FREEMAN, WALLACE LARRY. Lattice Dynamics in Gallium Using the "6-exp" Potential with Parameters Determined by the "Least Squares" Method. (1971) Directed by: Dr. Clifton Bob Clark. Pp. 91

The equations of motion for the dumbbell molecules of gallium are derived using the harmonic approximation. The "6-exp" interaction potential energy function is used to derive analytic expressions for the interatomic coupling constants. The intermolecular coupling constants are then determined numerically. These are used to calculate the elements of the dynamical matrix. The dynamical matrix is solved for the normal mode frequencies. The "Least Squares" method is used with a computer program to select a set of "6-exp" parameters to best fit the frequencies measured by others. Since some imaginary frequencies occurred for all sets of parameters found, the model does not agree with experimental results. There are two possible reasons for this disagreement: (1) The "6-exp" interaction function may not be applicable to gallium or (2) it may be invalid to treat gallium as having a molecular structure.

LATTICE DYNAMICS IN GALLIUM USING THE "6-exp"

POTENTIAL WITH PARAMETERS DETERMINED BY

THE "LEAST SQUARES" METHOD

by

Wallace Larry Freeman

A Thesis Submitted to
the Faculty of the Graduate School at
The University of North Carolina at Greensboro
in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Greensboro
1971

Approved by

Clifton Bob Clark
Thesis Advisor

This thesis has been approved by the following committee of the Faculty of the Graduate School at The University of North Carolina at Greensboro.

Thesis Advisor _Clifton Bob Clark_

Oral Examination
Committee Members _Francis J McCormack_

Andrew F. Long, Jr

July 1, 1971
Date of Examination

ii

TABLE OF CONTENTS

396228

iv

LIST OF TABLES

LIST OF FIGURES

Page

vi

INTRODUCTION

A crystal is a regular array of points in space with
atoms and/or molecules located at these points. It is
described using the concepts of the unit cell and transla-
tion vectors. The unit cell is a particular arrangement of
atoms and/or molecules which, when translated regularly
through space generates the crystal. The translation
vectors describe the location of a unit cell relative to
some co-ordinate system. For gallium, a set of three
mutually orthogonal vectors is chosen along the crystal
axes so that the unit cell is located at every combination
of even-integer multiples of these vectors. It should be
noted that this is not the only set of translation vectors
which describe the location of a unit cell for gallium.
However, it is one of the simplest and most convenient,
particularly, when considering programming techniques in
locating specific molecules.

The lattice structure for gallium is base-centered
orthorhombic (Fig. 1). Molecules are located at the
corners of the structure and in the middle of the upper
and lower faces.

There are two distinct types of molecules which, for
the purpose of this thesis, are labeled A and B. Both
types are treated as rigid dumbbells of length 2.442 Å [1]
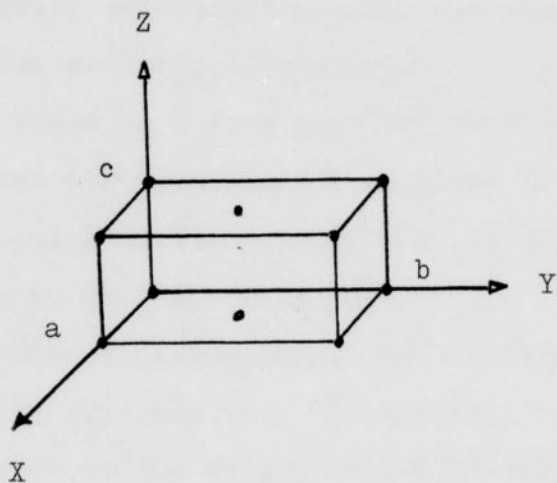
Fig. 1. The base-centered orthorhombic
lattice. $(a \neq b, a \neq c, b \neq c)$

and individual atomic masses of 115.7 X 10^{-24} grams.[2] The type A molecule is oriented so that the dumbbell axis makes an angle of approximately 16.9° counterclockwise with the Y axis (Fig. 2). The type B molecule is oriented so that the dumbbell axis makes an angle of approximately 16.9° clockwise with the Y axis (Fig. 2). The dumbbell axis of both types is always parallel to the Y-Z plane. This means that two orthorhombic lattices are combined to form the crystal structure of gallium. A unit cell of gallium is shown in Fig. 3. Note that in the figure a type A molecule is located at the origin of the co-ordinate system. A unit cell may also be constructed with a type B molecule located at the origin by replacing all type A molecules with type B molecules and vice versa. The a, b, and c lengths in Fig. 3 are called the lattice constants and are independent of the origin molecule.

As mentioned, a set of translation vectors is chosen so that a unit cell is located at every combination of even-integer multiples of these vectors. Therefore, in order to generate the crystal, the unit cell must be translated through space according to $\underline{T} = h\frac{a}{2}\hat{x} + k\frac{b}{2}\hat{y} + l\frac{c}{2}\hat{z}$ where h, k, and l are even integers and $\hat{x}$, $\hat{y}$, and $\hat{z}$ are the unit vectors along the axes of the crystal.

Exerting a force on a molecule in the crystal disturbs it from equilibrium. If there is a coupling between

and molecules and those just above them the dimensions to
be identical to the ......
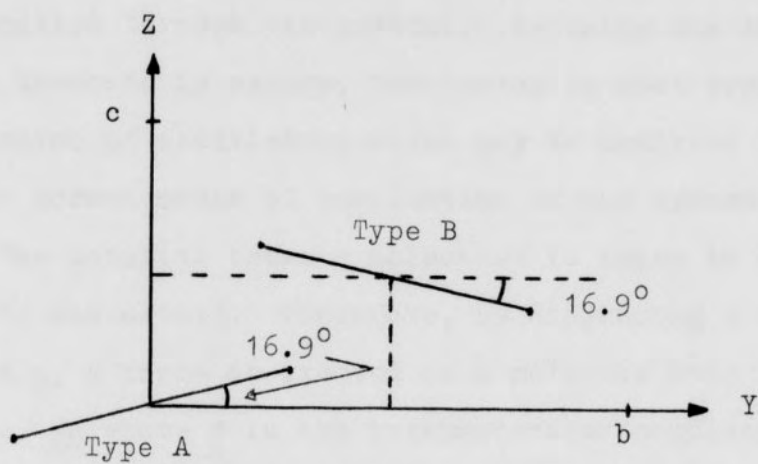
Fig. 2. The types of molecules.
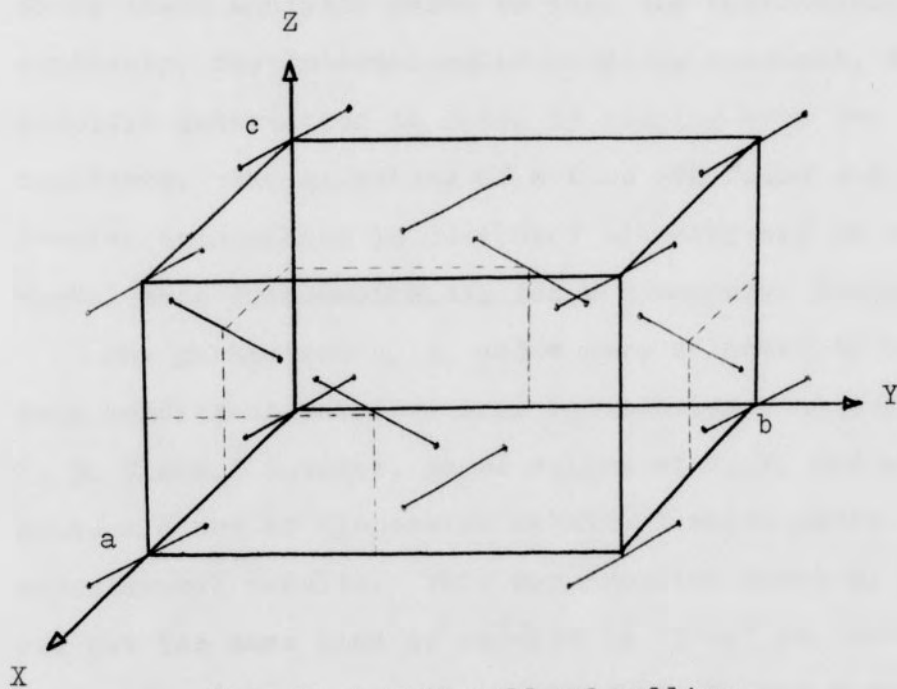
Fig. 3. A unit cell of gallium.

the molecules and those near them, then the disturbance is transmitted through the crystal. Assuming the disturbance to be harmonic in nature, the system is best treated as a collection of oscillators which may be analyzed in terms of the normal modes of oscillation of the system.

The coupling between molecules is taken to be of a Hooke's Law nature. Therefore, by displacing a molecule an amount $\underset{\sim}{u}$, a force is exerted on a molecule near it according to $\underset{\sim}{F} = -\underset{\approx}{\phi}\underset{\sim}{u}$ where $\underset{\approx}{\phi}$ is the intermolecular coupling constant. For a particular molecule-molecule interaction, analytic expressions for the interatomic forces are developed using the "6-exp" potential model given by $V = -\frac{A}{r^6} + Be^{-\alpha r}$ where A, B, and α are parameters and r is the atomic separation. Using these analytic forms to find the interatomic coupling constants, the intermolecular coupling constant, for a specific interaction is found by summing over the atomic constants. The equations of motion are found and the secular determinant is developed allowing one to find the normal mode frequencies, ω, for a given wave vector $\underset{\sim}{q}$.

The parameters A, B, and α were selected to meet certain conditions computed from equilibrium considerations by C. B. Clark.[3] However, these values of A, B, and α do not produce a set of dispersion relations which agree with experimental results. This was expected since D. E. Thompson got the same kind of results in 1970.[4] To further test the model it is necessary to change A, B, and α so as to

make the calculated dispersion relations converge to the
experimental relations. The method of "Least Squares" is
selected for this purpose. The details of this method are
discussed in CHAPTER II.

CHAPTER I

The Dynamical Matrix

As stated in the INTRODUCTION, gallium is being treated as if it were built of rigid dumbbell molecules. Thus, there are only three degrees of translational and three degrees of librational freedom per molecule to be concerned with. The translational motion will be considered first by treating the molecules as point masses located at the center of the dumbbell. The resulting equations of motion will be completely general and easily extended to cover librational motion.

Consider the motion of a molecule at r_j due to the displacement, $u_{j'}$, of the molecule at $r_{j'}$. The vectors r_j and $r_{j'}$ are relative to the origin of a co-ordinate system appropriately located in the crystal and the vector $u_{j'}$ is relative to $r_{j'}$. The force equation which governs the motion of the j molecule is

$$F_j = M_j u_j = -\sum_{j'} \phi(jj') u_{j'} \tag{1}$$

where the following definitions are made:

$$M_j = \begin{bmatrix} m & 0 & 0 \\ 0 & m & 0 \\ 0 & 0 & m \end{bmatrix}$$

where m is the mass of the gallium molecule.

$$\underset{\sim}{\phi}(jj') = \begin{bmatrix} \phi_{11} & \phi_{12} & \phi_{13} \\ \phi_{21} & \phi_{22} & \phi_{23} \\ \phi_{31} & \phi_{32} & \phi_{33} \end{bmatrix}$$

where ϕ_{ik} represents the force constant for the i component of force on the j molecule due to the displacement of the j' molecule in the k direction.

The general harmonic expressions for displacements of the j and j' molecules are assumed to be

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

and

$$\underset{\sim}{u}_{j'} = \underset{\sim}{A}(j')e^{i(\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'} - \omega t)}, \tag{3}$$

respectively. Substituting Eqs. (2) and (3) into Eq. (1) yields

$$-\underset{\approx}{M}_j\underset{\sim}{A}(j)\omega^2 = -\sum_{j'}\underset{\approx}{\phi}(jj')\underset{\sim}{A}(j')e^{i\underset{\sim}{q} \cdot (\underset{\sim}{r}_{j'} - \underset{\sim}{r}_j)}. \tag{4}$$

Now, let us choose a specific co-ordinate system located along the crystal axes so that the j molecule is positioned at the origin. Equation (4) may then be written as

$$-\underset{\approx}{M}_j\underset{\sim}{A}(j)\omega^2 = -\sum_{j'}\underset{\approx}{\phi}(jj')\underset{\sim}{A}(j')e^{i\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}}. \tag{5}$$

Assuming that all $A(j')$ are equal, Eq. (5) may be written in component form as

$$-m\omega^2 A_i(j) = -\sum_k A_k \sum_{j'} \phi_{ik}(jj')e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} \qquad (6)$$

where i and k = 1-3. Thus, Eq. (6) yields a set of three secular equations which produce a 3X3 secular determinant.

Now, it is necessary to be more complete and consider the effects of the librational motion of the j' molecule. Torques are taken along the principal axes of the j molecule so that the moment of inertia tensor, $\underset{\approx}{M}$, is diagonal. Therefore, Eq. (1) may be written to include both forces and torques as

$$\underset{\sim}{F}_j = \underset{\approx}{M}_j \underset{\sim}{u}_j = -\sum_{j'} \underset{\approx}{\phi}(jj')\underset{\sim}{u}_{j'}, \qquad (7)$$

where the following new definitions are made:

$$\underset{\sim}{F}_j = \begin{bmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \\ F_5 \\ F_6 \end{bmatrix}$$

where F_1, F_2, and F_3 represent the component forces on the j molecule and F_4, F_5, and F_6 represent the component torques on the j molecule. (The component torques are along the principal axes of the molecule.)

$$\underset{\approx}{M}_j = \begin{bmatrix} m_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & m_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & m_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & m_4 & 0 & 0 \\ 0 & 0 & 0 & 0 & m_5 & 0 \\ 0 & 0 & 0 & 0 & 0 & m_6 \end{bmatrix}$$

where m_1, m_2, and m_3 represent the mass of the gallium molecule and m_4, m_5, and m_6 represent the moments of inertia about the α, β, and γ principal axes, respectively (Fig. 4).

$$\underset{\sim}{u} = \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix}$$

where u_1, u_2, and u_3 represent translational displacements and u_4, u_5, and u_6 represent rotational displacements about the principal axes of the j or j' molecule.

and
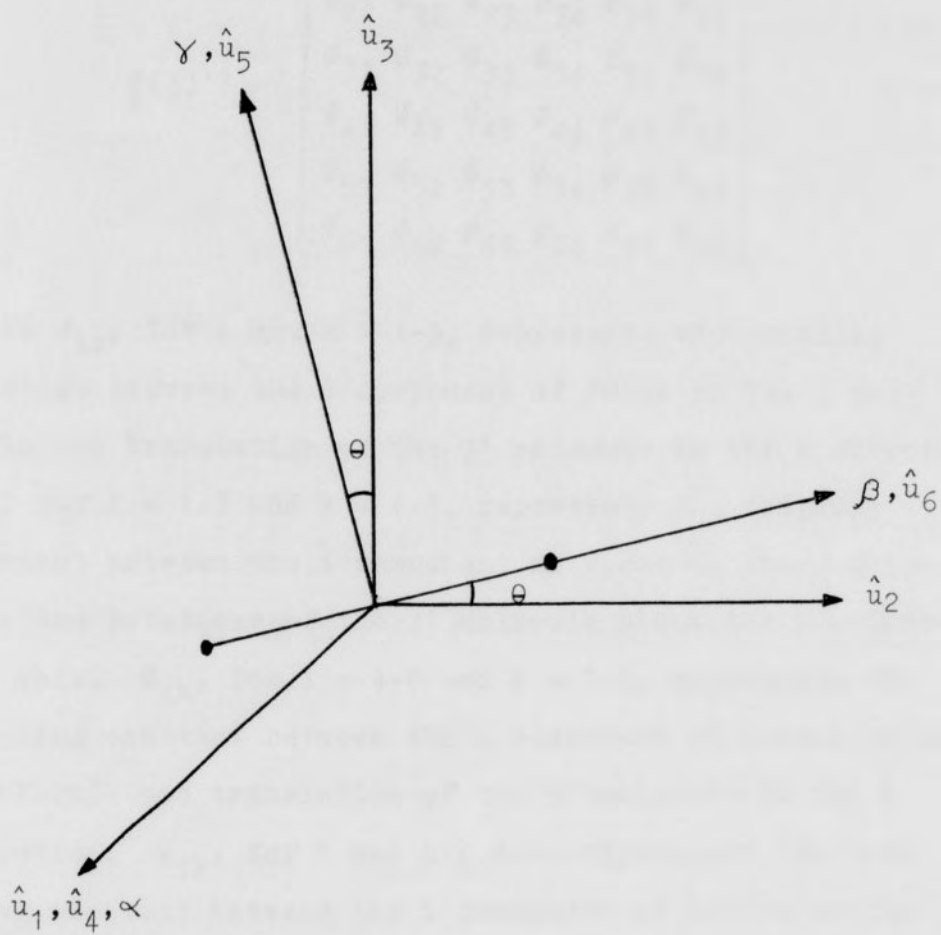
Fig. 4. The principal axes of the dumbbell molecule ((α, β, γ)
or ($\hat{u}_4, \hat{u}_6, \hat{u}_5$)) relative to the crystal axes given
by ($\hat{u}_1, \hat{u}_2, \hat{u}_3$).

