION

A crystal lattice may be described as a regular array of atoms and/or molecules. One may be described using two basic concepts - the unit cell and the translation vectors of the crystal. A particular arrangement of molecules (the "unit cell" of the crystal) is located at the origin of a coordinate system. This arrangement or unit cell is repeated at regular intervals in space. These intervals are described by three translation vectors. A unit cell is located at particular combinations of these vectors, as, for example, at every combination of integer multiples of the vectors. In the case of gallium, an orthogonal set of vectors will be chosen such that a unit cell is located at every combination of even-integer multiples of the translation vectors.

A force exerted on a molecule in such a crystal lattice, perhaps produced by a wave progressing past the molecules, disturbs the molecule from its equilibrium position. This disturbance propagates through the crystal at a speed which is dependent on the incident direction of the wave with respect to the crystal axes. In the harmonic approximation we may treat the molecules as if they were a collection of oscillators. The standard method of handling this is in terms of the normal modes of the oscillators.

In this thesis, gallium is treated as forming a crystal of diatomic molecules. The equations of motion for a molecule in the lattice are derived using the harmonic approximation. The inter-atomic forces are found analytically using the "6-exp" potential form, $V = -\frac{A}{r^6} + Be^{-\alpha r}$. Using these analytical forms the inter-molecular force constants are found numerically. The secular determinant is evaluated and an attempt is made to find the normal mode frequencies for selected values of the wave vector $\underset{\sim}{q}$.

The model of the gallium molecule is that of a rigid dumbbell of length 2.442 Å[1] and the mass of each atom is $115.735199 \times 10^{-24}$ grams.[2] In the crystal lattice (base-centered orthorhombic), there are two possible molecular orientations. With respect to the crystal axes (figure 1), both molecule positions lie parallel to the b-c plane. Type A is tipped ~ 16.9° counter-clockwise from the b-axis and type B ~ 16.9° clockwise from the same axis[3] (figure 2). The principal axes for each type are located such that one lies along the dumbbell axis (the β-axis). A second (the α-axis) passes through the center of the dumbbell parallel to the a-axis and the third (the γ-axis) is selected to form a right-handed system with the first two.

Lengths on the crystal axes are most conveniently measured in integer multiples of one-half the respective lattice constants. The integers are designated h, k, and ℓ. A unit cell containing four molecules can therefore be

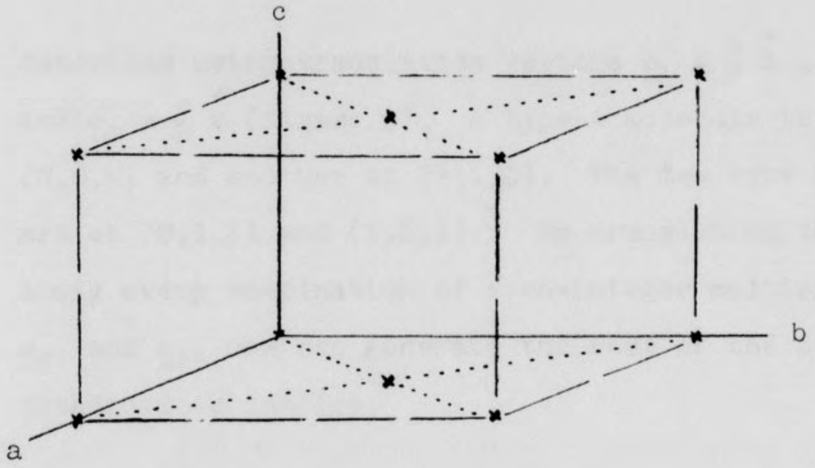

Figure 1: The base-centered orthorhombic lattice

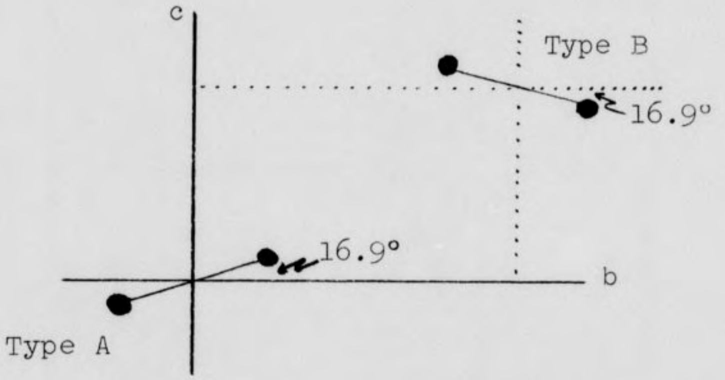

Figure 2: Relative molecular orientations in the gallium lattice

described using translation vectors $\underset{\sim}{e}_1 = \frac{a}{2}\hat{i}$, $\underset{\sim}{e}_2 = \frac{b}{2}\hat{j}$, and $\underset{\sim}{e}_3 = \frac{c}{2}\hat{k}$ (figure 3). A type A molecule is located at (0,0,0) and another at (1,1,0). The two type B molecules are at (0,1,1) and (1,0,1).[3] By translating this unit cell along every combination of even-integer multiples of $\underset{\sim}{e}_1$, $\underset{\sim}{e}_2$, and $\underset{\sim}{e}_3$, one can generate the rest of the base-centered orthorhombic lattice.

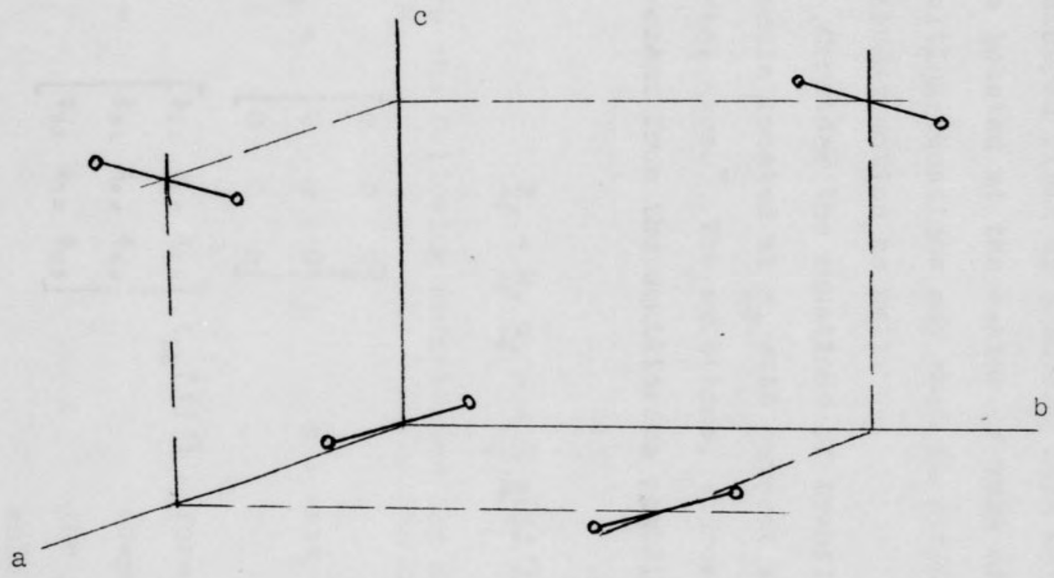

Figure 3: The basis for a unit cell of gallium

DEVELOPMENT OF THE DYNAMICAL MATRIX

Since the molecules are assumed rigid, there are only the three translational and three librational degrees of freedom per molecule. The translational motion will be considered first by assuming each molecule to be a point mass located at the center of mass of the molecule. The resulting equations may then be extended to include librational motion as well.

Consider the equations of translational motion of a molecule located at $\underset{\sim}{r}_j$ with respect to some origin in the crystal axes.[4] The equations, expressed in terms of displacement from the equilibrium position of the molecule, are

$$\underset{\sim}{F}_j = \underset{\approx}{M}_j \, \ddot{\underset{\sim}{u}}_j = - \sum_{j'} \underset{\approx}{\Phi}(jj') \, \underset{\sim}{u}_{j'} , \qquad (1)$$

where the following definitions are made:

$$\underset{\approx}{M}_j = \begin{bmatrix} m & 0 & 0 \\ 0 & m & 0 \\ 0 & 0 & m \end{bmatrix} \qquad m = \text{mass of Ga molecule}$$

$$\underset{\approx}{\Phi} = \begin{bmatrix} \Phi_{11} & \Phi_{12} & \Phi_{13} \\ \Phi_{21} & \Phi_{22} & \Phi_{23} \\ \Phi_{31} & \Phi_{32} & \Phi_{33} \end{bmatrix} \qquad \Phi_{ik}(jj') = $$

force constant for the i component of the force on the j (or "origin") molecule due to displacement of the j′ (or "source") molecule in the k direction

$\underset{\sim}{u}_{j'}$ = displacement of the molecule from its equilibrium position, components along the crystal axes.

The range of the j' index includes both j, the molecule being discussed, and its neighbors to any desired range. The harmonic expression for $\underset{\sim}{u}_j$

$$\underset{\sim}{u}_j = \underset{\sim}{A}_j \, e^{i(\underset{\sim}{q}_j \cdot \underset{\sim}{r}_j - \omega t)} \qquad (2)$$

is postulated. Substituting this into Equation (1) gives

$$\underset{\approx}{M} \, \underset{\sim}{A}_j \, \omega^2 \, e^{-i\omega t} \, e^{i\underset{\sim}{q} \cdot \underset{\sim}{r}_j} = e^{-i\omega t} \sum_{j'} \underset{\approx}{\Phi}(jj') \underset{\sim}{A}_{j'} \, e^{i\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}}$$

If the various $\underset{\sim}{A}_{j'}$ are assumed equal, this may be expressed in component form as

$$M\omega^2 A_k = \sum_{N=1}^{3} \sum_{j'} \Phi_{kN}(jj') \, A_N \, e^{i\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}} \qquad (3)$$

for $k = 1, 2,$ or 3 and where $\underset{\sim}{r}_{j'}$ now means $\underset{\sim}{r}_{j'} - \underset{\sim}{r}_j$. The coefficients of the three amplitude components may be collected to rearrange Equations (3) as

$$\Big[\sum_{j'} \Phi_{11}(jj') e^{i\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}} - M\omega^2\Big] A_1 + \Big[\sum_{j'} \Phi_{12}(jj') e^{i\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}}\Big] A_2 + \Big[\sum_{j'} \Phi_{13}(jj') \, e^{i\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}}\Big] A_3 = 0 \qquad (4)$$

$$\Big[\sum_{j'} \Phi_{21}(jj') e^{i\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}}\Big] A_1 + \Big[\sum_{j'} \Phi_{22}(jj') e^{i\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}} - M\omega^2\Big] A_2 + \Big[\sum_{j'} \Phi_{23}(jj') e^{i\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}}\Big] A_3 = 0$$

$$[\sum_{j'}\Phi_{31}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}}]A_1 + [\sum_{j'}\Phi_{32}(jj'(e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}}]A_2$$

$$+ [\sum_{j'}\Phi_{33}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} - M\omega^2]A_3 = 0$$

From Cramer's rule the secular determinant is therefore

$$\begin{bmatrix} \sum_{j'}\Phi_{11}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} - M\omega^2 & \sum_{j'}\Phi_{12}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} & \sum_{j'}\Phi_{13}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} \\ \sum_{j'}\Phi_{21}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} & \sum_{j'}\Phi_{22}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} - M\omega^2 & \sum_{j'}\Phi_{23}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} \\ \sum_{j'}\Phi_{31}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} & \sum_{j'}\Phi_{32}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} & \sum_{j'}\Phi_{33}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} - M\omega^2 \end{bmatrix} = 0 . \tag{5}$$

The molecular structure may be considered by extending these results to include librational motion as well. Torque components are taken along the principal axes of the molecule on which they are exerted so that the moment of inertia tensor $\underset{\approx}{I}$ of the molecule is diagonal. Equation (1) involving linear displacements and forces may be extended to include torques and molecular rotations as well. The resulting equation involves a 6x6 "force constant" matrix and is of the form

$$\begin{bmatrix} F_1 \\ F_2 \\ F_3 \\ L_\alpha \\ L_\beta \\ L_\gamma \end{bmatrix} = \begin{bmatrix} \begin{pmatrix} \text{constants} \\ \text{coupling} \\ \text{forces \&} \\ \text{displacements} \end{pmatrix} & \begin{pmatrix} \text{constants} \\ \text{coupling} \\ \text{forces \&} \\ \text{rotations} \end{pmatrix} \\ \begin{pmatrix} \text{constants} \\ \text{coupling} \\ \text{torques \&} \\ \text{displacements} \end{pmatrix} & \begin{pmatrix} \text{constants} \\ \text{coupling} \\ \text{torques \&} \\ \text{rotations} \end{pmatrix} \end{bmatrix} \bullet \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ \theta_1 \\ \theta_2 \\ \theta_3 \end{bmatrix} ,$$

where the 6x6 matrix $\underset{\approx}{\Phi}$ is divided into four 3x3 submatrices.