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

where ϕ_{ik}, for i and k = 1-3, represents the coupling constant between the i component of force on the j molecule and translation of the j' molecule in the k direction. ϕ_{ik}, for i = 1-3 and k = 4-6, represents the coupling constant between the i component of force on the j molecule and rotations of the j' molecule about the k principal axis. ϕ_{ik}, for i = 4-6 and k = 1-3, represents the coupling constant between the i component of torque on the j molecule and translation of the j' molecule in the k direction. ϕ_{ik}, for i and k = 4-6, represents the coupling constant between the i component of torque on the j molecule and rotations of the j' molecule about the k principal axis.

Since there are two distinct molecular types in a crystal of gallium, Eq. (5) must be written for both type A and type B origin (j) molecules as

$$-\underset{\approx}{M}\underset{\sim}{A}\omega^2 = -\sum_{j'} \underset{\approx}{\phi}(jj')\underset{\sim}{A}e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'}} - \sum_{l'} \underset{\approx}{\phi}(jl')\underset{\sim}{B}e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}_{l'}} \qquad (8)$$

and

$$-\underset{\sim}{M}\underset{\sim}{B}\omega^2 = -\sum_{j'}\underset{\sim}{\phi}(jj')\underset{\sim}{B}e^{i\underset{\sim}{q}\cdot \underset{\sim}{r}_{j'}} -\sum_{l'}\underset{\sim}{\phi}(jl')\underset{\sim}{A}e^{i\underset{\sim}{q}\cdot \underset{\sim}{r}_{l'}} \tag{9}$$

where A and B are six element column matrices representing the displacement amplitudes of the general harmonic form of Eqs. (2) and (3) for type A and type B molecules, respectively. The sum over j' is for source molecules of the same type as the j molecule and the sum over l' is for source molecules of a different type than the j molecule. Equation (8) produces six component equations of the form

$$\sum_k (\sum_{j'}\phi_{ik}(jj')e^{i\underset{\sim}{q}\cdot \underset{\sim}{r}_{j'}} - m_i\delta_{ik}\omega^2)A_k$$
$$+ \sum_k (\sum_{l'}\phi_{ik}(jl')e^{i\underset{\sim}{q}\cdot \underset{\sim}{r}_{l'}})B_k = 0 \tag{10}$$

and Eq. (9) produces six component equations of the form

$$\sum_k (\sum_{l'}\phi_{ik}(jl')e^{i\underset{\sim}{q}\cdot \underset{\sim}{r}_{l'}})A_k$$
$$+ \sum_k (\sum_{j'}\phi_{ik}(jj')e^{i\underset{\sim}{q}\cdot \underset{\sim}{r}_{j'}} - m_i\delta_{ik}\omega^2)B_k = 0 \tag{11}$$

where i and k = 1-6. Equations (10) and (11) form a 12X12 dynamical matrix whose secular determinant has elements of the form

$$\sum_{j'}\phi_{ik}(jj')e^{iq\ r_{j'}} - m_i\delta_{ik}\omega^2.$$

The order of the matrix may be reduced to 10X10 by considering molecular symmetry. Motion about the   or dumbbell axis is physically meaningless because the moment

of inertia about this axis is zero (Fig. 4). Therefore, the sixth and twelfth rows which involve components of torque about the   axis and the sixth and twelfth columns which involve rotations about the β axis may be omitted.

The 6X6 coupling constants matrix can be reduced to 5X5 for the same reason. Also, the number of independent elements of this matrix may be restricted by lattice symmetry as described by G. S. Pawley.[5] The type A symmetry reflects the molecules into themselves. Therefore, the system is unchanged so that the coupling constant matrix between the molecules is invariant under this symmetry operation. If the gallium lattice is reflected in a plane perpendicular to the a axis, the coupling constant matrices between molecules lying in the plane are of the form

$$
\underset{\sim}{\phi}(jj') = \begin{bmatrix} \phi_{11} & 0 & 0 & 0 & \phi_{15} \\ 0 & \phi_{22} & \phi_{23} & \phi_{24} & 0 \\ 0 & \phi_{32} & \phi_{33} & \phi_{34} & 0 \\ 0 & \phi_{42} & \phi_{43} & \phi_{44} & 0 \\ \phi_{51} & 0 & 0 & 0 & \phi_{55} \end{bmatrix} .
$$

The type B symmetry is an inversion through the origin. This type symmetry relates the interaction matrix between the molecule located at the origin, represented by O, and one located at (x,y,z), represented by j', to the interaction

matrix between the origin molecule and the molecule at $(-x,-y,-z)$, represented by $-j'$. A study of this symmetry shows that the two interaction matrices are related according to

$$\underset{\approx}{\emptyset}(0-j') = \begin{bmatrix} \emptyset_{11} & \emptyset_{12} & \emptyset_{13} & -\emptyset_{14} & -\emptyset_{15} \\ \emptyset_{21} & \emptyset_{22} & \emptyset_{23} & -\emptyset_{24} & -\emptyset_{25} \\ \emptyset_{31} & \emptyset_{32} & \emptyset_{33} & -\emptyset_{34} & -\emptyset_{35} \\ -\emptyset_{41} & -\emptyset_{42} & -\emptyset_{43} & \emptyset_{44} & \emptyset_{45} \\ -\emptyset_{51} & -\emptyset_{52} & -\emptyset_{53} & \emptyset_{54} & \emptyset_{55} \end{bmatrix}$$

where the elements within the brackets represent the components of the coupling constant matrix for the interaction between the origin and j' molecules. For interactions between molecules lying in a plane perpendicular to the a axis, types A and B symmetry operations yield

$$\underset{\approx}{\emptyset}(0-j') = \begin{bmatrix} \emptyset_{11} & 0 & 0 & 0 & \emptyset_{15} \\ 0 & \emptyset_{22} & \emptyset_{23} & -\emptyset_{24} & 0 \\ 0 & \emptyset_{32} & \emptyset_{33} & -\emptyset_{34} & 0 \\ 0 & -\emptyset_{42} & -\emptyset_{43} & \emptyset_{44} & 0 \\ -\emptyset_{51} & 0 & 0 & 0 & \emptyset_{55} \end{bmatrix}.$$

For interactions between like molecules, type B symmetry
reduces to nine the number of independent elements of the
coupling constant matrix for the interaction between the
origin molecule and a j' molecule. The interaction matrix
is given by

$$\underset{\approx}{\phi}(0j') = \begin{bmatrix} \phi_{11} & \phi_{12} & \phi_{13} & \phi_{14} & \phi_{15} \\ \phi_{21} & \phi_{22} & \phi_{23} & \phi_{24} & \phi_{25} \\ \phi_{13} & \phi_{23} & \phi_{33} & \phi_{34} & \phi_{35} \\ -\phi_{14} & -\phi_{24} & -\phi_{34} & \phi_{44} & \phi_{45} \\ -\phi_{15} & -\phi_{25} & -\phi_{35} & \phi_{45} & \phi_{55} \end{bmatrix} .$$

Again type A symmetry is applied when considering inter-
actions between like molecules lying in a plane perpendic-
ular to the a axis. The above matrix is reduced to

$$\underset{\approx}{\phi}(0j') = \begin{bmatrix} \phi_{11} & 0 & 0 & 0 & \phi_{15} \\ 0 & \phi_{22} & \phi_{23} & \phi_{24} & 0 \\ 0 & \phi_{23} & \phi_{33} & \phi_{34} & 0 \\ 0 & -\phi_{24} & -\phi_{34} & \phi_{44} & 0 \\ -\phi_{15} & 0 & 0 & 0 & \phi_{55} \end{bmatrix} .$$

Type C symmetry is used to relate the interaction matrix
for an A-B interaction to that for a B-A interaction. For
gallium it is best illustrated by the screw-diad operation
which transforms the molecule pair j-j' into the pair j'-j".
This symmetry allows one to show that the relationship be-
tween the interaction matrices of the j'-j" pair and a
different pair designated by j-l' (Fig. 5) is given by

$$
\phi(j'j") = \begin{bmatrix}
\phi_{11} & \phi_{21} & \phi_{31} & -\phi_{41} & -\phi_{51} \\
\phi_{12} & \phi_{22} & \phi_{32} & -\phi_{42} & -\phi_{52} \\
\phi_{13} & \phi_{23} & \phi_{33} & -\phi_{43} & -\phi_{53} \\
-\phi_{14} & -\phi_{24} & -\phi_{34} & \phi_{44} & \phi_{54} \\
-\phi_{15} & -\phi_{25} & -\phi_{35} & \phi_{45} & \phi_{55}
\end{bmatrix}
$$

where the elements within the brackets represent the
components of $\phi(jl')$. Type A symmetry is again applicable
to interactions between molecules lying in a plane perpen-
dicular to the a axis. The above matrix is reduced to
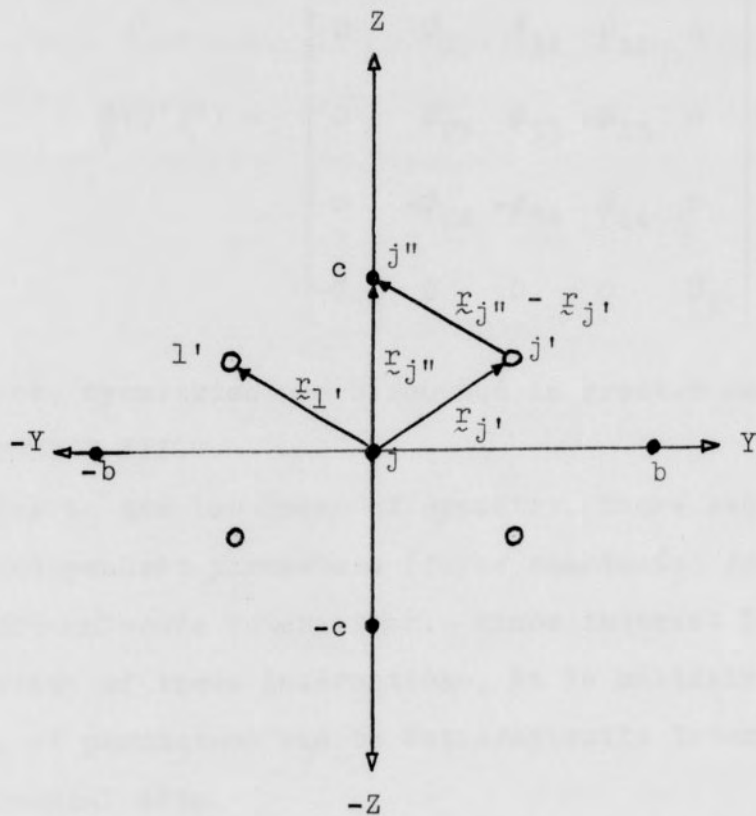
Fig. 5. A diagram for considering screw-diad symmetry.

(● and ○ represent the two types of molecules.)

$$\underset{\sim}{\emptyset}(j'j") = \begin{bmatrix} \emptyset_{11} & 0 & 0 & 0 & -\emptyset_{51} \\ 0 & \emptyset_{22} & \emptyset_{32} & -\emptyset_{42} & 0 \\ 0 & \emptyset_{23} & \emptyset_{33} & -\emptyset_{43} & 0 \\ 0 & -\emptyset_{24} & -\emptyset_{34} & \emptyset_{44} & 0 \\ -\emptyset_{15} & 0 & 0 & 0 & \emptyset_{55} \end{bmatrix}$$

The above symmetries are discussed in greater detail in APPENDIX III.

Due to the low order of symmetry, there are at least nine independent parameters (force constants) for each molecule-molecule interaction. Since interest lies in a collection of these interactions, it is unlikely that this number of parameters can be satisfactorily determined from experimental data.

Assuming the interaction forces to be derivable from a potential energy enables one to reduce the number of independent parameters of the problem. For the purpose of this thesis, the "6-exp" potential model, $V = -\frac{A}{r^6} + Be^{-\alpha r}$, is taken to give the interaction potential energy. Now there are only three independent parameters upon which the intermolecular force constants depend. It is, therefore, possible to determine the best set of parameters by comparing the calculated dispersion curves to the experimental dispersion curves using the method of "Least Squares".

The "6-exp" potential is used in APPENDIX I to derive the analytic expressions for the interatomic force constants for a particular molecule-molecule interaction. It is shown that the elements of the interatomic coupling constant matrix are of the following forms:[6]

a. $\qquad$ $i = 1\text{-}3$ and $j = 1\text{-}3$

$$\emptyset_{ij} = -\delta_{ij} f(r) - x_i x_j g(r)$$

b. $\qquad$ $i = 1\text{-}3$

$$\emptyset_{i4} = \emptyset_{i3} Y - \emptyset_{i2} Z$$
$$\emptyset_{i5} = -(Y \cos \Theta s + Z \sin \Theta s)\emptyset_{i1}$$

c. $\qquad$ $j = 1\text{-}5$

$$\emptyset_{4j} = \emptyset_{3j} Yo - \emptyset_{2j} Zo$$
$$\emptyset_{5j} = -(Yo \cos \Theta o + Zo \sin \Theta o)\emptyset_{1j}$$

where

$$f(r) = \frac{1}{r} \frac{\partial V}{\partial r} = 6\frac{A}{r^8} - B\frac{\alpha}{r} e^{-\alpha r}$$

and

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

The x_i and x_j are the position components of the source atom relative to the origin atom in a co-ordinate system along the crystal axes. (Yo,Zo) and (Y,Z) represent the

positions of the origin and source atoms, respectively, relative to their respective molecules. Θo and Θs are the angles that the dumbbell axes of the origin and source molecules, respectively, make with the b crystal axis.

The case for the displacement of the origin molecule while all other molecules are undisturbed must also be considered. The forces exerted on the origin molecule are called the "self" forces and must be calculated differently. They are written as $\underset{\sim}{F}(jj) = -\underset{\approx}{\phi}(jj)\underset{\sim}{u}_j$. The components of $\underset{\approx}{\phi}(jj)$ in terms of $\underset{\approx}{\phi}(jj')$ are of the following forms:[7]

a.　　　　type A origin molecules ($\Theta o = \Theta$)

　1.　　　　$i = 1-5$ and $k = 1-3$

$$\phi_{ik}(jj) = -\sum_{j'} \phi_{ik}$$

　2.　　　　$i = 1-5$

$$\phi_{i4}(jj) = -\sum_{j'} (\phi_{i4} - \phi_{i2}L\frac{c}{2} + \phi_{i3}K\frac{b}{2})$$

(Both sums are over types A and B source molecules.)

　3.　　　　$i = 1-5$

$$\phi_{i5}(jj) = -\sum_{j'} (\phi_{i5} - \phi_{i1}(K\frac{b}{2}\cos\,\Theta + L\frac{c}{2}\sin\,\Theta)$$
$$+ \phi_{i2}H\frac{a}{2}\cos\,\Theta + \phi_{i3}H\frac{a}{2}\sin\,\Theta)$$
$$-\sum_{j'} (\phi_{i5}\cos\,2\Theta - \phi_{i1}(K\frac{b}{2}\cos\,\Theta$$
$$+ L\frac{c}{2}\sin\,\Theta) + \phi_{i2}H\frac{a}{2}\cos\,\Theta + \phi_{i3}H\frac{a}{2}\sin\,\Theta)$$

(The first and second sums are over types A and B source molecules, respectively.)

b. type B origin molecules ($\Theta_0 = -\Theta$)

  1. $i = 1-5$ and $k = 1-3$

$$\emptyset_{ik}(jj) = -\sum_{j'} \emptyset_{ik}$$

  2. $i = 1-5$

$$\emptyset_{i4}(jj) = -\sum_{j'} (\emptyset_{i4} - \emptyset_{i2}L\frac{c}{2} + \emptyset_{i3}K\frac{b}{2})$$

(Both sums are over types A and B source molecules.)