There are two main variations from the method of the previous derivation. First, two equations of motion are used to describe translation and rotation of the "origin" molecule. In component form, these are[5]

$$F_i(j) = m\,\ddot{u}_i(j) = -\sum_{j'}\sum_{k}\sum_{\beta}\left[\Phi_{ik}(jj')u_k(j') + \Phi_{i\beta}(jj')\theta_\beta(j')\right]$$

$$C_\alpha(j) = I\,\ddot{\theta}_\alpha(j) = -\sum_{j'}\sum_{k}\sum_{\beta}\left[\Phi_{\alpha k}(jj')u_k(j') + \Phi_{\alpha\beta}(jj')\theta_\beta(j')\right]$$

where i, k, α, and β run from 1 to 3 and where the following definitions are made:

$C_\alpha(j)$ = net torque on the jth or origin molecule

$\Phi_{\alpha\beta}(jj')$ = "torque constant" relating the α component of torque on the origin molecule to a rotation of the j' or source molecule about the β principal axis

θ_β = rotation about the β principal axis

$\Phi_{i\beta}(jj')$ relates forces on the origin molecule to rotation of the source molecule

$\Phi_{\beta k}(jj')$ relates torques on the origin molecule to translation of the source molecule

It should be noted here that the k subscript connotes translation of the molecule, while the β subscript implies rotation. Thus Φ_{ik} does not equal $\Phi_{i\beta}$ nor does $\Phi_{\alpha k}$ equal $\Phi_{\alpha\beta}$ when k happens to equal β. For convenience these may be written

$$F_i(j) = -\sum_{j'}\sum_{k} \Phi_{ik}(jj')\, u_k(j')$$

where i and k range from 1 to 6 (1 to 3 imply translation and 4 to 6, libration). Second, the origin and source molecules are not necessarily identical, so that all amplitudes in the harmonic form may not be assumed equal. There must be equations of motion for each type of origin molecule, and there must be a different amplitude for each type of molecule in the lattice. The harmonic solution is now substituted, i.e.,

$$\underset{\sim}{u}_j = \underset{\sim}{A}_j\, e^{i(\underset{\sim}{q}\cdot\underset{\sim}{r}_j - \omega t)}$$

where $\underset{\sim}{u}_j$ and $\underset{\sim}{A}_j$ are now six-element column matrices. If the factor $e^{-i\omega t}$ is cancelled, the amplitudes of all type A molecules are assumed equal, and those of all type B molecules are assumed equal, then the resulting two equations are[5]

$$\begin{aligned} \underset{\approx}{M}\,\underset{\sim}{A}\,\omega^2 &= \sum_{j'} \underset{\approx}{\Phi}(jj')\,\underset{\sim}{A}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} + \sum_{\ell'} \underset{\approx}{\Phi}(j\ell')\,\underset{\sim}{B}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{\ell'}} \\ \underset{\approx}{M}\,\underset{\sim}{B}\,\omega^2 &= \sum_{\ell'} \underset{\approx}{\Phi}(j\ell')\,\underset{\sim}{A}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{\ell'}} + \sum_{j'} \underset{\approx}{\Phi}(jj')\,\underset{\sim}{B}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} \end{aligned} \qquad (6)$$

where in each case j' indicates only those molecules of the same type as the origin molecule, and ℓ' indicates only those not of the same type as the origin. The mass has been extended to a 6x6 diagonal matrix,

$$\underset{\approx}{M} = \begin{bmatrix} m & 0 & 0 & 0 & 0 & 0 \\ 0 & m & 0 & 0 & 0 & 0 \\ 0 & 0 & m & 0 & 0 & 0 \\ 0 & 0 & 0 & I_\alpha & 0 & 0 \\ 0 & 0 & 0 & 0 & I_\beta & 0 \\ 0 & 0 & 0 & 0 & 0 & I_\gamma \end{bmatrix} .$$

These equations may be written in component form and the coefficients of the components of $\underset{\sim}{A}$ and $\underset{\sim}{B}$ collected. There are now six equations of the form

$$\sum_k \{[\sum_{j'} \Phi_{ik}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} - M_i\,\omega^2\,\delta_{ik}]A_k\} + \sum_k \{[\sum_{\ell'} \Phi_{ik}(j\ell')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{\ell'}}]\}B_k = 0 \qquad (7)$$

and six of the form

$$\sum_k \{[\sum_{j'}\Phi_{ik}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}}]A_k\} + \sum_k\{[\sum_{\ell'} \Phi_{ik}(j\ell')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{\ell'}} - M_i\,\omega^2\,\delta_{ik}]B_k\} = 0.$$

where i, k = 1, 2, ..., 6. These equations give a 12x12 secular determinant whose elements are of the form

$$\sum_{j'} \Phi_{ik}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} - M_i\,\omega^2\,\delta_{ik} \quad . \qquad (8)$$

The order of the matrix may be reduced by considering molecular symmetry. Physically, motion about the β- or dumbbell axis can have no meaning since I_β is zero. Accordingly, the fifth and eleventh columns, which involve rotation about the β-axis, and the fifth and eleventh rows, which involve β-components of torque, may be omitted. The determinant is thus reduced to 10x10.

For the same reason, the fifth row and column of each inter-molecular force constant matrix may be omitted, reducing it to 5x5. Lattice symmetries further restrict the form of this matrix for certain locations of the source molecule. The symmetry notation described by Pawley[6] is used. The type B symmetry transformation, or inversion through a point in the lattice such as the origin, takes molecule n at (h, k, l) into molecule n′ at $(-h, -k, -\ell)$. Inversion through the origin indicates that $\underset{\approx}{\Phi}$ between the origin molecule and any other molecule in the lattice is of the form

$$\underset{\approx}{\Phi} = \begin{bmatrix} \Phi_{11} & \Phi_{12} & \Phi_{13} & \Phi_{14} & \Phi_{15} \\ \Phi_{12} & \Phi_{22} & \Phi_{23} & \Phi_{24} & \Phi_{25} \\ \Phi_{13} & \Phi_{23} & \Phi_{33} & \Phi_{34} & \Phi_{35} \\ -\Phi_{14} & -\Phi_{24} & -\Phi_{34} & \Phi_{44} & \Phi_{45} \\ -\Phi_{15} & -\Phi_{25} & -\Phi_{35} & \Phi_{45} & \Phi_{55} \end{bmatrix} .$$

A type A symmetry transformation brings the transformed molecules into self-coincidence, as in the case of reflection in the plane containing the molecules. This transformation leaves $\underset{\approx}{\Phi}$ unchanged. Reflecting the gallium lattice in a plane perpendicular to the a-axis indicates that the form of $\underset{\approx}{\Phi}$ between molecules lying in such a plane is

$$\underset{\approx}{\Phi} = \begin{bmatrix} \Phi_{11} & 0 & 0 & 0 & \Phi_{15} \\ 0 & \Phi_{22} & \Phi_{23} & \Phi_{24} & 0 \\ 0 & \Phi_{23} & \Phi_{33} & \Phi_{34} & 0 \\ 0 & -\Phi_{24} & -\Phi_{34} & \Phi_{44} & 0 \\ -\Phi_{15} & 0 & 0 & 0 & \Phi_{55} \end{bmatrix} .$$

Type C symmetry, a screw diad transformation, relates the force constant matrix ($\underset{\approx}{\Phi}$) between a type A origin molecule and the source molecule located at (h, k, ℓ) with respect to this origin to the force constant matrix ($\underset{\approx}{\Phi}'$) between a type B origin molecule and a source molecule located at a corresponding position with respect to this type B origin. The application of this symmetry transformation indicates that the following relationship must hold between $\underset{\approx}{\Phi}$ and $\underset{\approx}{\Phi}'$:

$$\underset{\approx}{\Phi} = \begin{bmatrix} \Phi_{11} & \Phi_{12} & \Phi_{13} & \Phi_{14} & \Phi_{15} \\ \Phi_{12} & \Phi_{22} & \Phi_{23} & \Phi_{24} & \Phi_{25} \\ \Phi_{13} & \Phi_{23} & \Phi_{33} & \Phi_{34} & \Phi_{35} \\ -\Phi_{14} & -\Phi_{24} & -\Phi_{34} & \Phi_{44} & \Phi_{45} \\ -\Phi_{15} & -\Phi_{25} & -\Phi_{35} & \Phi_{45} & \Phi_{55} \end{bmatrix} = \begin{bmatrix} \Phi'_{11} & \Phi'_{12} & \Phi'_{13} & -\Phi'_{14} & -\Phi'_{15} \\ \Phi'_{12} & \Phi'_{22} & \Phi'_{23} & -\Phi'_{24} & -\Phi'_{25} \\ \Phi'_{13} & \Phi'_{23} & \Phi'_{33} & -\Phi'_{34} & -\Phi'_{35} \\ \Phi'_{14} & \Phi'_{24} & \Phi'_{34} & \Phi'_{44} & \Phi'_{45} \\ \Phi'_{15} & \Phi'_{25} & \Phi'_{35} & \Phi'_{45} & \Phi'_{55} \end{bmatrix} = \underset{\approx}{\Phi}'.$$

The details of these symmetry transformations are shown in Appendix I.

The large number of independent parameters involved in molecule-molecule (m-m) interactions is not further reducible due to the low order of symmetry of the crystal. There are at least nine parameters involved in each m-m interaction. If only fifth-nearest neighbors are included in the dynamical matrix, a total of 101 independent parameters are involved. It is unlikely that this many independent parameters can satisfactorily be determined from experimental data.

If, however, a particular potential is assumed for interactions between atoms, the parameters in the m-m expressions become dependent on the potential used. The number of variables is thus greatly reduced.

The atoms are assumed to interact via the "6-exp" potential energy form, which is

$$V = -\frac{A}{r^6} + B\, e^{-\alpha r} \quad .$$

There are now only three independent parameters, with the intermolecular constants dependent on these. The potential energy of the crystal may be expressed in a Taylor series expansion about the equilibrium position as[7]

$$u = u_e + \sum_i x_i \frac{\partial u}{\partial x_i} + \frac{1}{2} \sum_i \sum_j x_i\, x_j \frac{\partial^2 u}{\partial x_i \partial x_j} + \cdot\ \cdot\ \cdot\ \cdot$$

evaluated at the equilibrium position of the molecule. Since both u and $\frac{\partial u}{\partial x_i}$ are zero when evaluated at the equilibrium position, the first non-vanishing term is the "harmonic oscillator" term. The harmonic approximation then implies that the inter-atomic force constants are the second derivatives of the potential. From this, one can show that the force constants (Φ_{ij}) between an atom in the origin molecule and one in the source molecule are of the following form:

a. $i = 1, 2, 3$ $\quad j = 1, 2, 3$

$$\Phi_{ij} = \delta_{ij}\, f(r) + x_i\, x_j\, g(r)$$

b. $i = 4, 5$ $\quad j = 1, 2, 3$

$$\Phi_{4j} = y_0 \Phi_{3j} - z_0 \Phi_{2j}$$
$$\Phi_{5j} = -(y_0 \cos\theta + z_0 \sin\theta)\, \Phi_{1j}$$

y_0, z_0 = position of the origin atom relative to the center of mass of the origin atom

c. $i = 1, 2, \ldots 5$ $\quad j = 4, 5$

$$\Phi_{j4} = y\, \Phi_{j3} - z\, \Phi_{j2}$$
$$\Phi_{j5} = -(y \cos\theta + z \sin\theta)\, \Phi_{j1}$$

y, z = position of the source atom relative to the center of mass of the source atom

where

$$f(r) = \frac{1}{r}\frac{\partial V}{\partial r} = \frac{6A}{r^8} - \frac{B\alpha}{r}\, e^{-\alpha r}$$
$$g(r) = \frac{1}{r}\frac{\partial f}{\partial r} = -\frac{48A}{r^{10}} + \frac{B\alpha e^{-\alpha r}}{r^3} + \frac{B\alpha^2 e^{-\alpha r}}{r^2}$$

and the x_i are the components (with respect to the crystal axes) of the position of the source atom relative to the origin atom. This derivation is carried out in greater detail in Appendix II.

The force constants between the origin molecule and the source (or displaced) molecule may be found by including the four inter-atomic interactions possible between the two molecules. If however the origin molecule is itself displaced and the rest of the lattice molecules remain in equilibrium, the forces exerted on the origin molecule (called the "self-forces") must be calculated differently.