  3. $i = 1-5$

$$\emptyset_{i5}(jj) = -\sum_{j'} (\emptyset_{i5}\cos 2\Theta - \emptyset_{i1}(K\frac{b}{2}\cos \Theta$$
$$- L\frac{c}{2}\sin \Theta) + \emptyset_{i2}H\frac{a}{2}\cos \Theta - \emptyset_{i3}H\frac{a}{2}\sin \Theta)$$
$$- \sum_{j'} (\emptyset_{i5} - \emptyset_{i1}(K\frac{b}{2}\cos \Theta - L\frac{c}{2}\sin \Theta)$$
$$+ \emptyset_{i2}H\frac{a}{2}\cos \Theta - \emptyset_{i3}H\frac{a}{2}\sin \Theta)$$

(The first and second sums are over types A and B
source molecules, respectively.)

where $\emptyset$ is written on the right hand side of the above
equations to represent $\emptyset(jj')$. H, K, and L are integers
and Θ_0 is the angle that the dumbbell axis of the origin
molecule makes with the b crystal axis. The above equa-
tions are derived in more detail in APPENDIX II.

It is useful to write Eqs. (10) and (11) in a more
general and compact matrix notation as $(\underset{\approx}{D}' - \underset{\approx}{M}\omega^2)\underset{\approx}{A} = 0$
where $\underset{\approx}{D}'$ represents a 10X10 matrix with elements involving

the intermolecular and "self" force constants. $\underset{\approx}{M}$ is the
10X10 mass matrix given by

$$
\underset{\approx}{M} = \begin{bmatrix}
m_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & m_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & m_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & m_4 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & m_5 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & m_1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & m_2 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & m_3 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & m_4 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & m_5
\end{bmatrix}
$$

and $\underset{\sim}{A}$ is a 10 element column matrix representing the dis-
placement amplitudes of both types A and B molecules and is
given by

$$
\begin{bmatrix}
A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \\ A_6 \\ A_7 \\ A_8 \\ A_9 \\ A_{10}
\end{bmatrix}
=
\begin{bmatrix}
A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \\ B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5
\end{bmatrix}
$$

Letting $a_n = A_n\sqrt{m_n}$ for $n = 1\text{-}3$ and $n = 6\text{-}8$ and $a_n = iA_n\sqrt{m_n}$
for $n = 4,5$ and $n = 9,10$ enables one to write

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

which in component form is $(D_{mn} - \delta_{mn}\omega^2)a_n = 0$ where D_{mn}
are elements of $\underset{\approx}{D}$ and have the following forms:

a.   for type A origin and source molecules

$$m = 1-5 \text{ and } n = 1-5$$

$$D_{mn} = \left(\sum_{j'} \phi_{mn}(jj')Cj' + Cj\phi_{mn}(jj)\right)/\sqrt{m_m m_n}$$

(summed over type A source molecules)

$Cj' = \cos(\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'})$ and $Cj = 1$ $m = 1-3;\ n = 1-3$

                                            $m = 4,5;\ n = 4,5$

$Cj' = \sin(\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'})$ and $Cj = 0$ $m = 1-3;\ n = 4,5$

$Cj' = -\sin(\underset{\sim}{q}\cdot\underset{\sim}{r}_{j'})$ and $Cj = 0$ $m = 4,5;\ n = 1-3$

b.   for type A origin and type B source molecules

$$m = 1-5 \text{ and } n = 6-10$$

$$D_{mn} = \left(\sum_{l'} \phi_{m\ n-5}(jl')Cl'\right)/\sqrt{m_m m_{n-5}}$$

(summed over type B source molecules)

$Cl' = \cos(\underset{\sim}{q}\cdot\underset{\sim}{r}_{l'})$ $m = 1-3;\ n = 6-8$

                                      $m = 4,5;\ n = 9,10$

$Cl' = \sin(\underset{\sim}{q}\cdot\underset{\sim}{r}_{l'})$ $m = 1-3;\ n = 9,10$

$Cl' = -\sin(\underset{\sim}{q}\cdot\underset{\sim}{r}_{l'})$ $m = 4,5;\ n = 6-8$

c.   for type B origin and source molecules

$$m = 6-10 \text{ and } n = 6-10$$

$$D_{mn} = \left(\sum_{j'} \phi_{m-5\ n-5}(jj')Cj' + Cj\phi_{m-5\ n-5}(jj)\right)/\sqrt{m_{m-5}m_{n-5}}$$

(summed over type B source molecules)

$$Cj' = \cos(\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}) \text{ and } Cj = 1 \qquad m = 6\text{-}8; \; n = 6\text{-}8$$

$$m = 9,10; \; n = 9,10$$

$$Cj' = \sin(\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}) \text{ and } Cj = 0 \qquad m = 6\text{-}8; \; n = 9,10$$

$$Cj' = -\sin(\underset{\sim}{q} \cdot \underset{\sim}{r}_{j'}) \text{ and } Cj = 0 \qquad m = 9,10; \; n = 6\text{-}8$$

d.　　　for type B origin and type A source molecules

$$m = 6\text{-}10 \text{ and } n = 1\text{-}5$$

$$D_{mn} = \left(\sum_{1'} \emptyset_{m-5 \; n}(j1')Cl' \right) / \sqrt{m_{m-5}m_n}$$

(summed over type A source molecules)

$$Cl' = \cos(\underset{\sim}{q} \cdot \underset{\sim}{r}_{1'}) \qquad m = 6\text{-}8; \; n = 1\text{-}3$$

$$m = 9,10; \; n = 4,5$$

$$Cl' = \sin(\underset{\sim}{q} \cdot \underset{\sim}{r}_{1'}) \qquad m = 6\text{-}8; \; n = 4,5$$

$$Cl' = -\sin(\underset{\sim}{q} \cdot \underset{\sim}{r}_{1'}) \qquad m = 9,10; \; n = 1\text{-}3$$

CHAPTER II

The Method of Least Squares

Considering the results of CHAPTER I it is possible to calculate the dispersion relations for gallium and compare them to the experimentally determined dispersion relations. By changing the values of the parameters A, B, and α in the "6-exp" potential model, it may be possible to calculate a set of dispersion curves which correspond favorably with the experimentally determined curves. The method of "Least Squares" is used for determing the necessary changes in A, B, and α which produce the best set of calculated dispersion curves as compared to the experimental curves.

In general, the calculated frequencies are dependent upon the parameters of the model being used and the particular wave vector being considered. However, since the wave vectors are known specifically it is appropriate to consider the calculated frequencies as a function of the model parameters only. The accepted mathematical notation is

$$f_1 = f_1(p_1, p_2, p_3, \ldots p_i)$$

where p_i represent the model parameters and f_1 represents a particular frequency.

If f_{ol} and f_{cl} represent the experimentally observed and the calculated frequencies, respectively, the "Least Squares" criteria takes as the best set of parameters that which minimizes the quantity

$$S = \sum_l W_l (f_{ol} - f_{cl})^2.$$

W_l is a weighting factor associated with the l observation. It has been shown, by statistical methods, to be $1/\sigma_{ol}{}^2$, where σ_{ol} is the standard error of the observation f_{ol}.[8]

Since S must be a minimum in order to get the best set of parameters, the following must be true:

$$\frac{\partial S}{\partial p_i} = 0.$$

Performing the derivative and setting it equal to zero yields

$$W_l (f_{cl} - f_{ol}) \frac{\partial f_{cl}}{\partial p_i} = 0. \tag{13}$$

Recalling that the calculated frequencies are functions of the model parameters, the frequencies may be written as a Taylor series expansion about the values calculated using an initial set of parameters designated by p_{oj}. The resulting equation may be written as

$$f_{cl}(p_j) = f_{cl}(p_{oj}) + \sum_j \frac{\partial f_{cl}}{\partial p_j} \Delta p_j$$

where $\Delta p_j = p_j - p_{oj}$. (Note that all second order and higher terms are neglected. It is assumed that $p_{oj} \approx p_j$.)

If the potential model being used is applicable then an initial set of parameters can be chosen such that f_{ol} $f_{cl}(p_{oj})$. This leads to the result that

$$f_{cl}(p_j) - f_{ol} \approx \sum_j \frac{\partial f_{cl}}{\partial p_j} \Delta p_j. \tag{14}$$

Substituting Eq. (14) into Eq. (13) yields

$$\sum_l W_l (f_{cl} - f_{ol}) \frac{\partial f_{cl}}{\partial p_i} = \sum_l \sum_j W_l \frac{\partial f_{cl}}{\partial p_j} \frac{\partial f_{cl}}{\partial p_i} \Delta p_j. \tag{15}$$

Therefore, for N model parameters there exists a set of NXN equations whose solutions are the changes in the parameters which tend to minimize the quantity

$$S = \sum_l W_l (f_{ol} - f_{cl})^2.$$

Equation (15) may be written in matrix notation as

$$\underset{\sim}{a} \underset{\sim}{x} = \underset{\sim}{v} \tag{16}$$

where a is the NXN matrix with elements

$$a_{ij} = \sum_l W_l \frac{\partial f_{cl}}{\partial p_j} \frac{\partial f_{cl}}{\partial p_i}.$$

$\underset{\sim}{x}$ and $\underset{\sim}{v}$ are N-fold column matrices with elements

$$x_i = \Delta p_i$$

and

$$v_i = \sum_l W_l (f_{cl} - f_{ol}) \frac{f_{cl}}{p_i},$$

respectively. From Eq. (16) it is obvious that $\underset{\sim}{x} = \underset{\sim}{a}^{-1} \underset{\sim}{v}$ where $\underset{\sim}{a}^{-1}$ is the inverse of $\underset{\sim}{a}$.

Using numerical techniques it is possible to determine $\underset{\sim}{a}$, $\underset{\sim}{a}^{-1}$, and $\underset{\sim}{v}$. Upon carrying out the above matrix multiplication the necessary changes in the model parameters are determined.

SUMMARY AND CONCLUSIONS

The "6-exp" potential energy function, $V = -\frac{A}{r^6} + Be^{-\alpha r}$, was used to develop analytic expressions for the interatomic coupling constants. The interatomic coupling constants were calculated for each molecule-molecule interaction. The intermolecular coupling constants were determined numerically by summing the interatomic constants for each molecule-molecule interaction. The resulting constants were used to numerically determine the elements of the dynamical matrix for a specific wave vector $\underset{\sim}{q}$.

The initial calculation of the dispersion relations for gallium was done using the program in APPENDIX IV. The initial values of the parameters A, B, and α were chosen such that $\alpha = 2.562$ A^{-1} and $A/B = \frac{1}{2}$. These conditions were determined from equilibrium considerations by C. B. Clark.[9] The values of A and B are 5×10^{-14}erg-A^6 and 10^{-13}ergs, respectively.[*] The normal mode frequencies were calculated for plane waves along the a, b, and c crystal axes. The maximum value of the traveling wave vector for each direction was taken to be the distance from the origin of the co-ordinate system of Figs. 9 and 10 in APPENDIX V, to the first Brillouin zone boundary in the desired direction.

---

[*]These values were chosen because they produce the correct orders of magnitude for the frequencies.

These distances were found in APPENDIX V to be

$$Q_a = \frac{\pi}{a}(1 + a^2/b^2),$$

$$Q_b = 2\frac{\pi}{b},$$

and

$$Q_c = \frac{\pi}{c}.$$

Note that these distances have units of inverse length because they are measured in reciprocal space. The normal mode frequencies (ω) were calculated for wave vectors (q) at intervals of $\frac{1}{5}Q$ ranging from $\frac{1}{5}Q$ to Q in each direction.

The force constant matrices were determined for interactions between origin and source molecules separated by distances ranging from $\pm a$ to $\pm(a^2 + b^2 + c^2)^{\frac{1}{2}}$. Due to the short range of the "6-exp" potential, distances greater than the latter produced neglible changes in the calculated frequencies. All symmetry requirements for the above interactions were met for both type A and type B origin and source molecules. (These symmetries are discussed in APPENDIX III.) However, the resulting dispersion relations were invalid because many of the calculated frequencies were imaginary and did not agree with experimental results[10].

The method of "Least Squares" was used to choose new values for A and B that would produce a better set of dispersion curves. $\propto$ was not changed because the equilibrium considerations yielded the value quoted, but gave only the

ratio of A to B. The new values of A and B are 4.791 X 10^{-14}erg-A^6 and 9.987 X 10^{-14}ergs, respectively. Although these new values reduced the number of imaginary frequencies from nineteen to nine (out of one hundred and fifty frequency values calculated), it was not possible to eliminate all the imaginary frequencies by just changing A and B. The next step is to change all three parameters, but due to the large amount of computer time involved, funds are not available at present to do this.

The calculations already made seem to indicate that the model chosen for gallium is not correct. Thus, it may be invalid to treat gallium as having a molecular structure or possibly the "6-exp" interatomic potential energy function cannot be used to describe the molecular model for gallium.

The experimental data, the results of calculations made with the initial values of A, B, and α, and the results of calculations made with new values of A and B are shown in TABLE I

TABLE I

Calculated and Experimental Values of ω for Plane Waves Propagating Along the Crystal Axes

Units: ω in 10^{12} Hz; $\underset{\sim}{q}$ in A^{-1}

ω_e are the experimental frequencies.

ω_i are the calculated frequencies using initial A, B, and α.

ω_f are the calculated frequencies using new A and B.

$\hat{x}$, $\hat{y}$, and $\hat{z}$ are the unit vectors along the crystal axes.

The letter i before a number indicates that it is imaginary.

$\underset{\sim}{q}$	ω_e X 10^{-12}	ω_i X 10^{-12}	ω_f X 10^{-12}
0.1874 $\hat{x}$	5.680	5.317	4.340
	5.580	4.897	3.878
	4.690	4.512	3.746
	3.250	3.467	2.887
	3.050	2.590	2.326
	2.880	2.568	2.263
	2.650	2.557	2.101
	1.280	1.359	1.185
	0.800	0.417	0.342
	0.650	i 0.435	i 0.134
0.3748 $\hat{x}$	5.650	5.309	4.314
	5.280	4.839	3.968
	5.150	4.757	3.816
	3.100	3.047	2.619
	3.020	2.965	2.547

$\underset{\sim}{q}$	$\omega_e \times 10^{-12}$	$\omega_i \times 10^{-12}$	$\omega_f \times 10^{-12}$
$0.3748\,\hat{x}$	2.890	2.265	2.363
	2.690	2.617	2.168
	2.240	2.050	1.848
	1.400	0.762	0.654
	1.140	i 0.695	0.123
$0.5622\,\hat{x}$	5.680	5.264	4.259
	5.560	5.055	4.126
	4.950	4.520	3.694
	3.550	3.903	3.302
	3.100	2.774	2.417
	2.910	2.714	2.386
	2.710	2.670	2.247
	2.460	1.828	1.710
	1.820	0.960	0.895
	1.500	i 0.647	0.514
$0.7496\,\hat{x}$	5.600	5.154	4.186
	5.600	5.127	4.162
	4.650	4.627	3.848
	4.280	4.234	3.542
	3.130	2.893	2.445
	2.950	2.734	2.344
	2.630	2.546	2.230
	2.180	1.386	1.412
	1.920	0.943	1.010

$\underline{q}$	ω_e X 10^{-12}	ω_i X 10^{-12}	ω_f X 10^{-12}
0.7496 $\hat{x}$	1.800	0.477	0.884
0.9370 $\hat{x}$	5.460	5.069	4.156
	5.400	5.068	4.127
	4.900	4.959	4.012
	4.450	4.049	3.450
	3.140	2.873	2.486
	3.080	2.868	2.380
	2.650	2.561	2.157
	2.110	1.126	1.201
	1.850	0.745	1.049
	1.770	0.563	0.921
0.1640 $\hat{y}$	5.790	5.272	4.316
	5.600	4.992	3.932
	4.500	4.267	3.603
	3.080	3.719	3.027
	2.900	2.667	2.315
	2.880	2.563	2.263
	1.900	2.510	2.082
	1.150	1.240	1.162
	0.710	i 0.362	i 0.126
	0.550	i 0.450	i 0.235
0.3281 $\hat{y}$	5.800	5.151	4.231
	5.500	5.110	4.018
	4.500	4.311	3.610

q	$\omega_e \times 10^{-12}$	$\omega_i \times 10^{-12}$	$\omega_f \times 10^{-12}$
$0.3281\ \hat{y}$	3.110	3.620	2.982
	3.010	3.008	2.538
	2.680	2.648	2.112
	2.190	2.327	2.104
	2.010	2.092	1.965
	1.100	i 0.668	i 0.200
	0.940	i 0.822	i 0.429
$0.4921\ \hat{y}$	5.800	5.238	4.127
	5.400	4.994	4.114
	4.530	4.362	3.618
	3.520	3.568	3.046
	2.850	3.517	2.938
	2.500	2.737	2.161
	2.500	2.419	2.128
	2.360	2.048	1.879
	1.120	i 0.883	i 0.173
	1.100	i 1.108	i 0.563
$0.6561\ \hat{y}$	5.800	5.330	4.186
	5.200	4.861	4.048
	4.600	4.402	3.625
	4.050	3.958	3.383
	2.740	3.444	2.908
	2.600	2.801	2.190
	2.420	2.543	2.147

q	$\omega_e \times 10^{-12}$	$\omega_i \times 10^{-12}$	$\omega_f \times 10^{-12}$
$0.6561 \, \hat{y}$	2.420	1.759	1.633
	1.200	i 0.996	0.164
	1.100	i 1.238	i 0.639
$0.8202 \, \hat{y}$	5.800	5.363	4.212
	5.080	4.809	4.019
	4.670	4.418	3.628
	4.400	4.085	3.486
	2.760	3.418	2.898
	2.500	2.825	2.191
	2.400	2.579	2.155
	2.400	1.625	1.516
	1.200	i 1.026	0.265
	1.100	i 1.289	i 0.663
$0.1388 \, \hat{z}$	5.800	5.300	4.352
	5.570	4.919	3.879
	4.600	4.244	3.588
	3.200	3.808	3.080
	3.200	2.967	2.570
	2.650	2.466	2.024
	1.660	2.153	2.004
	0.850	1.084	0.955
	0.530	0.303	0.238
	0.530	i 2.573	0.089

$\underset{\sim}{q}$	ω_e X 10^{-12}	ω_i X 10^{-12}	ω_f X 10^{-12}
0.2776 $\hat{z}$	5.640	5.237	4.343
	5.370	4.851	3.829
	4.580	4.221	3.354
	3.500	3.928	3.165
	3.320	3.308	2.816
	2.250	2.307	1.892
	1.900	2.121	1.869
	1.900	1.685	1.689
	1.050	0.608	0.480
	1.050	i 0.477	0.206
0.4165 $\hat{z}$	5.450	5.091	4.275
	5.080	4.744	3.750
	4.540	4.178	3.504
	3.700	4.089	3.279
	3.600	3.594	3.029
	2.500	3.034	2.651
	2.080	2.083	1.704
	2.000	1.206	1.396
	1.390	0.916	0.729
	1.280	i 0.618	0.367
0.5553 $\hat{z}$	5.120	4.823	4.101
	4.580	4.604	3.648
	4.400	4.265	3.434
	4.180	4.106	3.404

$\underset{\sim}{q}$	$\omega_e \times 10^{-12}$	$\omega_i \times 10^{-12}$	$\omega_f \times 10^{-12}$
$0.5553 \, \hat{z}$	3.950	3.822	3.299
	3.250	3.801	3.202
	2.050	1.818	1.480
	1.850	1.224	1.101
	1.650	0.671	0.983
	1.480	i 0.632	0.575
$0.6941 \, \hat{z}$	4.750	4.441	3.782
	4.620	4.441	3.782
	4.200	4.399	3.530
	4.160	4.399	3.530
	3.950	3.990	3.336
	3.950	3.990	3.336
	1.890	1.528	1.236
	1.890	1.528	1.236
	1.650	i 0.390	0.824
	1.600	i 0.390	0.824

FOOTNOTES AND BIBLIOGRAPHY

1. R. C. Weast, ed., Handbook of Chemistry and Physics (The Chemical Rubber Co., Cleveland, Ohio, 1966), 47th ed..

2. Ibid.

3. C. B. Clark, private communication.

4. D. E. Thompson, "Lattice Dynamics in a Gallium Crystal Using the "6-exp" Potential" (Masters thesis, University of North Carolina at Greensboro, 1970), p. 21.

5. G. S. Pawley, Phys. Stat. Sol. 20, 347 (1967).

6. D. E. Thompson, p. 15.

7. Ibid., p. 36.

8. W. R. Busing, "Summary of Method of Least Squares" (unpublished article), p. 1.

9. C. B. Clark, private communication.

10. W. Reichardt, unpublished results obtained at Oak Ridge National Laboratories.

11. W. Cochran and G. S. Pawley, Proc. Roy. Soc. A280, 6 (1964).

12. Pawley, p. 350.

13. Cochran and Pawley, p. 7.

14. Ibid., p. 5.

15. D. E. Thompson, p. 24.

16. Pawley, p. 350.

17. The Jacobi method for finding the eigen values of a real, symmetric matrix is discussed in A. Ralston, _A First Course in Numerical Analysis_ (McGraw-Hill Book Co., New York, 1965), Chap. 10, pp. 487-492.

18. The program used for the computations is an adaptation of a program obtained from R. M. Nicklow of Oak Ridge National Laboratories.

19. C. Kittel, _Introduction to Solid State Physics_ (John Wiley & Sons, Inc., New York, 1966), 3rd ed., Chap. 2, p. 53.

20. Ibid.

APPENDIX I

Analytical Calculations of Interatomic Force Constants

The force between a particular atom-atom pair may be derived from the "6-exp" interaction potential energy form

$$V = -\frac{A}{r^6} + Be^{-\alpha r}$$

using

$$\mathbf{F} = \hat{r}\,\frac{V}{r} = -(x_1\hat{u}_1 + x_2\hat{u}_2 + x_3\hat{u}_3)(6\frac{A}{r^7} - B\alpha e^{-\alpha r}) \tag{1}$$

where $\mathbf{F}$ is the force on the origin atom due to the source atom and $\hat{u}_1$, $\hat{u}_2$, and $\hat{u}_3$ are the unit vectors along the crystal axes (CA). The quantity (x_1, x_2, x_3) represents the X, Y, and Z co-ordinates, respectively, of the source atom relative to the origin atom in the co-ordinate system defined by the CA. Equation (1) may be written in component form as

$$F_i = x_i f(r) \tag{2}$$

where $i = 1\text{-}3$ and $f(r) = 6\frac{A}{r^8} - B\frac{\alpha}{r}e^{-\alpha r}$.

Displacing the source atom by an amount $d\mathbf{x} = \mathbf{U}$ produces a net unbalanced force on the origin atom. The components of the force may be written as

$$dF_i = \sum_j \frac{\partial F_i}{\partial x_j}U_j \tag{3}$$

where i and j = 1-3. Inserting Eq. (2) into Eq. (3) yields

$$dF_i = \sum_j (\frac{\partial x_i}{\partial x_j} f(r) U_j + x_i \frac{\partial f}{\partial r}(r) \frac{\partial r}{\partial x_j} U_j).$$

This may be written in a more compact form as

$$dF_i = \sum_j (\delta_{ij} f(r) U_j + x_i x_j g(r) U_j) \tag{4}$$

where δ_{ij} is the Kronecker delta and $g(r) = \frac{1}{r} \frac{\partial f(r)}{\partial r}$.

The Hooke's Law coupling requires that the component forces on the origin atom be

$$dF_i = - \sum_j \phi_{ij} U_j \tag{5}$$

where ϕ_{ij} represent the elements of the force constant matrix and U_j is the displacement of the source atom. Comparing Eqs. (4) and (5) one obtains

$$\phi_{ij} = - \delta_{ij} f(r) - x_i x_j g(r) \tag{6}$$

where i and j = 1-3.

Equation (6) is derived on the basis of atomic displacements, which now must be related to generalized displacements of the source molecule. Translating the source molecule by an amount $\underset{\sim}{u}$ produces a net translation of $\underset{\sim}{u}$ for each of the component atoms. However, translating and rotating the source molecule produces a net translation of the component atoms which is different from that of the source molecule. The translation and rotation of the source molecule may be written as

$$\underset{\sim}{u} = u_1 \hat{u}_1 + u_2 \hat{u}_2 + u_3 \hat{u}_3 \tag{7}$$

and

$$\underset{\sim}{\varphi} = u_4 \hat{u}_4 + u_5 \hat{u}_5 + u_6 \hat{u}_6, \tag{8}$$

respectively, where $\hat{u}_1$, $\hat{u}_2$, and $\hat{u}_3$ represent the unit vectors along the CA and $\hat{u}_4$, $\hat{u}_5$, and $\hat{u}_6$ represent the unit vectors along the principal axes (PA) of the source molecule as defined in Fig. 6. The net translation of an atom is given by

$$\underset{\sim}{U} = \underset{\sim}{u} + \underset{\sim}{\varphi} \times \underset{\sim}{R} \tag{9}$$

where $\underset{\sim}{R}$ is defined in Fig. 6 and $\underset{\sim}{\varphi} \times \underset{\sim}{R}$ is the translation of the atom due to the rotation of the molecule. It is most appropriate to write $\underset{\sim}{U}$ in terms of the CA and therefore necessary to convert the PA unit vectors into components involving the CA unit vectors. One obtains from analysis of Fig. 6 the following:

$$\hat{u}_4 = \hat{u}_1$$
$$\hat{u}_5 = -\hat{u}_2 \sin \Theta s + \hat{u}_3 \cos \Theta s$$
$$\hat{u}_6 = \hat{u}_2 \cos \Theta s + \hat{u}_3 \sin \Theta s$$

where Θs is the equilibrium inclination of the source molecule relative to the $\hat{u}_2$ crystal axis. Therefore, in terms of the CA, $\underset{\sim}{\varphi}$ is given by

$$\underset{\sim}{\varphi} = u_4 \hat{u}_1 + (u_6 \cos \Theta s - u_5 \sin \Theta s)\hat{u}_2 + (u_6 \sin \Theta s + u_5 \cos \Theta s)\hat{u}_3$$
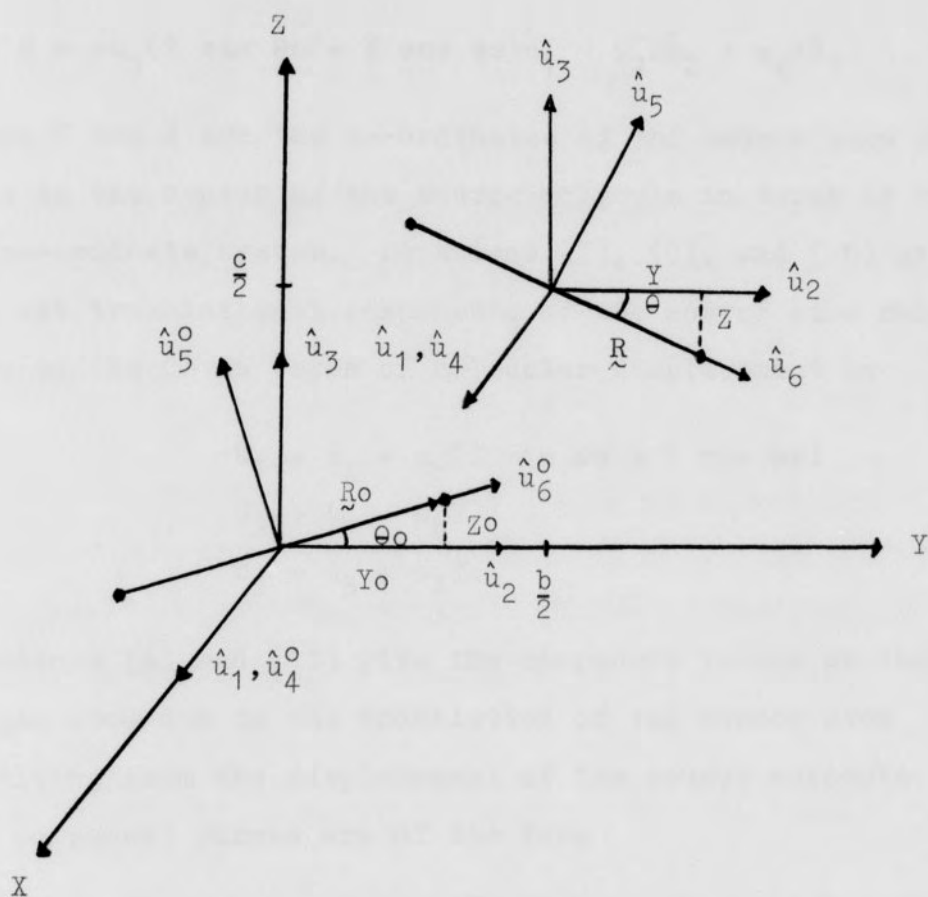
Fig. 6. A diagram defining the co-ordinate systems of the
origin and source molecules.

and

$$\underset{\sim}{\varphi} \times \underset{\sim}{R} = -u_5(Z \sin \Theta s + Y \cos \Theta s)\hat{u}_1 - u_4 Z \hat{u}_2 + u_4 Y \hat{u}_3 \qquad (10)$$

where Y and Z are the co-ordinates of the source atom rela-
tive to the center of the source molecule in terms of the
CA co-ordinate system. Equations (7), (9), and (10) give
the net translational components of the source atom rela-
tive to the CA in terms of molecular displacement as

$$
\begin{aligned}
U_1 &= u_1 - u_5(Z \sin \Theta s + Y \cos \Theta s) \\
U_2 &= u_2 - u_4 Z \\
U_3 &= u_3 + u_4 Y.
\end{aligned}
\qquad (11)
$$

Equations (4) and (11) give the component forces on the
origin atom due to the translation of the source atom
resulting from the displacement of the source molecule.
The component forces are of the form

$$dF_i = -\sum_j \phi_{ij} u_j \qquad (12)$$

where $i = 1-3$, $j = 1-5$, and u_j represent the displacement
components of the source molecule. The elements of the
interatomic force constant matrix are given by

    a. $i = 1-3$ and $j = 1-3$

$$\phi_{ij} = -\delta_{ij} f(r) - x_i x_j g(r)$$

b. $i = 1-3$

$$\phi_{i4} = \phi_{i3}Y - \phi_{i2}Z$$

$$\phi_{i5} = -(Y \cos \theta s + Z \sin \theta s)\phi_{i1}.$$

The contribution to the net unbalanced torque on the origin molecule made by the force on a single atom in the origin molecule is obtained from

$$d\underset{\sim}{T} = \underset{\sim}{R}o \ X \ d\underset{\sim}{F}$$

where $\underset{\sim}{R}o$ is the position of the origin atom relative to the center of the origin molecule (Fig. 6) and $d\underset{\sim}{F}$ is the net unbalanced force on the origin atom due to the displacement of the source atom. The resulting torque in terms of the CA is

$$d\underset{\sim}{T} = (Yo \ dF_3 - Zo \ dF_2)\hat{u}_1 + Zo \ dF_1\hat{u}_2 - Yo \ dF_1\hat{u}_3 \qquad (13)$$

where Yo and Zo are the co-ordinates of the origin atom relative to the center of the origin milecule (Fig. 6). It is more useful to know the torque contribution in terms of the PA of the origin molecule. Therefore, the CA must be written in terms of the PA of the origin molecule. One obtains from analysis of Fig. 6, the following:

$$\hat{u}_1 = \hat{u}_4^0$$
$$\hat{u}_2 = \hat{u}_6^0\cos \theta o - \hat{u}_5^0\sin \theta o \qquad (14)$$
$$\hat{u}_3 = \hat{u}_5^0\cos \theta o + \hat{u}_6^0\sin \theta o$$

where $\hat{u}_4^o$, $\hat{u}_5^o$, and $\hat{u}_6^o$ represent the PA of the origin molecule and Θo is the equilibrium angle of inclination of the origin molecule relative to the $\hat{u}_2$ crystal axis (Fig. 6). Equations (13) and (14) enable one to write the torque in terms of the PA of the origin molecule as

$$d\underset{\sim}{T} = (Yo\ dF_3 - Zo\ dF_2)\hat{u}_4 - (Yo\ \cos\ \Theta o + Zo\ \sin\ \Theta o)dF_1\hat{u}_5$$

which in component form may be written

$$dF_4 = Yo\ dF_3 - Zo\ dF_2$$
$$dF_5 = -(Yo\ \cos\ \Theta o + Zo\ \sin\ \Theta o)dF_1.$$