For a simple translation u_j of the origin molecule, the force on it is the same as if it were undisplaced and each neighbor were displaced by $u_{j'} = - u_j$. It is thus clear that

$$\Phi_{ik}(jj) = - \sum_{j'\neq j} \Phi_{ik}(jj') \text{ for } i,\ k = 1,\ 2,\ 3 \quad .$$

A pure rotation $\underset{\sim}{\theta}_j$ of the origin molecule is equivalent to each neighbor experiencing a translation of $-\underset{\sim}{\theta}_j \times \underset{\sim}{r}_{j'}$, and a pure rotation of $-\underset{\sim}{\theta}_j = \underset{\sim}{\theta}_{j'}$.[5] The resulting forces are derived in Appendix III.

The self-force and intermolecular force constants may now be used to compute the dynamical matrix for different values of the wave vector $\underset{\sim}{q}$. The 10x10 secular determinant elements have already been described (Equation (8)). It is convenient to redefine the amplitudes of the harmonic solutions ($\underset{\sim}{A}$) by

$$a_i = A_i \sqrt{M_i} \qquad \text{where } M_i = \begin{cases} m & \text{for } i = 1,\ 2,\ 3 \\ I_\alpha & i = 4 \\ I_\gamma & i = 5 \end{cases}$$

The secular equations may then be written

$$(\underset{\approx}{D} - \underset{\approx}{I}\omega^2)\ \underset{\sim}{a} = 0 \tag{9}$$

where $\underset{\approx}{I}$ is the identity matrix and the D_{ik} are of the form

$$D_{ik} = \{\sum_{j'} \Phi_{ik}(jj')\ e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}}\}/\sqrt{M_i M_k} \quad .$$

The elements of the dynamical matrix are either purely real or purely imaginary. By taking account of the 90° phase difference between the translational and rotational components of the molecular motion, one may redefine the rotational amplitudes as[5,6]

$$a_4 = i\, A_4 \sqrt{I_\alpha} \qquad a_9 = i\, A_9 \sqrt{I_\alpha}$$

$$a_5 = i\, A_5 \sqrt{I_\gamma} \qquad a_{10} = i\, A_{10} \sqrt{I_\gamma} \quad .$$

After making this substitution, we find the D_{ik} terms of Equation (9) are of the following forms:

a. for type A origin and source molecules: i, k = 1 - 5

$$D_{ik} = \{\sum_{j'} [\Phi_{ik}(jj')\, C_p\, e^{i \underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}}] - \Phi_{ik}(jj')\}/\sqrt{M_i M_k}$$

summed over type A molecules only.

b. for type A origin and type B source molecules:

$i = 1 - 5 \qquad k = 6 - 10$

$$D_{ik} = \{\sum_{j'} \Phi_{i(k-5)}(jj')\, C_p\, e^{i \underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}}\}/\sqrt{M_i M_{(k-5)}}$$

summed over type B molecules only.

c. for type B origin and source molecules: i, k = 6 - 10

$$D_{ik} = \{[\sum_{j'} \Phi_{(i-5)(k-5)}(jj')\, C_p\, e^{i \underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}}] - \Phi_{(i-5)(k-5)}(jj')\} / \sqrt{M_{(i-5)} M_{(k-5)}}$$

summed over type B molecules only.

d. for type B origin and type A source molecules:

$i = 6 - 10 \qquad k = 1 - 5$

$$D_{ik} = \{\sum_{j'} \Phi_{(i-5)k}(jj')\, C_p\, e^{i \underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}}\}/\sqrt{M_{(i-5)} M_k}$$

summed over type A molecules only.

The values of $\Phi_{1k}(jj')$ are given in Equations 6, Appendix III, and C_p is defined by:

$$C_p = \cos 2\theta \quad \text{if } i, k = 1, 2, 3, 6, 7, 8$$
$$\text{or if} \quad i, k = 4, 5, 9, 10$$
$$C_p = \sin 2\theta \quad \text{if } i = 4, 5, 9, 10$$
$$\text{and } k = 1, 2, 3, 6, 7, 8$$
$$C_p = -\sin 2\theta \quad \text{if } i = 1, 2, 3, 6, 7, 8$$
$$\text{and } k = 4, 5, 9, 10$$

The elements of the dynamical matrix may now be evaluated and the eigenvalues of the matrix found for specific values of $\underset{\sim}{q}$. These values are those of ω^2, where the ω's are the normal mode frequencies of the oscillators.

SUMMARY AND CONCLUSIONS

The intermolecular force constants for gallium may be obtained analytically using the "6-exp" potential form for inter-atomic interactions. These constants may be used to evaluate the dynamical matrix numerically and thus to obtain the dispersion relations for gallium.

An attempt was made to compute the dispersion relations for gallium using the program listed in Appendix IV. The values of the parameters A, B, and α were selected such that

$$\alpha = 2.562205 \text{ Å}^{-1} \quad \text{and} \quad \frac{A}{B} = \frac{1}{2} \quad . \tag{1}$$

These values were computed from equilibrium considerations by C. B. Clark.[8]

The normal mode frequencies were calculated for plane waves propagating parallel to each of the crystal axes. The maximum value of the wave vector (q_{max}) was taken to be the boundary of the first Brillouin zone on that axis. These values are found in Appendix V to be

$$q_1 = \frac{\pi}{a}\left[\frac{1 + (a^2/b^2)}{2}\right]$$

$$q_2 = \frac{\pi}{b}$$

$$q_3 = \frac{\pi}{c} \quad .$$

The frequencies were evaluated for waves at intervals of $\frac{1}{5}$ q_{max} along each axis.

The force constant matrices and the dynamical matrix found with the above parameters did not obey the restrictions indicated by the inversion and glide plane symmetries. (These restrictions are discussed in Appendix I.) Several methods were used to force the matrices to follow these restrictions, but no satisfactory values of ω^2 were obtained. The most nearly satisfactory results are listed in Table 1. In each case, some values of ω^2 are negative.

We are unable to obtain values for A, B, and α which would yield ten values of ω^2 with a uniform sign for one of the incident wave vectors. Final results in which all values of ω^2 are negative might suggest that the "6-exp" potential is appropriate for gallium only with a dominant repulsive term rather than a dominant attractive term. These parameters might be found by relating calculated values of ω^2 to those determined empirically. A selection criterion, such as a least squares fit, could be used to minimize the difference between the calculated values of ω^2 and the empirical values[9] to give a "best value" of A, B, and α. This, however, is beyond the scope of this paper.

TABLE 1

Calculated Values of ω^2 for Plane Waves Propagating Along the Crystal Axes*

units: ω^2 in 10^{24} Hz^2 ; $\underset{\sim}{q}$ in $\mathring{A}^{-1}$

$\underset{\sim}{q}$	ω^2	$\underset{\sim}{q}$	ω^2	$\underset{\sim}{q}$	ω^2
$.0674\hat{i}$	$.4954 \times 10^{1}$	$.1000\hat{j}$	$.5072 \times 10^{1}$	$.1000\hat{k}$	$.5037 \times 10^{1}$
	$-.1371$		$.5795 \times 10^{-1}$		$.1258$
	$-.1234 \times 10^{2}$		$-.3239$		$-.9219 \times 10^{1}$
	$-.5700 \times 10^{1}$		$-.3674 \times 10^{1}$		$-.6952 \times 10^{1}$
	$-.2753 \times 10^{-1}$		$-.3316$		$-.6846$
	$-.1088 \times 10^{2}$		$-.9403 \times 10^{1}$		$-.1516 \times 10^{2}$
	$-.3484 \times 10^{1}$		$-.5768 \times 10^{1}$		$-.2660 \times 10^{1}$
	$-.1543 \times 10^{2}$		$-.1524 \times 10^{2}$		$-.2731 \times 10^{2}$
	$-.3104$		$-.2786 \times 10^{2}$		$-.9997$
	$-.2794 \times 10^{2}$		$-.1396 \times 10^{2}$		$-.1335 \times 10^{2}$
$.1348\hat{i}$	$.5482 \times 10^{1}$	$.2000\hat{j}$	$.5906 \times 10^{1}$	$.2000\hat{k}$	$.5308 \times 10^{1}$
	$-.5301$		$.2289$		$.4544$
	$-.1237 \times 10^{2}$		$-.7475 \times 10^{1}$		$-.6525 \times 10^{1}$
	$-.5252 \times 10^{1}$		$-.5581 \times 10^{1}$		$-.8715 \times 10^{1}$
	$-.1070$		$-.1187 \times 10^{1}$		$-.1286 \times 10^{1}$
	$-.1079 \times 10^{2}$		$-.1542 \times 10^{2}$		$-.1510 \times 10^{2}$
	$-.3064 \times 10^{1}$		$-.3842 \times 10^{1}$		$-.2671 \times 10^{1}$
	$-.1616 \times 10^{2}$		$-.2748 \times 10^{2}$		$-.2532 \times 10^{2}$
	$-.1063 \times 10^{1}$		$-.1111 \times 10^{1}$		$-.3254 \times 10^{1}$
	$-.2777 \times 10^{2}$		$-.1618 \times 10^{2}$		$-.1406 \times 10^{2}$

* The values for the parameters were $\alpha = 2.562205\ \mathring{A}^{-1}$, $A = 5.00 \times 10^{-18}$ ergs $\mathring{A}^{6}$, and $B = 1.00 \times 10^{-17}$ ergs.

$\underset{\sim}{q}$	ω^2	$\underset{\sim}{q}$	ω^2	$\underset{\sim}{q}$	ω^2
$.2022\hat{i}$	$.6054 \times 10^{1}$	$.3000\hat{j}$	$.6926 \times 10^{1}$	$.3000\hat{k}$	$.4924 \times 10^{1}$
	$-.1028 \times 10^{1}$		$.5017$		$.8656$
	$-.1241 \times 10^{2}$		$-.2150 \times 10^{1}$		$-.5972 \times 10^{1}$
	$-.4460 \times 10^{1}$		$-.4350 \times 10^{1}$		$-.1041 \times 10^{2}$
	$-.2266$		$-.2038 \times 10^{1}$		$-.2023$
	$-.1081 \times 10^{2}$		$-.5675 \times 10^{1}$		$-.1491 \times 10^{2}$
	$-.2618 \times 10^{1}$		$-.5455 \times 10^{1}$		$-.5764 \times 10^{1}$
	$-.1726 \times 10^{2}$		$-.1569 \times 10^{2}$		$-.2223 \times 10^{2}$
	$-.1955 \times 10^{1}$		$-.2687 \times 10^{2}$		$-.3579 \times 10^{1}$
	$-.2745 \times 10^{2}$		$-.1845 \times 10^{2}$		$-.1391 \times 10^{2}$
$.2696\hat{i}$	$.6515 \times 10^{1}$	$.4000\hat{j}$	$.7969 \times 10^{1}$	$.4000\hat{k}$	$.3740 \times 10^{1}$
	$-.9290$		$.8536$		$.1212 \times 10^{1}$
	$-.1242 \times 10^{2}$		$-.2672 \times 10^{1}$		$-.4579$
	$-.3722 \times 10^{1}$		$-.4491 \times 10^{1}$		$-.9657 \times 10^{1}$
	$-.3501$		$-.2910 \times 10^{1}$		$-.7215$
	$-.1103 \times 10^{2}$		$-.4099 \times 10^{1}$		$-.8678 \times 10^{1}$
	$-.2941 \times 10^{1}$		$-.6541 \times 10^{1}$		$-.1178 \times 10^{2}$
	$-.1861 \times 10^{2}$		$-.1602 \times 10^{2}$		$-.1454 \times 10^{2}$
	$-.2435 \times 10^{1}$		$-.2607 \times 10^{2}$		$-.1833 \times 10^{2}$
	$-.2696 \times 10^{2}$		$-.2067 \times 10^{2}$		$-.1288 \times 10^{2}$
$.3370\hat{i}$	$.6790 \times 10^{1}$	$.5000\hat{j}$	$.8948 \times 10^{1}$	$.5000\hat{k}$	$.1623 \times 10^{1}$
	$-.2179$		$.1250 \times 10^{1}$		$.1351 \times 10^{1}$
	$-.1234 \times 10^{2}$		$-.3954 \times 10^{1}$		$-.1240 \times 10^{2}$
	$-.4183 \times 10^{1}$		$-.8668 \times 10^{1}$		$-.6736$
	$-.2599$		$-.2857 \times 10^{1}$		$-.1978 \times 10^{1}$
	$-.1144 \times 10^{2}$		$-.1637 \times 10^{2}$		$-.1096 \times 10^{2}$
	$-.4120 \times 10^{1}$		$-.4181 \times 10^{1}$		$-.1383 \times 10^{2}$
	$-.2014 \times 10^{2}$		$-.2514 \times 10^{2}$		$-.1440 \times 10^{2}$
	$-.1555 \times 10^{1}$		$-.2470 \times 10^{1}$		$-.1404 \times 10^{2}$
	$-.2628 \times 10^{2}$		$-.2277 \times 10^{2}$		$-.1118 \times 10^{2}$

FOOTNOTES AND BIBLIOGRAPHY

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APPENDIX I

Symmetry Transformations On The Gallium Lattice

There are three lattice symmetry operations which may be applied to the gallium crystal in order to reduce the number of independent elements in the intermolecular force constant matrices. Two of these are described by Cochran and Pawley[5] and the third by Pawley.[6] A class A symmetry operation is used to bring the origin and source molecules into self-coincidence, as, for example, molecules located in a mirror plane are reflected into themselves. The operation has no effect on the intermolecular interactions and so yields[6]

$$\underset{\approx}{T}\,\underset{\approx}{\Phi}(jj')\,\underset{\approx}{\tilde{T}} = \underset{\approx}{\Phi}(jj') \quad . \qquad (1)$$

Class B is symmetry about a point in the lattice such as the origin. It is applied to gallium as inversion through the origin and takes the molecule located at $r_{j'}$, or (h, k, ℓ), into the one at $r_{j''}$ or $(-h, -k, -\ell)$. The force constant matrix of molecule j' can be shown to obey[5]

$$\underset{\approx}{T}\,\underset{\approx}{\Phi}(jj')\,\underset{\approx}{\tilde{T}} = \underset{\approx}{\tilde{\Phi}}(jj') \quad . \qquad (2)$$

Type C symmetry relates the interaction tensors or force constant matrices between two different pairs of molecules (i.e., it relates $\Phi(jj')$ and $\Phi(j''j''')$) by[6]

$$\underset{\approx}{T}\,\underset{\approx}{\Phi}(jj')\,\underset{\approx}{\tilde{T}} = \underset{\approx}{\Phi}(j''j''') \quad . \qquad (3)$$

An example of this is the screw diad transformation, which takes, for instance, the molecules located at the origin and (0, 1, 1) (molecules j and j′, respectively) into those of opposite orientation located at (0, 1, 1) and (0, 0, 2) (molecules j″ and j‴) respectively. From Equation (3) it may be shown[6] that the relationship between the interaction tensors of the two pairs of molecules is

$$\underset{\approx}{\Phi}(j''j''') = \underset{\approx}{I}\,\underset{\approx}{\Phi}(jj')\,\underset{\approx}{\tilde{I}} \;. \qquad (4)$$

where

$$\underset{\approx}{I} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} .$$

In each of equations (1 - 3), the matrix $\underset{\approx}{T}$ is the six-dimensional symmetry transformation. It is formed from $\underset{\approx}{S}$, the three-dimensional rotation matrix for polar vectors. If det $\underset{\approx}{S} = 1$ (a proper rotation), $\underset{\approx}{S}$ is also appropriate for axial vectors. For an improper rotation (det $\underset{\approx}{S} = -1$), $-\underset{\approx}{S}$ is needed for axial vectors. Thus $\underset{\approx}{S}$ det $\underset{\approx}{S}$ may always be used for axial vectors.[5] In the case of gallium, however, the axial and polar vectors are not measured in the same coordinate system (since the principal and crystal axes do not coincide). A vector $\underset{\sim}{V}$ measured with respect to the crystal axes transforms to the principal axes through

$$\underset{\sim}{V}_{PA} = \underset{\approx}{\alpha}\ \underset{\sim}{V}_{CA} \tag{5}$$

where

$$\underset{\approx}{\alpha} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{bmatrix}$$

Beginning then with the transformation of

$$\underset{\sim}{V}'_{CA} = \underset{\approx}{S} \det \underset{\approx}{S}\, \underset{\sim}{V}_{CA} \ ,$$

and substituting from Equation (5), one finds

$$\begin{aligned} \underset{\sim}{V}'_{PA} &= \underset{\approx}{\alpha}\, \underset{\sim}{V}'_{CA} = \underset{\approx}{\alpha}(\underset{\approx}{S} \det \underset{\approx}{S})\ \underset{\sim}{V}_{CA} \\ &= \underset{\approx}{\alpha}(\underset{\approx}{S} \det \underset{\approx}{S})\ \underset{\approx}{\alpha}^{-1}\ \underset{\approx}{\alpha}\, \underset{\sim}{V}_{CA} \\ &= \underset{\approx}{\alpha}(\underset{\approx}{S} \det \underset{\approx}{S})\ \underset{\approx}{\alpha}^{-1}\ \underset{\sim}{V}_{PA} \end{aligned}$$

Therefore $\underset{\approx}{T}$, the transformation matrix for some symmetry operation $\underset{\approx}{S}$, is given by

$$\underset{\approx}{T} = \begin{bmatrix} \underset{\approx}{S} & 0 \\ 0 & \underset{\approx}{\alpha}(\underset{\approx}{S} \det \underset{\approx}{S})\ \underset{\approx}{\alpha}^{-1} \end{bmatrix} \ .$$

The three classes of symmetry may be applied to the gallium lattice using this form of $\underset{\approx}{T}$. The application of class B symmetry in the form of inversion of the lattice through the origin gives the most general results of the three. The matrices used in forming $\underset{\approx}{T}$ are

$$\underset{\approx}{S} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

and

$$\underset{\approx}{\alpha}(\underset{\approx}{S} \det \underset{\approx}{S})\underset{\approx}{\alpha}^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} .$$

$\underset{\approx}{T}$ is therefore defined by

$$\underset{\approx}{T} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

and $\underset{\approx}{T}\,\underset{\approx}{\Phi}(jj')\,\underset{\approx}{\tilde{T}}$ is given by

$$\underset{\approx}{T}\,\underset{\approx}{\Phi}\,\underset{\approx}{\tilde{T}} = \begin{bmatrix} \Phi_{11} & \Phi_{12} & \Phi_{13} & -\Phi_{14} & -\Phi_{15} & -\Phi_{16} \\ \Phi_{21} & \Phi_{22} & \Phi_{23} & -\Phi_{24} & -\Phi_{25} & -\Phi_{26} \\ \Phi_{31} & \Phi_{32} & \Phi_{33} & -\Phi_{34} & -\Phi_{35} & -\Phi_{36} \\ -\Phi_{41} & -\Phi_{42} & -\Phi_{43} & \Phi_{44} & \Phi_{45} & \Phi_{46} \\ -\Phi_{51} & -\Phi_{52} & -\Phi_{53} & \Phi_{54} & \Phi_{55} & \Phi_{56} \\ -\Phi_{61} & -\Phi_{62} & -\Phi_{63} & \Phi_{64} & \Phi_{65} & \Phi_{66} \end{bmatrix} .$$

From Equation(2) this must equal $\underset{\approx}{\tilde{\Phi}}(jj')$ so that one has

$$\begin{bmatrix} \Phi_{11} & \Phi_{12} & \Phi_{13} & -\Phi_{14} & -\Phi_{15} & -\Phi_{16} \\ \Phi_{21} & \Phi_{22} & \Phi_{23} & -\Phi_{24} & -\Phi_{25} & -\Phi_{26} \\ \Phi_{31} & \Phi_{32} & \Phi_{33} & -\Phi_{34} & -\Phi_{35} & -\Phi_{36} \\ -\Phi_{41} & -\Phi_{42} & -\Phi_{43} & \Phi_{44} & \Phi_{45} & \Phi_{46} \\ -\Phi_{51} & -\Phi_{52} & -\Phi_{53} & \Phi_{54} & \Phi_{55} & \Phi_{56} \\ -\Phi_{61} & -\Phi_{62} & -\Phi_{63} & \Phi_{64} & \Phi_{65} & \Phi_{66} \end{bmatrix} = \begin{bmatrix} \Phi_{11} & \Phi_{21} & \Phi_{31} & \Phi_{41} & \Phi_{51} & \Phi_{61} \\ \Phi_{12} & \Phi_{22} & \Phi_{32} & \Phi_{42} & \Phi_{52} & \Phi_{62} \\ \Phi_{13} & \Phi_{23} & \Phi_{33} & \Phi_{43} & \Phi_{53} & \Phi_{63} \\ \Phi_{14} & \Phi_{24} & \Phi_{34} & \Phi_{44} & \Phi_{54} & \Phi_{64} \\ \Phi_{15} & \Phi_{25} & \Phi_{35} & \Phi_{45} & \Phi_{55} & \Phi_{65} \\ \Phi_{16} & \Phi_{26} & \Phi_{36} & \Phi_{46} & \Phi_{56} & \Phi_{66} \end{bmatrix} .$$

The form of the force constant matrix between the origin molecule and any source molecule is therefore

$$\underset{\approx}{\Phi}(jj') = \begin{bmatrix} \Phi_{11} & \Phi_{12} & \Phi_{13} & \Phi_{14} & \Phi_{15} & \Phi_{16} \\ \Phi_{12} & \Phi_{22} & \Phi_{23} & \Phi_{24} & \Phi_{25} & \Phi_{26} \\ \Phi_{13} & \Phi_{23} & \Phi_{33} & \Phi_{34} & \Phi_{35} & \Phi_{36} \\ -\Phi_{14} & -\Phi_{24} & -\Phi_{34} & \Phi_{44} & \Phi_{45} & \Phi_{46} \\ -\Phi_{15} & -\Phi_{25} & -\Phi_{35} & \Phi_{45} & \Phi_{55} & \Phi_{56} \\ -\Phi_{16} & -\Phi_{26} & -\Phi_{36} & \Phi_{46} & \Phi_{56} & \Phi_{66} \end{bmatrix} . \qquad (6)$$

Reflection of the lattice in a plane perpendicular to the a-axis is class A symmetry. The transformation matrices are

$$\underset{\approx}{S} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ and } \underset{\approx}{\alpha}(\underset{\approx}{S} \det \underset{\approx}{S})\underset{\approx}{\alpha}^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

so that $\underset{\approx}{T}$ is given by

$$\underset{\approx}{T} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix} .$$

From Equation (1), it is known that

$$\underset{\approx}{T}\,\underset{\approx}{\Phi}(jj')\underset{\approx}{\tilde{T}} = \begin{bmatrix} \Phi_{11} & -\Phi_{12} & -\Phi_{13} & -\Phi_{14} & \Phi_{15} & \Phi_{16} \\ -\Phi_{12} & \Phi_{22} & \Phi_{23} & \Phi_{24} & -\Phi_{25} & -\Phi_{26} \\ -\Phi_{13} & \Phi_{23} & \Phi_{33} & \Phi_{34} & -\Phi_{35} & -\Phi_{36} \\ -\Phi_{14} & \Phi_{24} & \Phi_{34} & \Phi_{44} & -\Phi_{45} & -\Phi_{46} \\ \Phi_{15} & -\Phi_{25} & -\Phi_{35} & -\Phi_{45} & \Phi_{55} & \Phi_{56} \\ \Phi_{16} & -\Phi_{26} & -\Phi_{36} & -\Phi_{46} & \Phi_{56} & \Phi_{66} \end{bmatrix}$$

is equal to $\underset{\approx}{\Phi}(jj')$. This indicates that the form of $\underset{\approx}{\Phi}$ between any two molecules in a plane perpendicular to the a-axis is

$$\underset{\approx}{\Phi}(jj') = \begin{bmatrix} \Phi_{11} & 0 & 0 & 0 & \Phi_{15} & \Phi_{16} \\ 0 & \Phi_{22} & \Phi_{23} & \Phi_{24} & 0 & 0 \\ 0 & \Phi_{23} & \Phi_{33} & \Phi_{34} & 0 & 0 \\ 0 & -\Phi_{24} & -\Phi_{34} & \Phi_{44} & 0 & 0 \\ -\Phi_{15} & 0 & 0 & 0 & \Phi_{55} & \Phi_{55} \\ -\Phi_{16} & 0 & 0 & 0 & \Phi_{56} & {}_{66} \end{bmatrix} .$$

Type C symmetry may be used to relate the interaction tensor $\underset{\approx}{\Phi}(jj')$ between a type A origin molecule (j) and some source molecule (j') located at (h, k, ℓ) with respect to the origin and the tensor $\underset{\approx}{\Phi}(n\,n')$ between a type B origin molecule (n) and the source molecule (n′) located at some (h, k, ℓ) with respect to it (molecule n). A screw diad transformation about an axis parallel to the b-axis and crossing the c-axis at (0, 0, $\frac{1}{2}$) will transform the pair of molecules (jj′) at (0, 0, 0) and (0, 1, 1) into the pair (j″ j‴) at (0, 1, 1) and (0, 0, 2). With respect to an origin located on the j″ molecule (of type B) at (0, 1, 1), the j‴ molecule (of type A) would be located at (0, 1, -1). From Equation (4) this indicates that the interaction tensors for the two pairs are related. Upon calculating

$$\underset{\approx}{I}\,\underset{\approx}{\Phi}(jj')\,\tilde{\underset{\approx}{I}} = \begin{bmatrix} \Phi_{11} & \Phi_{12} & \Phi_{13} & -\Phi_{14} & -\Phi_{15} & -\Phi_{16} \\ \Phi_{12} & \Phi_{22} & \Phi_{23} & -\Phi_{24} & -\Phi_{25} & -\Phi_{26} \\ \Phi_{13} & \Phi_{23} & \Phi_{33} & -\Phi_{34} & -\Phi_{35} & -\Phi_{36} \\ \Phi_{14} & \Phi_{24} & \Phi_{34} & \Phi_{44} & \Phi_{45} & \Phi_{46} \\ \Phi_{15} & \Phi_{25} & \Phi_{35} & \Phi_{45} & \Phi_{55} & \Phi_{56} \\ \Phi_{16} & \Phi_{26} & \Phi_{36} & \Phi_{46} & \Phi_{56} & \Phi_{66} \end{bmatrix}$$

and comparing this to $\underset{\approx}{\Phi}\,(j''j''')$ (which is of the same form as Equation (6)), one finds that the force constant matrices differ only in the signs associated with certain elements.