Equation (12) enables one to rewrite the component equations as

$$dF_4 = \sum_j (Zo\ \emptyset_{2j} - Yo\ \emptyset_{3j})u_j$$

and

$$dF_5 = \sum_j (Yo\ \cos\ \Theta o + Zo\ \sin\ \Theta o)\emptyset_{1j}u_j$$

where $j = 1-5$. Comparing the two preceding equations to the form of Eq. (12), it is clear that for $j = 1-5$

$$\emptyset_{4j} = Yo\ \emptyset_{3j} - Zo\ \emptyset_{2j}$$

and

$$\emptyset_{5j} = -(Yo\ \cos\ \Theta o + Zo\ \sin\ \Theta o)\emptyset_{1j}.$$

APPENDIX II

Determination of Self Force Constants

The Hooke's Law approximation requires that the net unbalanced force on the origin molecule be of the form

$$\underset{\sim}{F}_j = - \sum_{j'} \underset{\approx}{\phi}(jj') \underset{\sim}{u}_{j'}$$

where the sum includes $j'=j$. Therefore the equation may be rewritten as

$$\underset{\sim}{F}_j = - \sum_{j'} \underset{\approx}{\phi}(jj') \underset{\sim}{u}_{j'} - \underset{\approx}{\phi}(jj) \underset{\sim}{u}_j$$

where $j' \neq j$. The second term in the preceding equation is called the "self" force term and results from the displacement of the origin molecule while the source molecules are undisturbed. The "self" force expression is best treated in terms of displacements of the source molecules. Clearly, translation of the origin molecule while the source molecules are undisturbed has the same effect as holding the origin molecule fixed and translating all source molecules in the opposite direction. If, however, the origin molecule is rotated by an amount $\underset{\sim}{\varphi}_j$ then the corresponding displacement of the source molecules is given by a rotation, $-\underset{\sim}{\varphi}_j$, plus a translation, $-\underset{\sim}{\varphi}_j \times \underset{\sim}{r}_{j'}$ where $\underset{\sim}{r}_{j'}$ is the vector connecting a source molecule to the origin molecule. If $\underset{\sim}{V}_j$

represents the translation of the origin molecule then the "self" force may be written in terms of the source molecule displacements as

$$-\underset{\sim}{\phi}(jj)\underset{\sim}{u}_j = -\sum_{j'} \underset{\sim}{\phi}(jj') \; (-\underset{\sim}{V}_j - \underset{\sim}{\varphi}_j \; X \; \underset{\sim}{r}_{j'} - \underset{\sim}{\varphi}_j) \qquad (1)$$

where

$$\begin{aligned}
\underset{\sim}{V}_j &= u_1^o \hat{u}_1 + u_2^o \hat{u}_2 + u_3^o \hat{u}_3 \\
\underset{\sim}{\varphi}_j &= u_4^o \hat{u}_4^o + u_5^o \hat{u}_5^o + u_6^o \hat{u}_6^o \\
\underset{\sim}{r}_{j'} &= H\frac{a}{2}\hat{u}_1 + K\frac{b}{2}\hat{u}_2 + L\frac{c}{2}\hat{u}_3
\end{aligned} \qquad (2)$$

and where $\hat{u}_1$, $\hat{u}_2$, and $\hat{u}_3$ are the unit vectors along the crystal axes (CA) and $\hat{u}_4^o$, $\hat{u}_5^o$, and $\hat{u}_6^o$ are the unit vectors along the principal axes (PA) of the origin molecule. H, K, and L are integers and a, b, and c are the lattice constants. Since $-\underset{\sim}{\varphi}_j \; X \; \underset{\sim}{r}_{j'}$ represents a translation, it is convenient to evaluate it in terms of the CA. From analysis of Fig. 6 in APPENDIX I it is clear that

$$\begin{aligned}
\hat{u}_4^o &= \hat{u}_1 \\
\hat{u}_5^o &= -\hat{u}_2 \sin \Theta o + \hat{u}_3 \cos \Theta o
\end{aligned}$$

and

$$\hat{u}_6^o = \hat{u}_2 \cos \Theta o + \hat{u}_3 \sin \Theta o.$$

This enables one to write $-\underset{\sim}{\varphi}_j \; X \; \underset{\sim}{r}_{j'}$ in terms of the CA as

$$-\underset{\sim}{\varphi}_j \times \underset{\sim}{r}_{j'} = (u_5^o(K_{\frac{b}{2}}\cos\theta_o + L_{\frac{c}{2}}\sin\theta_o))\hat{u}_1$$
$$+ (L_{\frac{c}{2}}u_4^o - H_{\frac{a}{2}}u_5^o\cos\theta_o)\hat{u}_2 \qquad (3)$$
$$- (K_{\frac{b}{2}}u_4^o + H_{\frac{a}{2}}u_5^o\sin\theta_o)\hat{u}_3$$

where terms involving u_6^o have been neglected because rotations about the dumbbell axis have no effect on the system. θ_o is the equilibrium inclination of the origin molecule relative to the b crystal axis and is positive for type A origin molecules and negative for type B origin molecules. The "self" force is written in terms of displacements of the source molecules and therefore the rotational displacements must be expressed in terms of the PA of the source molecules while the translational displacements are expressed in terms of the CA. For origin and source molecules that are alike, the two sets of PA are always parallel. Thus, angular displacements are the same relative to either set of PA. Therefore, $\underset{\sim}{\varphi}_j = u_4^o\hat{u}_4 + u_5^o\hat{u}_5$ where angular displacements about the $\hat{u}_6$ or dumbbell axis are neglected. For unlike origin and source molecules, however, the PA of the origin molecule must be converted to the PA of the source molecule. This is done by expressing the PA of the origin molecule in terms of the CA and then converting the CA to PA of the source molecule. The results are

$$\hat{u}_4^o = \hat{u}_4$$

and

$$\hat{u}_5^o = \cos 2\theta \; \hat{u}_5$$

where θ is the magnitude of the equilibrium inclination of the origin and source molecules. Components involving rotations about the dumbbell axis have been omitted. Thus, for unlike interactions

$$\underset{\sim}{\varphi}_j = u_4^o \hat{u}_4 + u_5^o \cos 2\theta \; \hat{u}_5.$$

By substituting Eqs. (2) and (3) into Eq. (1) and performing the indicated matrix multiplication, it is possible to determine the "self" force constants by comparing the coefficients of u_i^o. The results for the various interactions are given below.

a. type A origin molecules ($\theta o = \theta$)

1. $i = 1-5$ and $k = 1-3$

$$\emptyset_{ik}(jj) = -\sum_{j'} \emptyset_{ik}$$

2. $i = 1-5$

$$\emptyset_{i4}(jj) = -\sum_{j'} (\emptyset_{i4} - \emptyset_{i2}L_2^c + \emptyset_{i3}K_2^b)$$

(Both sums are over types A and B source molecules.)

3. $i = 1-5$

$$\phi_{i5}(jj) = -\sum_{j'}(\phi_{i5} - \phi_{i1}(K\frac{b}{2}\cos\theta + L\frac{c}{2}\sin\theta)$$
$$+ \phi_{i2}H\frac{a}{2}\cos\theta + \phi_{i3}H\frac{a}{2}\sin\theta)$$
$$- \sum_{j'}(\phi_{i5}\cos 2\theta - \phi_{i1}(K\frac{b}{2}\cos\theta$$
$$+ L\frac{c}{2}\sin\theta) + \phi_{i2}H\frac{a}{2}\cos\theta + \phi_{i3}H\frac{a}{2}\sin\theta)$$

(The first and second sums are over types A and B source molecules, respectively.)

b.   type B origin molecules ($\theta_0 = -\theta$)

    1. $i = 1-5$ and $k = 1-3$

$$\phi_{ik}(jj) = -\sum_{j'}\phi_{ik}$$

    2. $i = 1-5$

$$\phi_{i4}(jj) = -\sum_{j'}(\phi_{i4} - \phi_{i2}L\frac{c}{2} + \phi_{i3}K\frac{b}{2})$$

(Both sums are over types A and B source molecules.)

    3. $i = 1-5$

$$\phi_{i5}(jj) = -\sum_{j'}(\phi_{i5}\cos 2\theta - \phi_{i1}(K\frac{b}{2}\cos\theta$$
$$- L\frac{c}{2}\sin\theta) + \phi_{i2}H\frac{a}{2}\cos\theta - \phi_{i3}H\frac{a}{2}\sin\theta)$$
$$- \sum_{j'}(\phi_{i5} - \phi_{i1}(K\frac{b}{2}\cos\theta - L\frac{c}{2}\sin\theta)$$
$$+ \phi_{i2}H\frac{a}{2}\cos\theta - \phi_{i3}H\frac{a}{2}\sin\theta)$$

(The first and second sums are over types A and B source molecules, respectively.)

$\emptyset$ is written on the right hand side of the above equations
to represent $\emptyset(jj')$. H, K, and L are integers and Θo is
the angle that the dumbbell axis of the origin molecule
makes with the b crystal axis.

APPENDIX III

Symmetry of the Gallium Lattice

Symmetry requires that the force constant matrices for a particular pair of interactions be related by

$$\underset{\sim}{\phi}' = \underset{\sim}{T}\underset{\sim}{\phi}\underset{\sim}{\tilde{T}} \tag{1}$$

where $\underset{\sim}{\phi}'$ is the force constant matrix for one interaction and $\underset{\sim}{\phi}$ is the force constant matrix for the other. $\underset{\sim}{T}$ is a six dimensional transformation matrix formed from $\underset{\sim}{S}$, the three dimensional rotation matrix for polar vectors. If det $\underset{\sim}{S} = 1$ ($\underset{\sim}{S}$ performs a proper rotation), $\underset{\sim}{S}$ is appropriate for transforming both polar and axial vectors. However, if det $\underset{\sim}{S} = -1$ ($\underset{\sim}{S}$ performs an improper rotation), $-\underset{\sim}{S}$ is needed in transforming the axial vectors. Therefore, $\underset{\sim}{S}$ det $\underset{\sim}{S}$ may always be used for transforming axial vectors if they are expressed relative to the same orthogonal co-ordinate system as the polar vectors. For this study of gallium, the polar vectors (translations) are measured relative to the crystal axes (CA) and the axial vectors (rotations) are measured relative to the principal axes (PA) of the source molecule. Therefore, if $\underset{\sim}{S}$ is expressed relative to the CA, $\underset{\sim}{S}$ det $\underset{\sim}{S}$ must be transformed to the PA system before using it with axial vectors whose components are taken along the PA. Consider the axial vector $\underset{\sim}{r}$ with respect to the CA.

It transforms to PA according to

$$r_{PA} = a r_{CA} \qquad (2)$$

where

$$a = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{bmatrix} . \quad (\text{Fig. 7})$$

If S is the rotation matrix which transforms the polar vector v into the polar vector v' then r is transformed into r' according to

$$r'_{CA} = S \det S \, r_{CA} . \qquad (3)$$

The general form of Eq. (2) requires that

$$r'_{PA} = a r'_{CA} . \qquad (4)$$

Equations (2), (3), and (4) then yield

$$r'_{PA} = a \, S \det S \, r_{CA}$$

and

$$r'_{PA} = a \, S \det S \, a^{-1} r_{PA} .$$

Therefore, the correct form of the symmetry transformation is
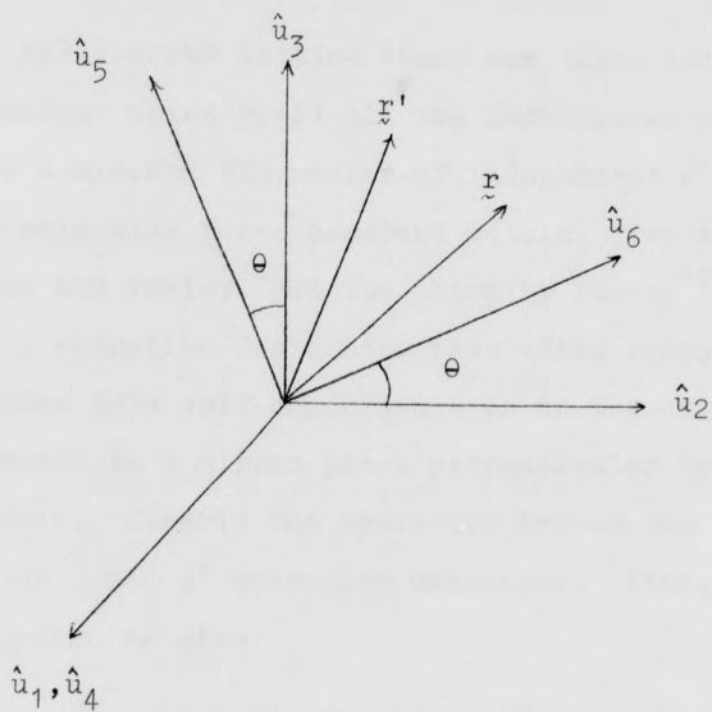
Fig. 7. A diagram for converting crystal axes to principal
axes. (($\hat{u}_1, \hat{u}_2, \hat{u}_3$) represent the crystal axes and
($\hat{u}_4, \hat{u}_6, \hat{u}_5$) represent the principal axes.)

$$
\underset{\sim}{T} = \begin{bmatrix} \underset{\sim}{S} & & 0 \\ & & \\ & & \\ 0 & & \underset{\sim}{a}\,\underset{\sim}{S}\,\det\underset{\sim}{S}\,\underset{\sim}{a}^{-1} \end{bmatrix}.
\tag{5}
$$

For the gallium lattice there are three lattice symmetry operations which yield all the information needed to reduce to a minimum the number of independent elements in the intermolecular force constant matrix. Two are discussed by Cochran and Pawley[11] and the third by Pawley[12]. The class A symmetry operation designates that which brings the j and j' molecules into self-coincidence as in the case of molecules located in a mirror plane perpendicular to the a crystal axis. Clearly the operation leaves the interaction between the j and j' molecules unchanged. Thus, Eq. (1) may be applied to give

$$
\underset{\sim}{\emptyset}(jj') = \underset{\sim}{T}\underset{\sim}{\emptyset}(jj')\underset{\sim}{\widetilde{T}}
\tag{6}
$$

Specifically, consider a mirror plane through the origin perpendicular to the a crystal axis. The reflection operation reverses the x co-ordinate so that

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

and

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

Therefore, the symmetry transformation matrix is given by

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

For a j molecule and a j' molecule located in the b-c plane
(the mirror plane) the interaction is unchanged by the
operation. Thus, Eq. (6) yields

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

Comparing elements, it is obvious that the above is true
if and only if

$$
\underset{\sim}{\emptyset}(jj') =
\begin{bmatrix}
\emptyset_{11} & 0 & 0 & 0 & \emptyset_{15} & \emptyset_{16} \\
0 & \emptyset_{22} & \emptyset_{23} & \emptyset_{24} & 0 & 0 \\
0 & \emptyset_{32} & \emptyset_{33} & \emptyset_{34} & 0 & 0 \\
0 & \emptyset_{42} & \emptyset_{43} & \emptyset_{44} & 0 & 0 \\
\emptyset_{51} & 0 & 0 & 0 & \emptyset_{55} & \emptyset_{56} \\
\emptyset_{61} & 0 & 0 & 0 & \emptyset_{65} & \emptyset_{66}
\end{bmatrix}. \tag{7}
$$

Equation (7) is the general form of the force constant matrix for intermolecular interactions between molecules located in the b-c plane. Class B symmetry designates an inversion through a center (such as the origin) so that the interaction between a j molecule located at the origin and a j' molecule located at (x,y,z) is transformed into the interaction between the origin molecule and the -j' molecule located at (-x,-y,-z). Equation (1) may be written for class B symmetry as

$$
\underset{\sim}{\emptyset}(0-j') = \underset{\sim}{T}\underset{\sim}{\emptyset}(0j')\underset{\sim}{\tilde{T}}. \tag{8}
$$

The inversion operation reverses the co-ordinates of any polar vector so that

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

and

$$\underset{\widetilde{\sim}}{a} \; \underset{\widetilde{\sim}}{S} \; \det \underset{\widetilde{\sim}}{S} \; \underset{\widetilde{\sim}}{a}^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