These are the only reductions possible from symmetry operations on the gallium lattice.

APPENDIX II

Analytical Calculation of the Interatomic Force Constants

Using the "6-exp" form for potential, one may derive the analytical expressions used in calculating the contributions from the interatomic forces to the intermolecular force and torque constants. The forces may be derived from the potential form

$$V = -\frac{A}{r^6} + B\,e^{-\alpha r}$$

using

$$\underset{\sim}{F} = -\underset{\sim}{\nabla}V = -\hat{r}\,\frac{dV}{dr} = \left[\frac{x_1}{r}\,\hat{e}_1 + \frac{x_2}{r}\,\hat{e}_2 + \frac{x_3}{r}\,\hat{e}_3\right]\left[\frac{6A}{r^7} - B\alpha e^{-\alpha r}\right]$$

where $\hat{e}_1$, $\hat{e}_2$, and $\hat{e}_3$ are unit vectors along the a, b, and c crystal axes. This may be written in component form as

$$F_i = x_i f(r) \qquad \text{where } f(r) = \frac{6A}{r^8} - \frac{B\alpha}{r}\,e^{-\alpha r} \quad .$$

If the source atom is displaced by some infinitesimal amount $\underset{\sim}{U}$, then the force increments generated on the atom at the origin are

$$dF_i = \sum_j \frac{\partial F_i}{\partial x_j}\,dx_j = \sum_j \frac{\partial F_i}{\partial x_j}\,U_j$$

$$= \sum_j \left[\frac{\partial x_i}{\partial x_j}\,f(r) + x_i\,\frac{\partial f}{\partial r}\,\frac{\partial r}{\partial x_j}\right] U_j \quad . \qquad (1)$$

If g(r) is defined by

$$g(r) = \frac{1}{r}\frac{\partial f}{\partial r} = -\frac{48A}{r^{10}} + \frac{B\alpha}{r^3}e^{-\alpha r} + \frac{B\alpha^2}{r^2}e^{-\alpha r}$$

then Equation (1) becomes

$$dF_i = \sum_j \left[\delta_{ij}\, f(r) + x_i\, x_j\, g(r)\right] U_j \quad .$$

By comparing this to the Hooke's law approximation, which gives

$$dF_i = -\sum_j \Phi_{ij}\, U_j \quad , \tag{2}$$

one can say that the force constants are represented by

$$\Phi_{ij} = -\delta_{ij}\, f(r) - x_i\, x_j\, g(r) \qquad \begin{array}{l} i = 1, 2, 3 \\ j = 1, 2, 3 \quad . \end{array}$$

The U_j, which are atomic displacements, must now be related to generalized displacements of the source molecule. Consider the atom located at (o, y, z) relative to the center of the dumbbell. The displacements of the atom with respect to the crystal axes due to translation of the molecule are the same as those of the molecule center and are designated by u_1, u_2, and u_3. The displacements of the atom due to some rotation $\underset{\sim}{\omega}$ of the molecule must also be included. Let $u_4\hat{i}$ and $u_5\hat{k}$ be the components of $\underset{\sim}{\omega}$ about the principal axes which have non-zero moments of inertia associated with them. (Note that $\hat{i}$, a principal axis, is coincident with $\hat{e}_1$. See Figure 4 for the relative orientation of axes.) The contribution may be found by taking $\underset{\sim}{D} = \underset{\sim}{\omega} \times (y\cos\theta + z\sin\theta)\hat{j}$ and converting the result to the crystal axis coordinates (see Figure 4). This is found to be

$$\underset{\sim}{D} = (u_4 \hat{i} + u_5 \hat{k}) \times (y\cos\theta + z\sin\theta)\hat{j}$$

$$= -u_5\ (y\cos\theta + z\sin\theta)\ \hat{i} + u_4\ (y\cos\theta + z\sin\theta)\ \hat{k} \quad .$$

Using the conversion equations

$$\hat{i} = \hat{e}_1$$

$$\hat{k} = -\sin\theta\ \hat{e}_2 + \cos\theta\ \hat{e}_3 \ ,$$

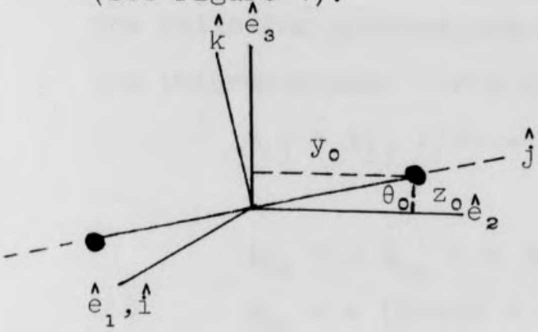

Figure 4: Principal axis orientation

one can show that

$$\underset{\sim}{D} = -\ u_5\ (y\cos\theta + z\sin\theta)\ \hat{e}_1 - u_4 z\ \hat{e}_2 + u_4 y\ \hat{e}_3 \quad .$$

The total component displacement of the atom due to translation and rotation of the molecule are therefore

$$U_1 = u_1 - u_5\ (y\cos\theta + z\sin\theta)$$

$$U_2 = u_2 - z u_4$$

$$U_3 = u_3 + y u_3 \quad .$$

The $\hat{e}_1$- force component may now be written as follows:

$$dF_1 = [f(r) + x_1{}^2\ g(r)][u_1 - u_5\ (y\cos\theta + z\sin\theta)]$$

$$+ x_1\ x_2\ g(r)\ [u_2 - z u_4] + x_1\ x_3\ g(r)\ [u_3 + u_4]$$

$$= [f(r) + x_1{}^2\ g(r)]\ u_1 + [x_1\ x_2\ g(r)]\ u_2$$

$$+ [x_1\ x_3\ g(r)]\ u_3 + [x_1\ g(r)(x_3\ y - x_2\ z)]\ u_4$$

$$- (y\cos\theta + z\sin\theta)\ [f(r) + x_1{}^2\ g(r)]\ u_5 \quad .$$

The $\hat{e}_2$- and $\hat{e}_3$- components may be written similarly and the following expressions found for the contributions to the intermolecular force constants:

$$\Phi_{ij} = \delta_{ij}\, f(r) + x_i\, x_j\, g(r) \qquad \begin{array}{l} k = 1,\ 2,\ 3 \\ j = 1,\ 2,\ 3 \quad . \end{array}$$

$$\Phi_{i4} = y\ \Phi_{i3} - z\ \Phi_{i2}$$

and $$\Phi_{i5} = -\ (y\cos\theta + z\sin\theta)\ \Phi_{i1}$$

where y and z represent the position of the source atom with respect to the center of mass of its molecule and θ is the angle of inclination of the source molecule.

The torque increments along the $\hat{i}$ and $\hat{k}$ axes of the origin molecule may be found using

$$d\underset{\sim}{\tau}\cdot\hat{e}_j = [(y_0\hat{e}_2 + z_0\hat{e}_3)\times d\underset{\sim}{F}_1]\cdot\hat{e}_j \text{ for } j = 4,\ 5 \text{ where } \begin{array}{l}\hat{e}_4 = \hat{i} \\ \hat{e}_5 = \hat{k}\end{array} .$$

where y_0 and z_0 represent the position of the origin atom with respect to the center of mass of the origin molecule

and $$d\underset{\sim}{F} = dF_1\ \hat{e}_1 + dF_2\ \hat{e}_2 + dF_3\ \hat{e}_3 \quad .$$

One then finds

$$d\underset{\sim}{\tau} = (y_0 dF_3 - z_0 dF_2)\hat{e}_1 + z_0\ dF_1\ \hat{e}_2 - y_0\ dF_1\ \hat{e}_3\ . \quad (3)$$

Converting this expression to principal axes gives

$$d\underset{\sim}{\tau} = [y_0 dF_3 - z_0 dF_2]\ \hat{i} + [-y_0 dF_1\ \cos\theta_0 - z_0 dF_1\ \sin\theta_0]\ \hat{j}$$
$$+ [-(y_0\ \cos\theta_0 + z_0\ \sin\theta_0)\ dF_1]\ \hat{k}$$

where θ_0 is the angle of inclination of the origin molecule. Since we may neglect the $\hat{j}$- or β- axis ($I_\beta = 0$), the torque components are

$$d\tau_1 = dF_4 = y_0 dF_3 - z_0 dF_2$$

$$d\tau_2 = dF_5 = -(y_0 \cos\theta_0 + z_0 \sin\theta) dF_1$$

The "torque constants" may then be found by substituting for dF_1, dF_2, and dF_3. After substituting these expressions into

$$dF_i = \sum_j \Phi_{ij} u_j \qquad \text{for } i = 1, 2, 3$$

one finds the torque constants to be

$$\Phi_{4j} = y_0 \Phi_{3j} - z_0 \Phi_{2j}$$

and $$\Phi_{5j} = -(y_0 \cos\theta_0 + z_0 \sin\theta_0) \Phi_{1j} \text{ for } j = 1\text{-}5.$$

APPENDIX III

Calculation Of The Self-Force Terms

The self-forces result from the motion $\underset{\sim}{u}_j$ of the origin molecule while the source molecules are undisplaced. Clearly, for a purely translational $\underset{\sim}{u}_j$, the force of the origin molecule is the same as if it were undisplaced and the source molecules were all translated by $-\underset{\sim}{u}_j$. If, however, $\underset{\sim}{u}_j$ has a rotational part, $\underset{\sim}{\omega}_j$, the corresponding shifts of the source molecules are both rotational and translational.[5] The molecules must be rotated by an amount $-\underset{\sim}{\omega}_j$ and translated by $-\underset{\sim}{\omega}_j \times \underset{\sim}{r}_{j'}$.

If $\underset{\sim}{v}_j$ represents the translational part of $\underset{\sim}{u}_j$, then the total forces on the origin molecule (including both those due to source molecules and $\underset{\sim}{F}_s$, the self-force) are

$$\underset{\sim}{F}_j = -\sum_{j'} \underset{\approx}{\Phi}(jj')\, \underset{\sim}{u}_{j'} + \underset{\sim}{F}_s = -\sum_{j'} \underset{\approx}{\Phi}(jj')\left[(\underset{\sim}{v}_{j'} - \underset{\sim}{v}_j) - \underset{\sim}{\omega}_j \times \underset{\sim}{r}_{j'} + (\underset{\sim}{\omega}_{j'} - \underset{\sim}{\omega}_j)\right] \quad . \qquad (1)$$

All the displacement terms must be expressed in terms of the $\hat{u}_i$ ($i = 1 - 5$) of the source molecule. For the translational terms, $[(\underset{\sim}{v}_{j'} - \underset{\sim}{v}_j) - (\underset{\sim}{\omega}_j \times \underset{\sim}{r}_{j'})]$, this is straightforward. If $\underset{\sim}{\omega}_j$ and $\underset{\sim}{r}_{j'}$ are defined by

$$\underset{\sim}{\omega}_j = \overset{\circ}{u}_4\, \hat{i} + \overset{\circ}{u}_5\, \hat{k} = \overset{\circ}{u}_4\, \hat{u}_1 \mp \overset{\circ}{u}_5 \sin\theta\, \hat{u}_2 + \overset{\circ}{u}_5 \cos\theta\, \hat{u}_3$$

$$\text{and } \underset{\sim}{r}_{j'} = H\, \hat{u}_1 + K\, \hat{u}_2 + L\, \hat{u}_3, \qquad (2)$$

then

$$
\begin{aligned}
-\underset{\sim}{\omega}_j \times \underset{\sim}{r}_{j'} = {} & u_5^\circ[K \cos\theta \pm L \sin\theta]\hat{u}_1 \\
& - [- u_4^\circ L + u_5^\circ H \cos\theta]\hat{u}_2 \\
& - [u_4^\circ K \mp u_5^\circ H \sin\theta]\hat{u}_3 \quad .
\end{aligned}
$$

Where there is a choice of sign, the top sign goes with a type A origin molecule (tipped at $+\theta$ with respect to the b-axis) and the bottom one with a type B origin molecule (at $-\theta$ with respect to the b-axis). Thus the translation components are given by

$$
\begin{aligned}
u_1 &= v_1(j') - v_1(j) + u_5^\circ[K \cos\theta + L \sin\theta] \\
u_2 &= v_2(j') - v_2(j) + u_4^\circ L - u_5^\circ H \cos\theta \\
u_3 &= v_3(j') - v_3(j) - u_4^\circ K - u_5^\circ H \sin\theta \quad .
\end{aligned}
\tag{3}
$$

The rotational terms must both be expressed with respect to the principal axes of the source molecule. If those of the origin molecule are parallel, then the components of rotation are

$$
\begin{aligned}
u_4 &= u_4(j') - u_4^\circ \\
u_5 &= u_5(j') - u_5^\circ \quad .
\end{aligned}
\tag{4}
$$

If the source molecule is not the same type as the origin, $\underset{\sim}{\omega}_j$ must be converted first to crystal axis components and then to components along $\hat{u}_4$ and $\hat{u}_5$. If $\underset{\sim}{\omega}_j$ is defined as in Equation 2, then it may be converted to the desired coordinate system using Equation (5), Appendix I. The resulting components for $(\underset{\sim}{\omega}_{j'} - \underset{\sim}{\omega}_j)$ are

$$
\begin{aligned}
u_4 &= u_4(j') - u_4^\circ \\
u_5 &= u_5(j') - u_5^\circ \cos 2\theta \quad .
\end{aligned}
\tag{5}
$$

Substituting the harmonic solution into Equation (1) as in Appendix I will leave a factor of $e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}}$ multiplying each term. If $\underset{\approx}{\Phi}(jj') = [\Phi_{ik}]$ is the force constant matrix between the j and j' molecules, then the contribution to the D_{ik} term of the dynamical matrix from source molecule motion is $\Phi_{ik}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}}$. The contribution due to motion of the original molecule may be expressed in terms of Φ_{ik}.

These self-force contributions to the dynamical matrix may be found by writing out Equation (1) in matrix form using $\underset{\approx}{\Phi} = [\Phi_{ik}]$ and the $\underset{\sim}{u}_i$ given in Equations (3) and (4) or (5). If the components of $\underset{\sim}{F}_j$ are now written in terms of source molecule and self-force contributions, as

$$F_i = - \sum_{j'} \sum_{k} \Phi_{ik}(jj')\, u_k(j') + \sum_{k} \Phi_{ik}(jj)\, u_k(j) \quad .$$

Comparison of the force components written from Equation (3) and those in Equation (4) shows that the self-force contributions to the dynamical matrix are of the following forms:

a. for type A origin molecules:

$i = 1, 2, 3, 4, 5 \qquad k = 1 - 10$

1. $\Phi_{ik}(jj) = \sum_{j'} \Phi_{ik}(jj')$ for $k = 1, 2, 3$

2. $\Phi_{i4}(jj) = \sum_{j'}[\Phi_{i4}(jj') - L\, \Phi_{i2}(jj') + K\, \Phi_{i3}(jj')$

(summed over both types A and B)

3. $$\begin{aligned} \Phi_{i5}(jj) = \sum_{j'(A)} [& \Phi_{i5}(jj') - \Phi_{i1}(jj') L \sin\theta \\ & - \Phi_{i1}(jj') K \cos\theta + \Phi_{i2}(jj') H \cos\theta \\ & + \Phi_{i3}(jj') H \sin\theta] \\ & + \sum_{j'(B)} [\Phi_{i5}(jj') \cos 2\theta - \Phi_{i1}(jj') L \sin\theta \\ & - \Phi_{i1}(jj') K \cos\theta + \Phi_{i2}(jj') H \cos\theta \\ & + \Phi_{i3}(jj') H \sin\theta \end{aligned}$$

(where the first sum is over type A molecules only and the second over type B only)

4. $\Phi_{ik}(jj) = 0 \qquad k = 6, 7, 8, 9, 10$

b. for type B origin molecules:

$i = 6, 7, 8, 9, 10 \quad k = 1 - 10$

It is convenient to define $m = i-5$ and $n = k-5$.

1. $\Phi_{mn}(jj) = \sum_{j'} \Phi_{mn}(jj')$ for $k = 6, 7, 8$

(summed over types A and B molecules)

2. $\Phi_{m9}(jj) = \sum_{j'} [\Phi_{m4}(jj') - L\, \Phi_{m2}(jj') + K\, \Phi_{m3}(jj')]$

(summed over types A and B)

3. $$\begin{aligned} \Phi_{m10}(jj) = \sum_{j'} [& \Phi_{m5}(jj') \cos 2\theta + \Phi_{m1}(jj') L \sin\theta \\ & - \Phi_{m1}(jj') K \cos\theta + \Phi_{m2}(jj') H \cos\theta \\ & - \Phi_{m3}(jj') H \sin\theta] \\ & + \sum_{j'} [\Phi_{m5}(jj') + \Phi_{m1}(jj') L \sin\theta \\ & - \Phi_{m1}(jj') K \cos\theta + \Phi_{m2}(jj') H \cos\theta \\ & - \Phi_{m3}(jj') H \sin\theta] \end{aligned}$$

(where the first sum is over type A only and the second over type B only)

4. $\Phi_{1k}(jj) = 0$ for $k = 1, 2, 3, 4, 5$.

APPENDIX IV

Programming Considerations

The normal mode frequencies of the lattice under the influence of an incident wave of momentum $\underset{\sim}{q}$ were calculated using the IBM 360/75 located at Triangle Universities Computation Center. The computation is divided into three main parts:

a. Calculation and storage of the intermolecular force constant matrices and of the self-force matrix.

b. Calculation of the dynamical matrix for a specific wave vector $\underset{\sim}{q}$.

c. Determination of the eigenvalues of the dynamical matrix for this $\underset{\sim}{q}$.

The program listing is included in this appendix.

The calculation and storage of the intermolecular force constant matrix for each pair of atoms are accomplished using three nested do-loops to select values of h, k, and ℓ. The interatomic force constants for the four possible combinations of origin and source atoms are computed and summed to give the intermolecular constants. These are used to calculate the self-force term and are then stored to be used in computing the dynamical matrix.

Each term of the dynamical matrix involves the corresponding term of the self-force matrix and the corresponding term of each intermolecular matrix multiplied by the factor $e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}$, where r is the location of the source molecule relative to the origin molecule. This exponential must be evaluated for each molecule. The dynamical matrix is accumulated for the specific $\underset{\sim}{q}$ involved.