The symmetry transformation matrix is given by

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

Applying Eq. (8) yields the result that

$$\underset{\sim}{\phi}(0-j') = \begin{bmatrix} \phi_{11} & \phi_{12} & \phi_{13} & -\phi_{14} & -\phi_{15} & -\phi_{16} \\ \phi_{21} & \phi_{22} & \phi_{23} & -\phi_{24} & -\phi_{25} & -\phi_{26} \\ \phi_{31} & \phi_{32} & \phi_{33} & -\phi_{34} & -\phi_{35} & -\phi_{36} \\ -\phi_{41} & -\phi_{42} & -\phi_{43} & \phi_{44} & \phi_{45} & \phi_{46} \\ -\phi_{51} & -\phi_{52} & -\phi_{53} & \phi_{54} & \phi_{55} & \phi_{56} \\ -\phi_{61} & -\phi_{62} & -\phi_{63} & \phi_{64} & \phi_{65} & \phi_{66} \end{bmatrix} \tag{9}$$

where the ϕ_{ik} within the brackets represent $\phi_{ik}(0j')$.
By considering interactions in the b-c plane Eq. (7) may
be applied to give

$$\underset{\sim}{\phi}(0-j') = \begin{bmatrix} \phi_{11} & 0 & 0 & 0 & -\phi_{15} & -\phi_{16} \\ 0 & \phi_{22} & \phi_{23} & -\phi_{24} & 0 & 0 \\ 0 & \phi_{32} & \phi_{33} & -\phi_{34} & 0 & 0 \\ 0 & -\phi_{42} & -\phi_{43} & \phi_{44} & 0 & 0 \\ -\phi_{51} & 0 & 0 & 0 & \phi_{55} & \phi_{56} \\ -\phi_{61} & 0 & 0 & 0 & \phi_{65} & \phi_{66} \end{bmatrix} \circ \qquad (10)$$

Inversion symmetry for interactions between like molecules exhibits the property of translational invariance as defined by Cochran and Pawley.[13] It is expressed simply as

$$\underset{\sim}{\phi}(0-j') = \underset{\sim}{\phi}(j'0).^{*}$$

It can be shown that

$$\underset{\sim}{\phi}(j'j) = \underset{\sim}{\tilde{\phi}}(jj').^{14}$$

Therefore, for interactions between like molecules Eq. (9) may be equated to $\underset{\sim}{\tilde{\phi}}(0j')$ to yield

$$\underset{\sim}{\phi}(0j') = \begin{bmatrix} \phi_{11} & \phi_{12} & \phi_{13} & \phi_{14} & \phi_{15} & \phi_{16} \\ \phi_{12} & \phi_{22} & \phi_{23} & \phi_{24} & \phi_{25} & \phi_{26} \\ \phi_{13} & \phi_{23} & \phi_{33} & \phi_{34} & \phi_{35} & \phi_{36} \\ -\phi_{14} & -\phi_{24} & -\phi_{34} & \phi_{44} & \phi_{45} & \phi_{46} \\ -\phi_{15} & -\phi_{25} & -\phi_{35} & \phi_{45} & \phi_{55} & \phi_{56} \\ -\phi_{16} & -\phi_{26} & -\phi_{36} & \phi_{46} & \phi_{56} & \phi_{66} \end{bmatrix} \circ \qquad (11)$$

---

*It should be noted that D. E. Thompson[15] assumed this property to be valid for all interactions. This resulted in the misinterpretation of the symmetry properties.

By again considering interactions in the b-c plane Eq. (11) is reduced to

$$
\underset{\sim}{\phi}(0j') = \begin{bmatrix} \phi_{11} & 0 & 0 & 0 & \phi_{15} & \phi_{16} \\ 0 & \phi_{22} & \phi_{23} & \phi_{24} & 0 & 0 \\ 0 & \phi_{32} & \phi_{33} & \phi_{34} & 0 & 0 \\ 0 & -\phi_{24} & -\phi_{34} & \phi_{44} & 0 & 0 \\ -\phi_{15} & 0 & 0 & 0 & \phi_{55} & \phi_{56} \\ -\phi_{16} & 0 & 0 & 0 & \phi_{56} & \phi_{66} \end{bmatrix} .
$$

Class C symmetry, as defined by Pawley[16], relates the interaction matrix for an A-B interaction to that for a B-A interaction. It is best illustrated by the screw-diad operation which transforms the molecule pair j-j' into the molecule pair j'-j" (These are represented in Fig. 5 of CHAPTER I.) Since j represents the molecule located at the origin and j' and j" represent the molecules located at $\underset{\sim}{r}_{j'}$ and $\underset{\sim}{r}_{j''}$, respectively, Eq. (1) may be written as

$$
\underset{\sim}{\phi}(\underset{\sim}{r}_{j'},\underset{\sim}{r}_{j''}) = \underset{\sim}{T}\underset{\sim}{\phi}(0\underset{\sim}{r}_{j'})\underset{\sim}{\tilde{T}} \tag{12}
$$

where $\underset{\sim}{T}$ is the screw-diad symmetry transformation. If $\underset{\sim}{S}$ represents the operation that transforms $\underset{\sim}{r}_{j'}$ into $\underset{\sim}{r}_{j''} - \underset{\sim}{r}_{j'}$ then $\underset{\sim}{r}_{j''} = \underset{\sim}{r}_{j'} + \underset{\sim}{S}\underset{\sim}{r}_{j'}$. Therefore Eq. (12) may be written as

$$
\underset{\sim}{\phi}(\underset{\sim}{r}_{j'},\ \underset{\sim}{r}_{j'} + \underset{\sim}{S}\underset{\sim}{r}_{j'}) = \underset{\sim}{T}\underset{\sim}{\phi}(0\underset{\sim}{r}_{j'})\underset{\sim}{\tilde{T}}. \tag{13}
$$

Since $\underset{\sim}{r}_{j'} + \underset{\sim}{S}\underset{\sim}{r}_{j'}$ is a lattice translation vector, $-(\underset{\sim}{r}_{j'} + \underset{\sim}{S}\underset{\sim}{r}_{j'})$ may be added to the expressions in parenthesis on the left hand side of Eq. (13) to give

$$\underset{\sim}{\phi}(-\underset{\sim}{S}\underset{\sim}{r}_{j'},0) = \underset{\sim}{T}\underset{\sim}{\phi}(0\underset{\sim}{r}_{j'})\underset{\sim}{\tilde{T}} = \underset{\sim}{\tilde{\phi}}(0-\underset{\sim}{S}\underset{\sim}{r}_{j'}). \tag{14}$$

Using the property of class B symmetry given by Eq. (8), it is clear that

$$\underset{\sim}{\tilde{\phi}}(0-\underset{\sim}{S}\underset{\sim}{r}_{j'}) = \underset{\sim}{I}\underset{\sim}{\tilde{\phi}}(0\underset{\sim}{S}\underset{\sim}{r}_{j'})\underset{\sim}{\tilde{I}} \tag{15}$$

where

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

as developed for an inversion through the origin. Therefore, Eqs. (12), (14), and (15) give

$$\underset{\sim}{\phi}(\underset{\sim}{r}_{j'}\underset{\sim}{r}_{j''}) = \underset{\sim}{I}\underset{\sim}{\tilde{\phi}}(0\underset{\sim}{S}\underset{\sim}{r}_{j'})\underset{\sim}{\tilde{I}}.$$

The symmetry of Fig. 5 in CHAPTER I requires that $\underset{\sim}{S}\underset{\sim}{r}_{j'} = \underset{\sim}{r}_{j''} - \underset{\sim}{r}_{j'} = \underset{\sim}{r}_{1'}$, therefore, it is more convenient to write

$$\underset{\sim}{\phi}(j'j'') = \underset{\sim}{I}\underset{\sim}{\tilde{\phi}}(j1')\underset{\sim}{\tilde{I}}$$

where $\underset{\sim}{\phi}(j'j'')$ represents the interaction matrix for any

A-B or B-A interaction and $\emptyset(jl')$ represents the interaction matrix for any corresponding B-A or A-B interaction. The result of this relationship is given by

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

If interactions in a plane perpendicular to the a crystal axis are considered, class A symmetry requires that

$$\emptyset(j'j") = \begin{bmatrix} \emptyset_{11} & 0 & 0 & 0 & -\emptyset_{51} & -\emptyset_{61} \\ 0 & \emptyset_{22} & \emptyset_{32} & -\emptyset_{42} & 0 & 0 \\ 0 & \emptyset_{23} & \emptyset_{33} & -\emptyset_{43} & 0 & 0 \\ 0 & -\emptyset_{24} & -\emptyset_{34} & \emptyset_{44} & 0 & 0 \\ -\emptyset_{15} & 0 & 0 & 0 & \emptyset_{55} & \emptyset_{65} \\ -\emptyset_{16} & 0 & 0 & 0 & \emptyset_{56} & \emptyset_{66} \end{bmatrix} .$$

The terms within the brackets of the above two equations represent elements of $\emptyset(jl')$. Note that all through this appendix the matrices are 6X6. They are reduced to 5X5 when used because there is no coupling about the dumbbell axis of gallium.

APPENDIX IV

Programming Considerations

All computations were made by the IBM 360/75 computer located at Triangle Universities Computation Center in Durham, North Carolina. Entrance into the computer was gained through the IBM 2780 terminal system located on the campus of the University of North Carolina at Greensboro. The computer program is divided into five main sections:

a. Calculation and storage of the intermolecular and "self" force constants for like interactions.

b. Calculation and storage of the intermolecular and "self" force constants for unlike interactions.

c. Calculation of the dynamical matrix elements.

d. Solving the dynamical matrix for its frequency eigenvalues.

e. Comparing the calculated dispersion curves to the experimental dispersion curves, using the "Least Squares" criteria for determining the best set of model parameters.

The intermolecular force constants are calculated using three nested do-loops in each section a. and b. to select values of h, k, and l representing a specific molecule-molecule interaction. The interatomic force

constants for the four possible combinations of the origin and source atoms are calculated[*] and summed to give a specific intermolecular force constant which is then stored. This is done for all specified values of h, k, and l. The intermolecular force constants are then used to calculate the "self" force constants, which are then stored. The intermolecular and "self" force constants are then used in calculating the elements of the dynamical matrix for a specific wave vector, q, which enters through $e^{i q \cdot r}$, where r is the location of the source molecule relative to the origin molecule.

The eigenvalues of the dynamical matrix are then found for each q value using a subroutine, JACOBI, obtained from Oak Ridge National Laboratories.[17]

After all eigenvalues are calculated they are compared to the experimental eigenvalues using another program obtained from Oak Ridge National Laboratories. The program uses the method of "Least Squares" as outlined in Chap. II to determine a set of model parameters which produce dispersion curves similar to the experimental curves.[18]

A listing of the completed program follows.