The eigenvalues of the matrix are found using a subroutine, JACOBI, which was obtained from Oak Ridge National Laboratories, where it has been used extensively in lattice dynamics calculations.[10]

```
$JOB      COP.UNCG.PY600020/CLARK,TIME=010,PAGES=999
C
C
CGAFCN - SECULAR DETERMINANT AND DISPERSION RELATIONS
C FOR GALLIUM
C
C     VARIABLE AND ARRAY NAMES
C     IDNATM(3,4)      MOLEC & ATOMIC IDENTIFYING #S
C                      FOR EACH PAIR
C     SEPAR(3,4)       ATOMIC SEPARATIONS
C     RFG(3,4)         RADII,F(R), AND G(R) FOR EACH ATOM PAIR
C     FCON(5,5,4)      FORCE CONSTANTS FOR EACH PAIR
C     PHI(5,5)         FORCE CONSTANTS FOR EACH MOLECULE PAIR
C     AXIS(3)          UNIT AXIS LENGTHS (1/2 CUBE EDGE LENGTH)
C     H,K,L            POSITION OF SOURCE MOLECULE
C     HMAX,KMAX,LMAX   HIGHEST VALUE CONSIDERED FOR H,K,L
C     A,B,ALFA         CONSTANTS IN 6-EXP POTENTIAL FUNCTION
C     POSIT(4,4)       POSITIONS OF ATOMS IN ORIGIN AND
C                      SOURCE MOLECULES
C     Y(4)             ATOM DISPLACEMENTS RELATIVE TO
C                      CM OF MOLECULE
C                      Y(1),Y(2)    EQUIL POS OF ORIGIN ATOMS
C                      Y(3),Y(4)    POS OF SOURCE ATOMS
C     SINE,COSINE      SIN AND COS OF ANGLE BETW PRIN
C                      AND CRYSTAL AXES
C     D                ONE-HALF DUMBBELL LENGTH
C     SELF(10,10)      SELF FORCE TERMS
C     DYNAM(10,10)     DYNAMICAL MATRIX
C     WAVE(3)          INCIDENT WAVE COMPONENTS
C     AMASS(10)        MASSES AND MOMENTS OF INERTIA
C     PHISTR(5,5,100,2)
C                      STORAGE FOR INTERMOLEC CONSTANTS
C
      IMPLICIT REAL*8(A-H,O-Z)
      REAL TT
      INTEGER H,HM,HMAX
      DIMENSION IDNATM(3,4),SEPAR(3,4),RFG(3,4),FCON(5,5,4),
     1AXIS(3),PHI(5,5),Y(4),SELF(10,10),DYNAM(10,10),WAVE(3),
     2PHISTR(5,5,100,2),NUMBER(2),SC(5,5),POSIT(4,4),AMASS(10),
C EXTRA ARRAYS REQUIRED BY MATRIX SOLUTION SBR
     3EIGEN(10),WORK(10,10)
C INITIALIZE SC AND IDNATM
      DO 20J=1,2
      DO 20I=1,3
      IDNATM(I,J)=1
 20   IDNATM(I,J+2)=2
      DO 25I=1,10
      DO 25J=1,10
 25   SELF(I,J)=0.
      DO 35I=1,3
      DO 30J=1,3
 30   SC(I,J)=1.
      DO 35J=4,5
      SC(I,J)=-1.
 35   SC(J,I)=-1.
      DO 36I=4,5
```

```
      DO 36J=4,5
 36   SC(I,J)=1.
      READ(1,6101)A,B
      READ(1,6102)ALFA,(AXIS(I),I=1,3),HMAX,KMAX,LMAX,(Y(I), 44
     1I=1,4)
      READ(1,6104) (AMASS(I),I=1,2)
 6104 FORMAT(2F11.7)
 6101 FORMAT(2F10.0)
 6102 FORMAT(F8.6,F5.3,F6.4,F5.3,3I1,4F5.4)
       WRITE(3,950)
 950  FORMAT(1X,' A       B            ALFA           AX A       AX B',
     1'      AX C')
       WRITE(3,955)A,B,ALFA,(AXIS(I),I=1,3)
 955  FORMAT(1X,2F13.2,4F13.9)
       WRITE(3,951)
 951  FORMAT(1X,'    Y0       Z0       Y       Z           MAX H     K     L')
      WRITE(3,960) (Y(I),I=1,4),HMAX,KMAX,LMAX
 960  FORMAT(1X,4F13.9 ,3I5)
C SET UP MASS MATRIX
      AMASS(4) = AMASS(2)
      AMASS(5) = AMASS(2)
      AMASS(2) = AMASS(1)
      AMASS(3) = AMASS(1)
      DO 3I=1,5
 3    AMASS(5+I)=AMASS(I)
      Y4 = Y(1)*4.
      Z4 = Y(2)*4.
      DO 5I=1,2
      Y(I+2) = Y(I+2)*AXIS(I+1)*2
 5    Y(I) = Y(I)*2*AXIS(I+1)
      DO 10I=1,4
      DO 10J=1,4
 10   POSIT(I,J) = Y(J)
      DO 15I=1,2
      DO 15J=1,2
      POSIT(J+2,I) = -POSIT(J+2,I)
 15   POSIT(J*2,I+2) = -POSIT(J*2,I+2)
      HM = HMAX+1
      KM = KMAX+1
      LM = LMAX+1
      D = Y(1)*Y(1) + Y(2)*Y(2)
      D =DSQRT(D)
      SINE = Y(2)/D
      COSINE = Y(1)/D
      ARG = DARCOS(COSINE)
      COS2 = DCOS(2*ARG)
C
C SELECT H,K,L FOR SOURCE MOLECULE
C
      DO 2000MTYPE=1,2
      MOLEC = MTYPE-1
C INITIALIZE FLAGS, ETC.
      IDNATM(1,1) = 0
      IDNATM(3,1) = 0
      IDNATM(3,3) = 0
      IDNATM(3,2) = 1
```

```
          IDNATM(3,4) = 1
          LFLAG = 1
   50     DO 800NDX1=1,LM
          L = NDX1-1
          LFLAG = -LFLAG
          MXCODE=1
          CONST=COS2
          IF(LFLAG+1)60,55,60
   55     MXCODE = 0
          CONST = 1.
   60     DO 700NDX2=1,KM
          K = NDX2-1
   70     DO 600NDX3=1,HM
          H = NDX3-1
C SKIP THE 0-0-0 POSITION
          IF (L)78,72,78
   72     IF (K)78,73,78
   73     IF (H)78,75,78
   75     H = H+1
C TEST FOR EVEN H+K+L
   78     II = (H+K+L)/2
          TT = (H+K+L)/2.
          IF(TT.NE.II)GO TO 600
C RETURN POSITION FOR H-MIRROR CALCULATIONS
C OTHERS GO TO BEGINNING OF NEXT DO LOOP
C
C CLEAR MOLECULAR FORCE CONSTANTS
   88     DO 85J=1,5
          DO 85I=1,5
   85     PHI(I,J)=0.
C INCREMENT SOURCE MOLECULE AND ATOM#S
   80     IDNATM(1,1) = IDNATM(1,1)+1
          NUMBER(MTYPE) = IDNATM(1,1)
          DO 90I=1,4
   90     IDNATM(3,1) = IDNATM(3,1)+1
C STORE H,K,L AS ATOMIC SEPARATIONS
          DO 100J=1,4
          SEPAR(1,J) = H
          SEPAR(2,J) = K
  100     SEPAR(3,J) = L
C ADJUST ATOMIC SEPARATIONS
          SEPAR(2,2) = SEPAR(2,2) - Y4
          SEPAR(2,3) = SEPAR(2,3) + Y4
          IF(LFLAG+1)105,103,105
C LIKE MOLECULE ROUTINE (L = EVEN)
  103     SEPAR(3,2) = SEPAR(3,2) - Z4
          SEPAR(3,3) = SEPAR(3,3) + Z4
          GO TO 107
C UNLIKE MOLECULE ROUTINE (L = ODD)
  105     SEPAR(3,1) = SEPAR(3,1) - Z4
          SEPAR(3,4) = SEPAR(3,4) + Z4
C
C COMPUTE RADII,F, & G FOR EACH PAIR
C
  107     DO 110N = 1,4
          DO 110J=1,3
```

```
  110 SEPAR(J,N) = SEPAR(J,N) * AXIS(J)
      DO 150I=1,4
      RFG(1,I)= SEPAR(1,I) * SEPAR(1,I)
     $         + SEPAR(2,I) * SEPAR(2,I)
     $         + SEPAR(3,I) * SEPAR(3,I)
      RFG(1,I) = DSQRT(RFG(1,I))
      R= RFG(1,I)
      EXPO = DEXP(-ALFA*R)
      RFG(2,I) = (6.*A)/R**8 - B*ALFA*EXPO/R
  150 RFG(3,I) = (-48.*A)/R**10 + (B*ALFA*EXPO)/(R*R*R)
     $            +(B*ALFA*ALFA*EXPO)/(R*R)
C
C CALCULATE FORCE AND TORQUE CONSTANTS BETWEEN ATOM PAIRS
C
      SIN1 = SINE*((-1)**MOLEC)
      SIN2 = SIN1*LFLAG
  200 DO 400N=1,4
CCALCULATE FORCE CONSTS
      DO 260I=1,3
      DO 260J=1,3
C EVALUATION OF KRONECKER DELTA
      KDELTA = 0
      IF(I-J)210,205,210
  205 KDELTA = 1
 210  FCON(I,J,N) =-KDELTA*RFG(2,N) -
     1                  SEPAR(I,N)*SEPAR(J,N)*RFG(3,N)
  260 CONTINUE
C CALCULATE TORQUE CONSTANTS
C J4 & J5 FOR J = 1-5
      DO 325J=1,3
      FCON(J,4,N) = FCON(3,J,N)*POSIT(N,3) -
     1                  FCON(2,J,N)*POSIT(N,4)
  325 FCON(J,5,N) = FCON(1,J,N)*(POSIT(N,3)*COSINE +
     1                  POSIT(N,4)*SIN2)
C 4J & 5J FOR J = 4,5
      DO 300J=4,5
      FCON(4,J,N) = FCON(3,J,N)*POSIT(N,1) -
     1                  FCON(2,J,N)*POSIT(N,2)
  300 FCON(5,J,N) =    FCON(1,J,N)*(POSIT(N,1)*COSINE +
     1                  POSIT(N,2)*SIN1)
C ACCUMULATE MOLECULAR FORCE CONSTANTS
      DO 350I=1,5
      DO 350J=I,5
  350 PHI(I,J) = PHI(I,J) + FCON(I,J,N)
C
C FORCE SYMMETRY ON PHI MATRICES
C
      DO 420I=2,5
      JI=I-1
      DO 420J=1,JI
  420 PHI(I,J) = PHI(J,I)
      DO 400I=4,5
      DO 400J=1,3
      PHI(I,J) = -PHI(I,J)
  400 CONTINUE
C
```

```
C STORE FORCE CONSTANTS
C
      NO = NUMBER(MTYPE)
      DO 410 I=1,5
      DO 410 J=1,5
  410 PHISTR(I,J,NO     ,MTYPE) = PHI(I,J)
C
C COMPUTE AND ACCUM SELF-FORCE TERMS
C
      DO 460 I=1,5
      N1=I+(5*MOLEC)
      N2 = 5*MOLEC
      SELF(N1,4+N2) = SELF(N1,4+N2) - PHI(I,2)*L*AXIS(3) +
     1                     PHI(I,3)*K*AXIS(2) + PHI(I,4)
      SELF(N1,5+N2) = SELF(N1,5+N2) + PHI(I,1)*(-K*COSINE*
     1AXIS(2) + L*SINE*AXIS(3)*((-1)**MTYPE)) + PHI(I,2)*
     2H*COSINE*AXIS(1) + PHI(I,3)*H*SINE*AXIS(1)*((-1)**MOLEC)
     3+ PHI(I,5)*CONST
      DO 460 J=1,3
  460 SELF(N1,J+N2)=SELF(N1,J+N2) + PHI(I,J)
C
C DO H-MIRROR POSITION IF NOT PREVIOUSLY DONE
C
      H=-H
      IF(H)88,600,600
C OTHERWISE CONTINUE K-ROW
  600 CONTINUE
C
C DO -K ROW IF NOT YET DONE
C
      K=-K
      IF(K)70,700,700
  700 CONTINUE
C
C DO -L PLANE FINALLY
C
      L=-L
      IF(L)60,801,801
  801 DO 52I = 1,4
  52  POSIT(I,4) = -POSIT(I,4)
  800 CONTINUE
      Z4=-Z4
      DO 810I=1,4
      POSIT(I,2) = -POSIT(I,2)
  810 POSIT(I,4) = POSIT(I,4)*IFLAG
 2000 CONTINUE
 5566 FORMAT(5D24.16)
C
C BEGINCONSTRUCTING DYNAMICAL MATRIX
C
C READ COMPONENTS OF INCIDENT WAVE
 1000 READ(1,6103) (WAVE(I),I=1,3)
 6103 FORMAT(3F10.9)
      LFLAG=1
C CLEAR DYNAM FOR NEXT INCIDENT WAVE
      DO 1900I=1,10
```

```
      DO 1900J=1,10
 1900 DYNAM(I,J) = 0.
      N = 0
      WRITE(3,992)
      WRITE(3,993) (WAVE(I) ,I=1,3)
  992 FORMAT(1X,' QX       QY       QZ')
  993 FORMAT(3F8.5)
C
C SELECT H,K,L USING DO-LOOPS AS ABOVE
C
 1050 DO 1800NDX1=1,LM
      L = NDX1-1
      LFLAG=-LFLAG
      MXCODE=1
      IF(LFLAG.LT.0) MXCODE=0
 1060 DO 1700NDX2=1,KM
      K = NDX2-1
 1070 DO 1600NDX3=1,HM
      H = NDX3-1
C SKIP 0-0-0
      IF (L) 1078,1072,1078
 1072 IF(K) 1078,1073,1078
 1073 IF(H) 1078,1075,1078
 1075 H=H+1
C
C TEST FOR EVEN H+K+L
C
 1078 II = (H+K+L) /2
      TT = (H+K+L) /2.
      IF(TT.NE.II) GO TO 1600
C
C RETURN FOR -H POSITIONS; OTHERS GO TO NEXT DO LOOP
C
C COMPUTE COSINE(Q.R)
 1088 ARG = (WAVE(1)*H+WAVE(2)*K+WAVE(3)*L) * (3.1415927)
      RCOS = DCOS(ARG)
      RSIN = DSIN(ARG)
C
C ACCUM DYNAMICAL MATRIX TERMS -
C       NOTE DYNAM IS INITIALIZED TO ZERO
C
      N = N+1
      DO 450 I = 1,5
      I5 = I+5
      DO 450 J = 1,5
      N1 = J+5*MXCODE
      N2 = J+5*(1-MXCODE)
      FACTOR = RCOS
      IF(SC(I,J))421,440,440
  421 FACTOR = RSIN
  440 DYNAM(I,N1)= DYNAM(I,N1) +
     1       PHISTR(I,J,N,1     )*FACTOR
  450 DYNAM(I5,N2)  = DYNAM(I5,N2)
     1+PHISTR(I,J,N,2) *FACTOR
C DO -H POSITIONS
      H=-H
```

```
      IF (H) 1088,1600,1600
 1600 CONTINUE
C DO -K ALSO
      K=-K
      IF (K) 1070,1700,1700
 1700 CONTINUE
C FINALLY DO -L
      L=-L
      IF (L) 1060,1800,1800
 1800 CONTINUE
C
C
C COMPLETE DYNAMICAL MATRIX USING SELF-FORCE TERMS
      DO 825N=1,6,5
      DO 825K=1,6,5
      DO 825I=1,3
      DO 825J=4,5
      IK=I+K-1
      JN=J+N-1
  825 DYNAM(IK,JN) = -DYNAM(IK,JN)
      DO 850I=1,10
      DO 850J=1,10
      DENOM = AMASS(I)*AMASS(J)
      DENOM = DSQRT(DENOM)
      DYNAM(I,J) = (DYNAM(I,J) - SELF(I,J))/(DENOM)
      DYN= DABS(DYNAM(I,J))
      IF(DYN.LT.(1.D-13))DYNAM(I,J)=0.
  850 CONTINUE
C
C PRINT DYNAMICAL MX
C
      WRITE(3,990)
      DO 875I=1,10
      WRITE(3,991) (DYNAM(I,J),J=1,10)
  875 CONTINUE
  990 FORMAT(1X,' THE DYNAMICAL MATRIX IS')
  991 FORMAT(5D24.16)
C CALL MATRIX SOLUTION SUBROUTINE
      NCOL = 10
      CALL JACOBI(DYNAM,WORK,EIGEN,NCOL)
      WRITE(3,6100)
 6100 FORMAT(1X,' THE NORMAL MODE FRENQUENCIES ARE')
      WRITE(3,5566)(EIGEN(I),I=1,10)
      GO TO 1000
      END



      SUBROUTINE JACOBI(A,B,E,N)
C SOLUTION SUBROUTINE FROM OAKRIDGE NATIONAL LABORATORIES
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(N,N), B(N,N), E(N)
      S=0.0
      DO10I=1,N
   10 S= S+DABS(A(I,I))
      TEST=S/N
      DO12I=1.N
```

```
      DO11J=1,N
   11 B(I,J)=0.0
   12 B(I,I)=1.0
      GOTO15
   25 DO13I=2,N
      II=I-1
      DO13J=1,II
      P=A(I,J)
      IF ( DABS(P)-AMAX)  13,16,16
   16 Y=(A(J,J)-A(I,I))/2.0
      D=Y**2+P*A(J,I)
      IF(D)  18,18,77
   77 YSQ= Y+DSQRT(D)
      IF(YSQ)31,31,17
   31 DD  =  Y  **2  +  P*A(J,I)
      YY=DSQRT(DD)
      DENOM=Y+YY
      YSQ=DABS(DENOM)
      SSIGN=  P*A(I,J)
      IF  ( SSIGN )  32,17,17
   32 YSQ=-YSQ
   17 X=P/YSQ
      GOTO19
   18 X=P/Y
   19 U=  DSQRT(  1.  +X*X  )
      C=1/U
      S=X*C
      DO20K=1,N
      Y=A(K,I)
      Z=A(K,J)
      A(K,I)=C*Y-S*Z
      A(K,J)=S*Y+C*Z
      Y=B(K,I)
      Z=B(K,J)
      B(K,I)=C*Y-S*Z
   20 B(K,J)=S*Y+C*Z
      DO  1  K=1,N
      Y=A(I,K)
      Z=A(J,K)
      A(I,K)=C*Y-S*Z
    1 A(J,K)=S*Y+C*Z
   13 CONTINUE
   15 S=0.0
      DO21I=2,N
      II=I-1
      DO21J=1,II
      IF  ( DABS(  A(I,J))-S  )  21,21,22


   22 S=  DABS(A(I,J))
 21   CONTINUE
   23 R=S/TEST
      AMAX=S/5.0
      IF(R-1.0D-6) 24,24,25
   24 DO26I=1,N
   26 E(I)=A(I,I)
      RETURN
      END
```

APPENDIX V

Calculation of the First Brillouin Zone Boundaries

The limits of the wave vector $\underset{\sim}{q}$ for the first Brillouin zone are found in the usual manner.[11] A set of primitive translation vectors for the lattice is chosen, and those of the reciprocal lattice in momentum space are calculated. The boundary planes of the first Brillouin zone are the planes which perpendicularly bisect the vectors from the origin to the nearest base-centers and to the nearest cell corners on each axis.

A set of primitive translation vectors, $\underset{\sim}{a}_i$, for the lattice can be shown to be

$$\begin{aligned} \underset{\sim}{a}_1 &= (a/2)\,\hat{u}_1 - (b/2)\,\hat{u}_2 \\ \underset{\sim}{a}_2 &= b\hat{u}_2 \\ \underset{\sim}{a}_3 &= c\hat{u}_3 \end{aligned} \tag{1}$$

by computing the volume of the primitive cell which they form. Since there are two lattice points per unit cell (of volume abc), then the primitive cell, containing one lattice point should have a volume of abc/2. The volume of the cell described by Equation (1) is

$$\underset{\sim}{a}_1 \cdot \underset{\sim}{a}_2 \times \underset{\sim}{a}_3 = (a/2\,\hat{u}_1 - b/2\,\hat{u}_2)\cdot(b\hat{u}_2 \times c\hat{u}_3) = abc/2 \quad .$$

Using Equation (1), the reciprocal lattice primitive vectors, $\underset{\sim}{b}_i$, may be found from

$$\underset{\sim}{b}_i = \frac{\underset{\sim}{a}_j \times \underset{\sim}{a}_k}{\underset{\sim}{a}_1 \cdot \underset{\sim}{a}_2 \times \underset{\sim}{a}_3}$$

where i, j, k are cyclic in 1, 2, 3. The reciprocal lattice is found to be base-centered orthorhombic and the cell edge lengths are given values of $x = 4\pi/a$, $y = 4\pi/b$, and $z = 2\pi/c$. The reciprocal lattice may be described by primitive vectors

$$\underset{\sim}{b}_1 = (4\pi/a)\ \hat{u}_1$$
$$\underset{\sim}{b}_2 = (2\pi/b)\ \hat{u}_1 + (2\pi/a)\ \hat{u}_2$$
$$\underset{\sim}{b}_3 = (2\pi/c)\ \hat{u}_3$$

The reciprocal lattice is now plotted, and the distance from the origin to the first Brillouin zone along each of the axes may be found geometrically. The distance in the (100) and (010) directions are found using a plot of the x-y plane of the reciprocal lattice (in Figure 5). Two Brillouin zone boundary planes intersect the x-axis. The distance x_1' is by definition one-half the distance to the first lattice point, or

$$x_1' = \pi/a$$

geometrically, x_1 is found from

$$x_1 \cos\theta = \tfrac{1}{4}\left[\left(\frac{2\pi}{a}\right)^2 + \left(\frac{2\pi}{b}\right)^2\right]^{\frac{1}{2}} .$$

After substituting

$$\cos\theta = (2\pi/b)\ /\ [(2\pi/a)^2 + (2\pi/b)^2]^{\frac{1}{2}} ,$$

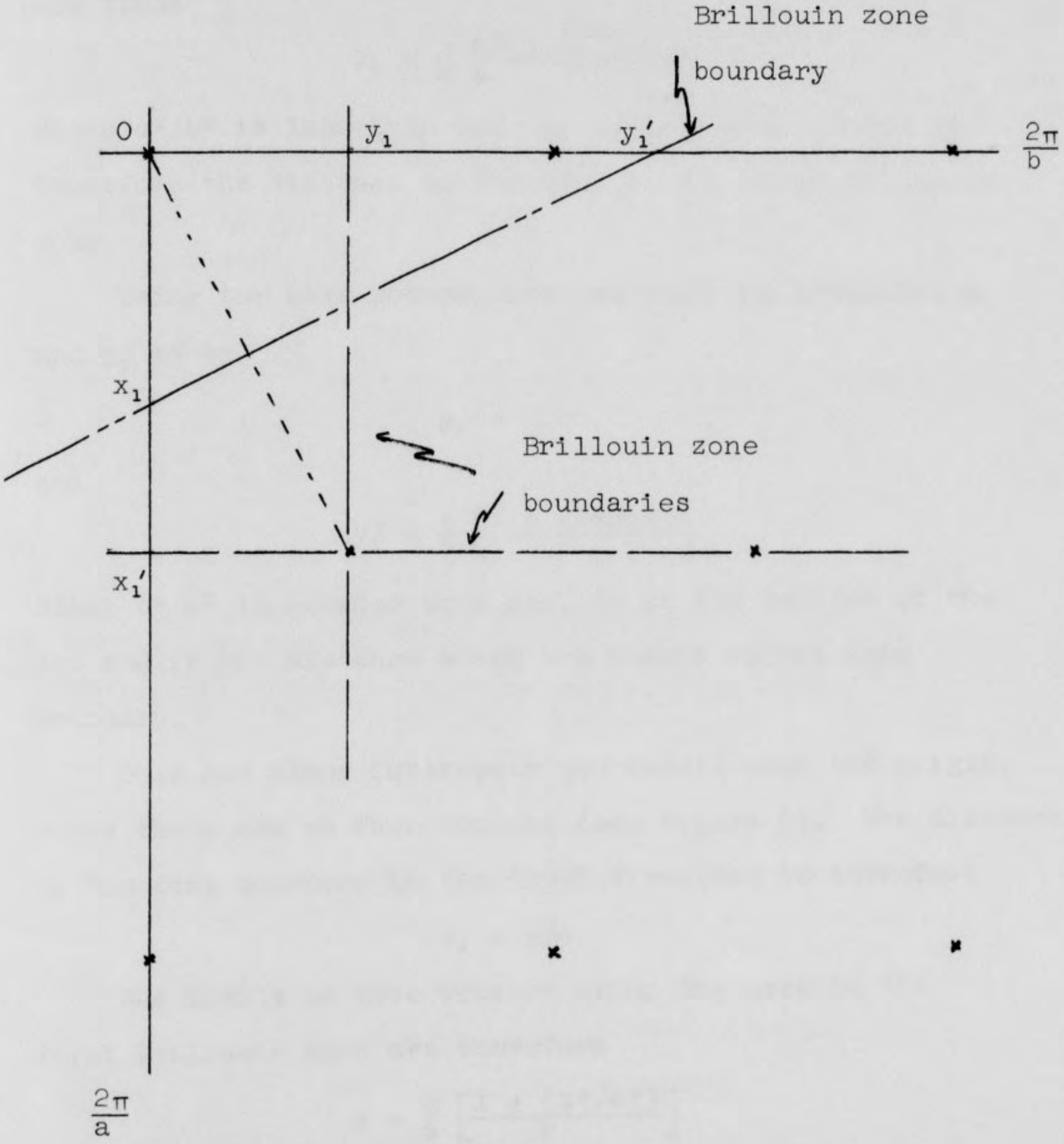

Figure 5: The first quadrant of the x-y plane of the reciprocal lattice showing the Brillouin zone boundaries

one finds

$$x_1 = \frac{\pi}{a}\left[\frac{1 + (a^2/b^2)}{2}\right] .$$

Since a^2/b^2 is less than one, x_1 is less than x_1' and is therefore the distance to the edge of the first Brillouin zone.

Using the same method, one can find the distances y_1 and y_1' to be

$$y_1 = \pi/b$$

and

$$y_1' = \frac{\pi}{b}\left[\frac{1 + (b^2/a^2)}{2}\right] .$$

Since b^2/a^2 is greater than one, y_1 is the smaller of the two and is the distance along the y-axis to the zone boundary.

Only one plane intersects the z-axis near the origin, since there are no face centers (see Figure 6). The distance to the zone boundary in the (001) direction is therefore

$$z_1 = \pi/c$$

The limits of wave vectors along the axes in the first Brillouin zone are therefore

$$x = \frac{\pi}{a}\left[\frac{1 + (a^2/b^2)}{2}\right]$$

$$y = \pi/b$$

$$z = \pi/c \quad .$$

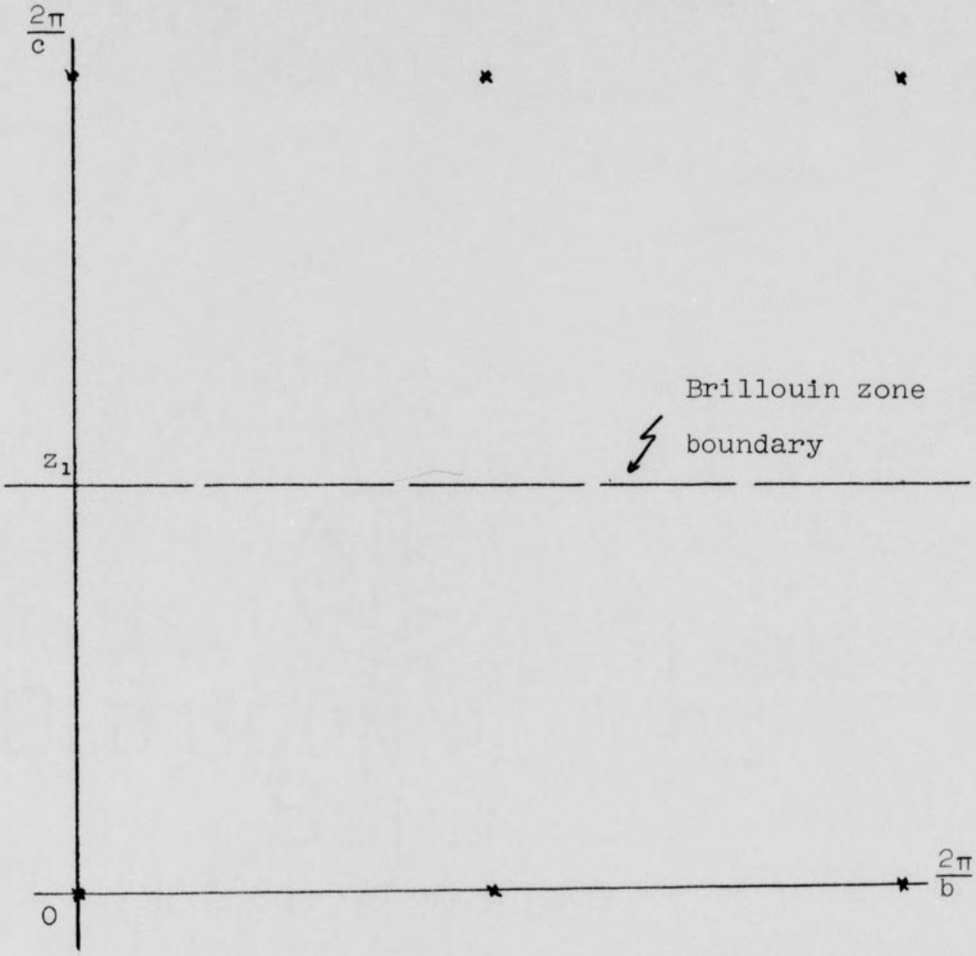

Figure 6: The first quadrant of the y-z plane of the reciprocal lattice showing the Brillouin zone boundary