---

[*]The expressions used in calculating the interatomic force constants were not the same as given in APPENDIX I. They differ in sign, however, this does not affect the final dynamical matrix eigenvalues.

```
$JOB       ECS.UNCG.PY620069/FREEMAN,KP=29,TIME=960,PAGES=100
C      AL IS THE LENGTH OF THE UNIT CELL IN THE X DIRECTION.
C      BL IS THE LENGTH OF THE UNIT CELL IN THE Y DIRECTION.
C      CL IS THE LENGTH OF THE UNIT CELL IN THE Z DIRECTION.
C      PX(1), PX(2), AND PX(3) ARE
C      THE PARAMETERS A, B, AND ALPHA.
C      BM(1),BM(2), AND BM(3) ARE MASS OF GALLIUM MOL.
C      BM(4) AND BM(5) ARE MOMENTS OF INERTIA ABOUT
C      THE PRINCIPAL AXES OF THE GALLIUM MOLECULE.
C      X(1) IS THE X CO-ORD. OF THE SOUR. ATOM RELTV. TO
C      THE ORIGIN ATOM.
C      X(2) IS THE Y CO-ORD. OF THE SOUR. ATOM RELTV. TO
C      THE ORIGIN ATOM.
C      X(3) IS THE Z CO-ORD. OF THE SOUR. ATOM RELTV. TO
C      THE ORIGIN ATOM.
C      X(4) IS THE DISTANCE BETWEEN THE SOUR. ATOM AND
C      THE ORIGIN ATOM
C      YO IS Y CO-ORD. OF ORIG. ATM. RELTV. TO CENT. OF
C      ORIGIN MOLECULE.
C      ZO IS Z CO-ORD. OF ORIG. ATM. RELTV. TO CENT. OF
C      THE ORIGIN MOLECULE.
C      YS IS Y CO-ORD. OF SOUR. ATM. RELTV. TO CENT. OF
C      THE SOURCE MOLECULE.
C      ZS IS Z CO-ORD. OF SOUR. ATM. RELTV. TO CENT. OF
C      THE SOURCE MOLECULE.
C      THETAO IS ANGL BTWEEN DUMBBELL AXIS OF
C      THE ORIGIN MOLECULE AND THE BL AXIS.
C      THETAS IS ANGL BTWEEN DUMBBELL AXIS OF
C      THE SOURCE MOLECULE AND THE BL AXIS.
C      QW(I) REPRESENT THE INCIDENT WAVE VECTORS.
C      RJ(1) IS THE X COMPONENT OF SEPARATION OF
C      THE ORIGIN AND SOURCE MOLECULES.
C      RJ(2) IS THE Y COMPONENT OF SEPARATION OF
C      THE ORIGIN AND SOURCE MOLECULES.
C      RJ(3) IS THE Z COMPONENT OF SEPARATION OF
C      THE ORIGIN AND SOURCE MOLECULES.
C      APHI(I,J) REPRESENT THE ELEMNTS OF THE
C      INTERATOMIC FORCE CONSTANT MATRIX.
C      PHI(I,J) REPRESENT THE ELEMENTS OF THE
C      INTERMOLECULAR FORCE CONSTANT MATRIX.
C      PSAA(I,J) ARE ELEMNTS OF THE
C      SELF FORCE CONSTANT MATRIX FOR A-A INTERACTIONS.
C      PSAB(I,J) ARE ELEMNTS OF THE
C      SELF FORCE CONSTANT MATRIX FOR A-B INTERACTIONS.
C      PSBB(I,J) ARE ELEMNTS OF THE
C      SELF FORCE CONSTANT MATRIX FOR B-B INTERACTIONS.
C      PSBA(I,J) ARE ELEMNTS OF THE
C      SELF FORCE CONSTANT MATRIX FOR B-A INTERACTIONS.
C      PSA(I,J) = PSAA(I,J) + PSAB(I,J)
C      PSB(I,J) = PSBB(I,J) + PSBA(I,J)
C      AAPHIC(I,J,H,K,L) IS ARRAY FOR
```

```
C        STORING FORCE CONSTANTS OF A-A INTERACTIONS.
C        ABPHIC(I,J,H,K,L) IS ARRAY FOR
C        STORING FORCE CONSTANTS OF A-B INTERACTIONS.
C        BBPHIC(I,J,H,K,L) IS ARRAY FOR
C        STORING FORCE CONSTANTS OF B-B INTERACTIONS.
C        BAPHIC(I,J,H,K,L) IS ARRAY FOR
C        STORING FORCE CONSTANTS OF B-A INTERACTIONS.
C        APSA(I,J) IS ARRAY FOR STRNG SLF FRCE CNSTS OF
C        TYPE A ORIGIN MOLECULES.
C        BPSB(I,J) IS ARRAY FOR STRNG SLF FRCE CNSTS FOR
C        TYPE B ORIGIN MOLECULES.
C        D(I,J) REPRESENT ELEMNTS OF THE DYNAMICAL MTRX.
C        EVSQ(I,J) REPRESENT EIGEN VALUES OF DYNMICAL MTRX.
C        EV(I,J) REPRESENT THE CALCULATED FREQUENCIES.
         IMPLICIT REAL*8 (A-G,O-Z)
         INTEGER HMAX
         DIMENSION VV(3,3),APX(3),DX(10,15,3),X(10,15),AV(10,15)
         DIMENSION Y(10,15),RM(3,3),W(10,15),WW(10,15),RMI(3,3)
         DIMENSION V(10,15),EV(10,15),PX(3),DEPX(3,3),A(3,6)
         DIMENSION BM(5),QW(3),EVSQ(10,15),Z(15)
         COMMON/BLK1/AL,BL,CL,Q,P,FR,GR,QW,JI
         COMMON/BLK6/YF,ZF,AM,BM,HMAX,KMAX,LMAX
         COMMON/BLK7/PX,NN,NTRL(3),NCODE(15)
         COMMON/BLK8/JCOUN,KCOUN,LCOUN
         DATA BR1/'(100)'/,BR2/'(010)'/,BR3/'(001)'/
         READ(1,1004)AL,BL,CL
         READ(1,1005)YF,ZF
         READ(1,1007)HMAX,KMAX,LMAX
         READ(1,1006)PX(1),PX(2),PX(3)
         READ(1,1004)AM
         READ(1,1007)M,NN,KK
         READ(1,1007)NTRL(1),NTRL(2),NTRL(3)
         READ(1,105)((V(I,J),W(I,J),Z(J),NCODE(J),J=1,M),I=1,10)
     105 FORMAT(D20.12,F5.3,D20.12,I3)
    1004 FORMAT(3D20.12)
    1005 FORMAT(2F10.6)
    1006 FORMAT(2D20.12,F10.6)
    1007 FORMAT(3I3)
         WRITE(3,1000)AL,BL,CL
         WRITE(3,1010)YF,ZF
         WRITE(3,1004)AM
         WRITE(3,1020)HMAX,KMAX,LMAX
         WRITE(3,1008)PX
    1008 FORMAT(' PX(1)=',D20.12,2X,'PX(2)=',D20.12,2X,'PX(3)
        1=',D20.12)
    1000 FORMAT(' AL=',F8.5,2X,'BL=',F8.5,2X,'CL=',F8.5,2X)
    1010 FORMAT(' YF=',F8.5,2X,'ZF=',F8.5,2X)
    1020 FORMAT(' HMAX=',I4,'KMAX=',I4,'LMAX=',I4)
    1003 FORMAT('0')
         WRITE(3,1003)
         DO 50 J=1,M
```

```
      DO 50 I=1,10
      X(I,J)=V(I,J)**2
      W(I,J)=W(I,J)*V(I,J)
      WW(I,J)=1.0/(W(I,J)*2*V(I,J))**2
   50 AV(I,J)=V(I,J)**2
      K=NN
      KK=0
      DO 5 I=1,K
      IF(NTRL(I).EQ.1)KK=KK+1
    5 CONTINUE
      KN=0
      YY=1.0D4
      LCOUN=0
   61 XX=0.0D0
      JCOUN=0
      DO 1 JI=1,3
      IF(JI.EQ.1)MN=1
      IF(JI.EQ.1)NM=5
      IF(JI.EQ.2)MN=6
      IF(JI.EQ.2)NM=10
      IF(JI.EQ.3)MN=11
      IF(JI.EQ.3)NM=15
      DO 1 J=MN,NM
      JCOUN=JCOUN+1
      QW(JI)=Z(J)
      CALL HFIT(J,X,DX)
      DO 1 I=1,10
      Y(I,J)=X(I,J)-AV(I,J)
      XX=XX+WW(I,J)*Y(I,J)**2
    1 CONTINUE
      WRITE(3,27)XX,KN
      IF(XX.GT.YY)GO TO 131
      IF(XX-YY)66,66,109
   66 WRITE(3,27)XX,KN
   27 FORMAT(' XX=',D20.12,4X,'KN=',I3)
      WRITE(3,110)(I,PX(I),I=1,NN)
  110 FORMAT(3(' PX(',I2,')=',D20.12,2X))
      DO 113 J=1,M
      DO 113 I=1,10
      IF(X(I,J))97,97,98
   97 EV(I,J)=-DSQRT(-X(I,J))
      GO TO 113
   98 EV(I,J)=DSQRT(X(I,J))
  113 CONTINUE
      DO 130 J=1,M
      NC=NCODE(J)
      IF(NC.EQ.1)BR=BR1
      IF(NC.EQ.2)BR=BR2
      IF(NC.EQ.3)BR=BR3
      WRITE(3,124)BR,Z(J)
  124 FORMAT(1H0,5X,A5,1X,'Q=',D20.12)
```

```
      WRITE(3,125)(I,J,V(I,J),I,J,W(I,J),I,J,EV(I,J),I=1,10)
  125 FORMAT(' V(',I2,',',I2,')=',D20.12,2X,'W(',I2,',',I2
     2,')=',F5.3,5X,'EV(',I2,',',I2,')=',D20.12)
  130 CONTINUE
      IF(DABS(1.D0-XX/YY)-1.D-5)131,131,60
   60 DO 45 I=1,K
      DO 45 J=1,K
      RM(I,J)=0.0
   45 VV(I,J)=0.0
      DO 30 J=1,M
      DO 30 I=1,10
      DO 30 II=1,KK
      DO 29 JJ=1,KK
   29 RM(II,JJ)=RM(II,JJ)+DX(I,J,II)*DX(I,J,JJ)*WW(I,J)
   30 VV(II,1)=VV(II,1)-DX(I,J,II)*Y(I,J)*WW(I,J)
      KKK=2*KK
      CALL DELPX(RM,VV,DEPX,KK,KKK,RMI,A)
      YY=XX
      KN=-1
  109 KN=KN+1
      IF(KN-1)77,74,74
   74 IF(KN-5)76,76,78
   77 DO 54 I=1,K
   54 APX(I)=PX(I)
   76 NK=0
      DO 85 I=1,K
      IF(NTRL(I))85,85,84
   84 NK=NK+1
      PX(I)=APX(I)+DEPX(NK,1)
   85 CONTINUE
      LCOUN=LCOUN+1
      GO TO 61
   78 WRITE(3,37)
   37 FORMAT('0DID NOT CONVERGE')
      WRITE(3,27)XX,KN
      WRITE(3,110)(I,PX(I),I=1,NN)
  131 STOP
      END
      SUBROUTINE HFIT(J,X,DX)
      IMPLICIT REAL*8 (A-G,O-Z)
      INTEGER HMAX
      DIMENSION DX(10,15,3),X(10,15),X1(10,15),BM(5)
      DIMENSION DPX(3),PX1(3),QW(3),EVSQ(10,15),PX(3)
      COMMON/BLK1/AL,BL,CL,Q,P,FR,GR,QW,JI
      COMMON/BLK6/YF,ZF,AM,BM,HMAX,KMAX,LMAX
      COMMON/BLK7/PX,K,NTRL(3),NCODE(15)
      COMMON/BLK8/JCOUN,KCOUN,LCOUN
      KCOUN=0
      CALL FREQC(PX,J,X)
      DO 78 I=1,10
   78 X1(I,J)=X(I,J)
```

```
         E=-1.0D-3
         DO 77 N=1,K
     77 PX1(N)=PX(N)
         NNK=0
         DO 76 N=1,K
         IF(NTRL(N))76,76,70
     70 NNK=NNK+1
         DPX(N)=PX(N)*E
         IF(DABS(DPX(N))-1.D-7)71,71,72
     71 DPX(N)=1.0D-7
     72 PX1(N)=PX(N)+DPX(N)
         KCOUN=1
         CALL FREQC(PX1,J,X1)
         DO 75 I=1,10
     75 DX(I,J,NNK)=(X1(I,J)-X(I,J))/DPX(N)
         PX1(N)=PX(N)
     76 CONTINUE
         RETURN
         END
         SUBROUTINE DELPX(RM,VV,DEPX,KK,KKK,RMI,A)
         IMPLICIT REAL*8 (A-H,O-Z)
         DIMENSION RM(KK,KK),RMI(KK,KK),VV(KK,KK)
         DIMENSION DEPX(KK,KK),A(KK,KKK)
         CALL MINV(A,RM,RMI,KK,KKK,IJ)
         CALL MPRD(RMI,VV,DEPX,KK)
         RETURN
         END
         SUBROUTINE MPRD(A,B,C,N)
C        THIS PROGRAM PERFORMS THE FOLLOWING OPERATION: A*B=C
C        'N' IS THE ORDER OF THE MATRICES
         IMPLICIT REAL*8 (A-H,O-Z)
         DIMENSION A(N,N),B(N,N),C(N,N)
         DO 1 I=1,N
         DO 1 J=1,N
         C(I,J)=0.DO
         DO 1 K=1,N
         C(I,J)=A(I,K)*B(K,J)+C(I,J)
         IF(DABS(C(I,J)).LT.1.D-11)C(I,J)=0.DO
      1 CONTINUE
         RETURN
         END
         SUBROUTINE MINV(A,AI,AINV,N,NN,IJ)
         IMPLICIT REAL*8 (A-H,O-Z)
         REAL*8 DABS
         DIMENSION A(N,NN),AINV(N,N),AI(N,N)
         NI=N+1
         N2=2*N
         DO 6 I=1,N
         DO 6 J=1,N
      6 A(I,J)=AI(I,J)
         DO 1 I=1,N
```

```
      DO 1 J=NI,N2
      A(I,J)=0.D0
      IF(I.EQ.(J-N))A(I,J)=1.D0
    1 CONTINUE
      DO 200 M=1,N
      B=DABS(A(M,M))
      DO 2 I=M,N
      IF(DABS(A(I,M)).LT.B)GO TO 2
      B=DABS(A(I,M))
      L=I
    2 CONTINUE
      IF(B.EQ.DABS(A(M,M)))GO TO 3
      DO 4 J=1,N2
      B=A(M,J)
      A(M,J)=A(L,J)
    4 A(L,J)=B
    3 B=A(M,M)
      IF(DABS(B).LT.1.D-11)GO TO 92
      GO TO 93
   92 IJ=0
      GO TO 94
   93 IJ=1
      DO 5 J=M,N2
    5 A(M,J)=A(M,J)/B
      DO 12 I=1,N
      IF(I.EQ.M)GO TO 12
      B=A(I,M)
      DO 13 J=M,N2
   13 A(I,J)=A(I,J)-B*A(M,J)
   12 CONTINUE
  200 CONTINUE
      DO 10 I=1,N
      DO 10 J=1,N
   10 AINV(I,J)=A(I,J+N)
   94 RETURN
      END
      SUBROUTINE FREQC(PX,JJ,EVSQ)
      IMPLICIT REAL*8 (A-G,O-Z)
      INTEGER H,HMAX,HH
      REAL*8 DSQRT,DCOS,DSIN,DEXP,DATAN,DABS
      DIMENSION PHI(5,5),X(4)
      DIMENSION AAPHI(5,5,7,7,7),BBPHI(5,5,7,7,7)
      DIMENSION ABPHI(5,5,7,7,7),BAPHI(5,5,7,7,7)
      DIMENSION FV(10,10),FREQ(10),EVSQ(10,15)
      DIMENSION APSA(5,5),BPSB(5,5)
      DIMENSION PSAA(5,5),PSAB(5,5),PSA(5,5)
      DIMENSION PSBB(5,5),PSBA(5,5),PSB(5,5)
      DIMENSION D(10,10),E(10,10),QW(3),RJ(3)
      DIMENSION BM(5),PX(3)
      COMMON/BLK1/AL,BL,CL,Q,P,FR,GR,QW,II
      COMMON/BLK2/NCOUN
```

```
      COMMON/BLK3/THETAO,YO,ZO
      COMMON/BLK4/THETAS,YS,ZS
      COMMON/BLK5/H,K,L
      COMMON/BLK6/YF,ZF,AM,BM,HMAX,KMAX,LMAX
      COMMON/BLK8/JCOUN,KCOUN,LCOUN
      IF(KCOUN.EQ.1)GO TO 108
      IF(JCOUN.GT.1)GO TO 108
      IF(LCOUN.GT.0)GO TO 108
      U=YF*BL
      V=ZF*CL
      BM(1)=2*AM
      BM(2)=BM(1)
      BM(3)=BM(1)
      BM(4)=2*AM*(U**2+V**2)
      BM(5)=BM(4)
      A=AL/2
      B=BL/2
      C=CL/2
      THETA=DATAN(ZF*CL/(YF*BL))
      HMAX=HMAX+1
      KMAX=KMAX+1
      LMAX=LMAX+1
  108 ICOUN=0
   23 DO 100 LL=1,LMAX
      L=LL-1
      LTEST=L/2
      RTEST=L/2.
      IF(LTEST.NE.RTEST)GO TO 100
   40 DO 90 KK=1,KMAX
      K=KK-1
   30 DO 80 HH=1,HMAX
      IF(HH.NE.1)GO TO 10
      IF(K.NE.0)GO TO 10
      IF(L.EQ.0)GO TO 80
   10 H=HH-1
      MTEST=(H+K)/2
      OTEST=(H+K)/2.
      IF(MTEST.NE.OTEST)GO TO 80
C     THIS PART COMPUTES FOR TYPE A MOLECULES
C     THIS PART COMPUTES DISTANCES BETWEEN  ATOMS 1 AND 3
C     DISTANCES 1 TO 3 EQUAL 2 TO 4 WHEN L IS EVEN
C     THE PRECEDING MEANS ORIGIN AND SOURCE ARE SAME TYPE
C     X,Y,AND Z ARE DISTANCE COORDINATES RELATIVE TO AN ATOM
   11 CONTINUE
      IH=H+4
      IK=K+4
      IL=L+4
      THETAO=THETA
      THETAS=THETA
      IF(KCOUN.EQ.1)GO TO 138
      IF(JCOUN.GT.1)GO TO 116
```

```
    138 CONTINUE
        X(1)=H*A
        X(2)=K*B
        X(3)=L*C
        X(4)=DSQRT(X(1)**2+X(2)**2+X(3)**2)
        NCOUN=0
        YO=U
        ZO=V
        YS=U
        ZS=V
        GO TO 26
     21 CONTINUE
        YO=-U
        ZO=-V
        YS=-U
        ZS=-V
     26 CONTINUE
        CALL PHIC(X,PHI,PX)
        NCOUN=NCOUN+1
        IF(NCOUN.EQ.1)GO TO 21
C       THIS PART COMPUTES DISTANCE BETWEEN ATOMS 1 AND 4
        X(1)=H*A
        X(2)=K*B-2*YF*BL
        ZS=-V
        X(3)=L*C+2*ZS
        X(4)=DSQRT(X(1)**2+X(2)**2+X(3)**2)
        YO=U
        ZO=V
        YS=-U
        CALL PHIC(X,PHI,PX)
        CONTINUE
C       THIS PART COMPUTES DISTANCE BETWEEN ATOMS 2 AND 3
      7 X(1)=H*A
        X(2)=K*B+2*YF*BL
        ZS=V
        X(3)=L*C+2*ZS
        X(4)=DSQRT(X(1)**2+X(2)**2+X(3)**2)
        YO=-U
        ZO=-V
        YS=U
        CALL PHIC(X,PHI,PX)
     17 CONTINUE
        DO 18 I=1,5
        DO 22 J=1,3
        IF(THETAO.LT.0)GO TO 47
        IF(ICOUN)18,27,28
     47 IF(ICOUN)18,48,49
     48 PSBB(I,J)=0.D0
     49 PSBB(I,J)=-PHI(I,J)+PSBB(I,J)
        GO TO 22
     27 PSAA(I,J)=0.D0
```

```
   28 PSAA(I,J)=-PHI(I,J)+PSAA(I,J)
   22 CONTINUE
      IF(THETAO.LT.0)GO TO 50
      IF(ICOUN)18,29,31
   50 IF(ICOUN)18,51,52
   51 PSBB(I,4)=0.D0
   52 PSBB(I,4)=-PHI(I,4)+PHI(I,2)*L*C-PHI(I,3)*K*B+PSBB(I,4)
      GO TO 53
   29 PSAA(I,4)=0.D0
   31 PSAA(I,4)=-PHI(I,4)+PHI(I,2)*L*C-PHI(I,3)*K*B+PSAA(I,4)
      IF(ICOUN)18,32,33
   53 IF(ICOUN)18,54,55
   54 PSBB(I,5)=0.D0
   55 PSBB(I,5)=-PHI(I,5)+PHI(I,1)*(K*B*DCOS(THETAO)+L*C*
     6DSIN(THETAO))-PHI(I,2)*H*A*DCOS(THETAO)-
     CPHI(I,3)*H*A*DSIN(THETAO)+PSBB(I,5)
      GO TO 18
   32 PSAA(I,5)=0.D0
   33 PSAA(I,5)=-PHI(I,5)+PHI(I,1)*(K*B*DCOS(THETAO)+L*C*
     3DSIN(THETAO))-PHI(I,2)*H*A*DCOS(THETAO)-
     DPHI(I,3)*H*A*DSIN(THETAO)+PSAA(I,5)
   18 CONTINUE
      IF(KCOUN.EQ.1)GO TO 116
      IF(THETAO)121,116,122
  121 DO 123 I=1,5
      DO 123 J=1,5
  123 BBPHI(I,J,IH,IK,IL)=PHI(I,J)
      GO TO 116
  122 DO 124 I=1,5
      DO 124 J=1,5
  124 AAPHI(I,J,IH,IK,IL)=PHI(I,J)
  116 CONTINUE
      RJ(1)=H*A
      RJ(2)=K*B
      RJ(3)=L*C
      QR=QW(II)*RJ(II)
      DO 93 I=1,5
      DO 72 J=1,5
      M=I+5
      N=J+5
      IF(I.GT.3)GO TO 74
      IF(J.GT.3)CJP=DSIN(QR)
      IF(J.LE.3)CJP=DCOS(QR)
      GO TO 73
   74 IF(J.LE.3)CJP=-DSIN(QR)
      IF(J.GT.3)CJP=DCOS(QR)
   73 IF(ICOUN.GT.0)GO TO 75
      IF(THETAO.LT.0)GO TO 76
      E(I,J)=0.D0
      GO TO 77
   76 E(M,N)=0.D0
```

```
      GO TO 78
   75 CONTINUE
      IF(THETAO.LT.0)GO TO 78
   77 IF(KCOUN.EQ.1)GO TO 139
      E(I,J)=AAPHI(I,J,IH,IK,IL)*CJP+E(I,J)
      GO TO 79
  139 E(I,J)=PHI(I,J)*CJP+E(I,J)
      GO TO 79
   78 IF(KCOUN.EQ.1)GO TO 141
      E(M,N)=BBPHI(I,J,IH,IK,IL)*CJP+E(M,N)
      GO TO 79
  141 E(M,N)=PHI(I,J)*CJP+E(M,N)
   79 CONTINUE
   72 CONTINUE
   93 CONTINUE
      ICOUN=ICOUN+1
      IF(H)80,80,12
   12 H=-H
      GO TO 11
   80 CONTINUE
      IF(K)90,90,13
   13 K=-K
      GO TO 30
   90 CONTINUE
      IF(L)100,100,20
   20 L=-L
      GO TO 40
  100 CONTINUE
      IF(THETA)101,101,102
  102 THETA=-THETA
      V=-V
      ICOUN=0
      GO TO 23
  101 CONTINUE
      THETA=-THETA
      V=-V
C     THIS SECTION COMPUTES DISTANCES BETWEEN UNLIKE MOLS.
  109 ICOUN=0
  104 DO 200 LL=1,LMAX
      L=LL-1
      LTEST=L/2
      RTEST=L/2.
      IF(RTEST.EQ.LTEST)GO TO 200
  140 DO 190 KK=1,KMAX
      K=KK-1
  130 DO 180 HH=1,HMAX
      IF(HH.NE.1)GO TO 110
      IF(K.NE.0)GO TO 110
      IF(L.EQ.0)GO TO 180
  110 H=HH-1
      MTEST=(H+K)/2
```

```
              OTEST=(H+K)/2.
              IF(MTEST.EQ.OTEST)GO TO 180
      C       THIS PART COMPUTES DISTANCE BETWEEN ATOMS 1 AND 3
        111 CONTINUE
              JH=H+4
              JK=K+4
              JL=L+4
              THETAO=THETA
              THETAS=-THETA
              IF(KCOUN.EQ.1)GO TO 142
              IF(JCOUN.GT.1)GO TO 118
        142 CONTINUE
              ZO=V
              X(1)=H*A
              X(2)=K*B
              X(3)=L*C-2*ZO
              X(4)=DSQRT(X(1)**2+X(2)**2+X(3)**2)
              YO=U
              YS=U
              ZS=-V
              NCOUN=0
              CALL PHIC(X,PHI,PX)
              NCOUN=NCOUN+1
      C       THIS PART COMPUTES DISTANCE BETWEEN ATOMS 1 AND 4
        114 X(1)=H*A
              X(2)=K*B-2*YF*BL
              X(3)=L*C
              X(4)=DSQRT(X(1)**2+X(2)**2+X(3)**2)
              YO=U
              ZO=V
              YS=-U
              ZS=V
              CALL PHIC(X,PHI,PX)
      C       THIS PART COMPUTES DISTANCE BETWEEN ATOMS 2 AND 3
        115 X(1)=H*A
              X(2)=K*B+2*YF*BL
              X(3)=L*C
              X(4)=DSQRT(X(1)**2+X(2)**2+X(3)**2)
              YO=-U
              ZO=-V
              YS=U
              ZS=-V
              CALL PHIC(X,PHI,PX)
      C       THIS PART COMPUTES DISTANCE BETWEEN ATOMS  2 AND 4
        117 CONTINUE
              ZO=-V
              X(1)=H*A
              X(2)=K*B
              X(3)=L*C-2*ZO
              X(4)=DSQRT(X(1)**2+X(2)**2+X(3)**2)
              YO=-U
```

```
      YS=-U
      ZS=V
      CALL PHIC(X,PHI,PX)
      DO 24 I=1,5
      DO 25 J=1,3
      IF(THETAO.LT.O)GO TO 56
      IF(ICOUN)24,34,35
   56 IF(ICOUN)24,57,58
   57 PSBA(I,J)=0.DO
   58 PSBA(I,J)=-PHI(I,J)+PSBA(I,J)
      GO TO 25
   34 PSAB(I,J)=0.DO
   35 PSAB(I,J)=-PHI(I,J)+PSAB(I,J)
   25 CONTINUE
      IF(THETAO.LT.O)GO TO 59
      IF(ICOUN)24,36,37
   59 IF(ICOUN)24,60,61
   60 PSBA(I,4)=0.DO
   61 PSBA(I,4)=-PHI(I,4)+PHI(I,2)*L*C-PHI(I,3)*K*B+PSBA(I,4)
      GO TO 62
   36 PSAB(I,4)=0.DO
   37 PSAB(I,4)=-PHI(I,4)+PHI(I,2)*L*C-PHI(I,3)*K*B+PSAB(I,4)
      IF(ICOUN)24,38,39
   62 IF(ICOUN)24,63,64
   63 PSBA(I,5)=0.DO
   64 PSBA(I,5)=-PHI(I,5)*DCOS(2*THETAO)+PHI(I,1)*(K*B*DCOS
     7(THETAO)+L*C*DSIN(THETAO))-PHI(I,2)*H*A*DCOS(THETAO)-
     8PHI(I,3)*H*A*DSIN(THETAO)+PSBA(I,5)
      GO TO 24
   38 PSAB(I,5)=0.DO
   39 PSAB(I,5)=-PHI(I,5)*DCOS(2*THETAO)+PHI(I,1)*(K*B*DCOS
     4(THETAO)+L*C*DSIN(THETAO))-PHI(I,2)*H*A*DCOS(THETAO)-
     5PHI(I,3)*H*A*DSIN(THETAO)+PSAB(I,5)
   24 CONTINUE
      IF(KCOUN.EQ.1)GO TO 118
      IF(THETAO)125,118,126
  125 DO 128 I=1,5
      DO 128 J=1,5
  128 BAPHI(I,J,JH,JK,JL)=PHI(I,J)
      GO TO 118
  126 DO 129 I=1,5
      DO 129 J=1,5
  129 ABPHI(I,J,JH,JK,JL)=PHI(I,J)
  118 CONTINUE
      RJ(1)=H*A
      RJ(2)=K*B
      RJ(3)=L*C
      QR=QW(II)*RJ(II)
      DO 81 I=1,5
      DO 82 J=1,5
      M=I+5
```

```
       N=J+5
       IF(I.GT.3)GO TO 83
       IF(J.GT.3)CJP=DSIN(QR)
       IF(J.LE.3)CJP=DCOS(QR)
       GO TO 84
   83  IF(J.LE.3)CJP=-DSIN(QR)
       IF(J.GT.3)CJP=DCOS(QR)
   84  IF(ICOUN.GT.0)GO TO 85
       IF(THETAO.LT.0)GO TO 86
       E(I,N)=0.D0
       GO TO 87
   86  E(M,J)=0.D0
       GO TO 88
   85  CONTINUE
       IF(THETAO.LT.0)GO TO 88
   87  IF(KCOUN.EQ.1)GO TO 143
       E(I,N)=ABPHI(I,J,JH,JK,JL)*CJP+E(I,N)
       GO TO 89
  143  E(I,N)=PHI(I,J)*CJP+E(I,N)
       GO TO 89
   88  IF(KCOUN.EQ.1)GO TO 144
       E(M,J)=BAPHI(I,J,JH,JK,JL)*CJP+E(M,J)
       GO TO 89
  144  E(M,J)=PHI(I,J)*CJP+E(M,J)
   89  CONTINUE
   82  CONTINUE
   81  CONTINUE
       ICOUN=ICOUN+1
       IF(H)180,180,112
  112  H=-H
       GO TO 111
  180  CONTINUE
       IF(K)190,190,113
  113  K=-K
       GO TO 130
  190  CONTINUE
       IF(L)200,200,120
  120  L=-L
       GO TO 140
  200  CONTINUE
       IF(THETA)65,65,103
  103  THETA=-THETA
       V=-V
       ICOUN=0
       GO TO 104
   65  CONTINUE
       THETA=-THETA
       V=-V
       DO 45 I=1,5
       DO 46 J=1,5
       IF(KCOUN.EQ.0)GO TO 147
```

```
      PSA(I,J)=PSAA(I,J)+PSAB(I,J)
      GO TO 146
147   IF(JCOUN.GT.1)GO TO 148
      APSA(I,J)=PSAA(I,J)+PSAB(I,J)
148   PSA(I,J)=APSA(I,J)
146   IF(DABS(PSA(I,J)).LT.1.D-11)PSA(I,J)=0.D0
 46   CONTINUE
 45   CONTINUE
      DO 70 I=1,5
      DO 71 J=1,5
      IF(KCOUN.EQ.0)GO TO 149
      PSB(I,J)=PSBB(I,J)+PSBA(I,J)
      GO TO 171
149   IF(JCOUN.GT.1)GO TO 150
      BPSB(I,J)=PSBB(I,J)+PSBA(I,J)
150   PSB(I,J)=BPSB(I,J)
171   IF(DABS(PSB(I,J)).LT.1.D-11)PSB(I,J)=0.D0
 71   CONTINUE
 70   CONTINUE
119   CONTINUE
      DO 91 I=1,10
      DO 92 J=1,10
      IF(DABS(E(I,J)).LT.1.D-11)E(I,J)=0.D0
 92   CONTINUE
 91   CONTINUE
      DO 98 I=1,5
      DO 99 J=1,5
      M=I+5
      N=J+5
      D(I,J)=(E(I,J)+PSA(I,J))/DSQRT(BM(I)*BM(J))
      D(I,N)=E(I,N)/DSQRT(BM(I)*BM(J))
      D(M,N)=(E(M,N)+PSB(I,J))/DSQRT(BM(I)*BM(J))
      D(M,J)=E(M,J)/DSQRT(BM(I)*BM(J))
 99   CONTINUE
 98   CONTINUE
      CALL JACOBI(D,FV,FREQ,10)
      DO 135 J=1,9
      FMAX=FREQ(J)
      M=J+1
      DO 136 I=M,10
      IF(FMAX.GE.FREQ(I))GO TO 136
      FOLD=FMAX
      FMAX=FREQ(I)
      FREQ(I)=FOLD
136   CONTINUE
      FREQ(J)=FMAX
135   CONTINUE
      DO 127 I=1,10
127   EVSQ(I,JJ)=FREQ(I)
202   CONTINUE
      RETURN
```

```
      END
      SUBROUTINE PHIC(X,PHI,PX)
      IMPLICIT REAL*8 (A-G,O-Z)
      INTEGER H
      REAL*8 DSIN,DCOS,DEXP
      DIMENSION DELT(3,3),APHI(5,5),PHI(5,5),X(4)
      DIMENSION PX(3),QW(3)
      COMMON/BLK1/AL,BL,CL,Q,P,FR,GR,QW,II
      COMMON/BLK2/NCOUN
      COMMON/BLK3/THETAO,YO,ZO
      COMMON/BLK4/THETAS,YS,ZS
      COMMON/BLK5/H,K,L
      AP=PX(1)
      BP=PX(2)
      ALP=PX(3)
      Q=6*AP/X(4)**8
      P=BP*ALP*DEXP(-ALP*X(4))/X(4)
      FR=Q-P
      GR=(-8*Q+P)/X(4)**2+ALP*P/X(4)
   19 DO 2 I=1,3
      DO 3 J=1,3
      IF(NCOUN)201,4,8
    4 PHI(I,J)=0.DO
    5 IF(I.NE.J)GO TO 6
      DELT(I,J)=1
      GO TO 8
    6 DELT(I,J)=0
    8 APHI(I,J)=DELT(I,J)*FR+X(I)*X(J)*GR
      PHI(I,J)=APHI(I,J)+PHI(I,J)
    3 CONTINUE
      IF(NCOUN)201,9,14
    9 PHI(I,4)=0.DO
      PHI(I,5)=0.DO
   14 APHI(I,4)=+APHI(I,3)*YS-APHI(I,2)*ZS
      APHI(I,5)=-(YS*DCOS(THETAS)+ZS*DSIN(THETAS))*APHI(I,1)
      PHI(I,4)=APHI(I,4)+PHI(I,4)
      PHI(I,5)=APHI(I,5)+PHI(I,5)
    2 CONTINUE
      DO 1 N=1,5
      IF(NCOUN)201,15,16
   15 PHI(4,N)=0.DO
      PHI(5,N)=0.DO
   16 APHI(4,N)=YO*APHI(3,N)-ZO*APHI(2,N)
      APHI(5,N)=-(YO*DCOS(THETAO)+ZO*DSIN(THETAO))*APHI(1,N)
      PHI(4,N)=APHI(4,N)+PHI(4,N)
      PHI(5,N)=APHI(5,N)+PHI(5,N)
    1 CONTINUE
  201 CONTINUE
      RETURN
      END
      SUBROUTINE JACOBI(A,B,E,N)
```

```
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(N,N), B(N,N), E(N)
      EQUIVALENCE (Y,YA)
      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 = YA**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( 1D0+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

The First Brillouin Zone Boundaries

Every crystal structure has two important lattices. The real lattice described by the fundamental vectors $\underset{\sim}{a}$, $\underset{\sim}{b}$, and $\underset{\sim}{c}$ and the reciprocal lattice described by the fundamental reciprocal lattice vectors $\underset{\sim}{A}$, $\underset{\sim}{B}$, and $\underset{\sim}{C}$. The reciprocal lattice vectors are related to the real lattice vectors by the following equations:

$$\underset{\sim}{A} = 2\pi \frac{\underset{\sim}{b} \times \underset{\sim}{c}}{\underset{\sim}{a} \cdot \underset{\sim}{b} \times \underset{\sim}{c}}$$

$$\underset{\sim}{B} = 2\pi \frac{\underset{\sim}{c} \times \underset{\sim}{a}}{\underset{\sim}{a} \cdot \underset{\sim}{b} \times \underset{\sim}{c}} \tag{1}$$

$$\underset{\sim}{C} = 2\pi \frac{\underset{\sim}{a} \times \underset{\sim}{b}}{\underset{\sim}{a} \cdot \underset{\sim}{b} \times \underset{\sim}{c}}. \text{[19]}$$

Reciprocal lattice points are generated using the reciprocal translation vectors given by

$$\underset{\sim}{G} = h\underset{\sim}{A} + k\underset{\sim}{B} + l\underset{\sim}{C} \text{ [20]} \tag{2}$$

where h, k, and l are positive or negative integers.

The primitive cell of the real lattice is defined as the cell of smallest volume containing one lattice point which, when translated parallel to its edges regularly through space, generates the complete lattice structure.

The unit cell of the base-centered orthorhombic lattice contains two lattice points. If the fundamental

lattice vectors are $\underset{\sim}{a}$, $\underset{\sim}{b}$, and $\underset{\sim}{c}$ then the volume of the unit cell is $\underset{\sim}{a} \cdot \underset{\sim}{b} \times \underset{\sim}{c} = a\,b\,c$. Since the primitive cell contains only one lattice point, its volume is $a\,b\,c/2$. A set of primitive lattice vectors, which describe a primitive cell of the base-centered orthorhombic lattice, is

$$\underset{\sim}{a}' = \frac{a}{2}\hat{x} + \frac{b}{2}\hat{y}$$

$$\underset{\sim}{b}' = b\hat{y} \tag{3}$$

and

$$\underset{\sim}{c}' = c\hat{y}.$$

$\hat{x}$, $\hat{y}$, and $\hat{z}$ are the unit vectors along the a, b, and c crystal axes, respectively (Fig. 8). A set of primitive reciprocal lattice vectors which describe a primitive cell in reciprocal space may be obtained using Eqs. (1) and (3) where a, b, and c are replaced by a', b', and c', respectively. The results are given by the following:

$$\underset{\sim}{A} = 4\frac{\pi}{a}\hat{x}$$

$$\underset{\sim}{B} = 2\pi\,(\frac{\hat{y}}{b} - \frac{\hat{x}}{a}) \tag{4}$$

$$\underset{\sim}{C} = 2\frac{\pi}{c}\hat{z}.$$

Therefore, from Eq. (2) the reciprocal translation vectors are given by

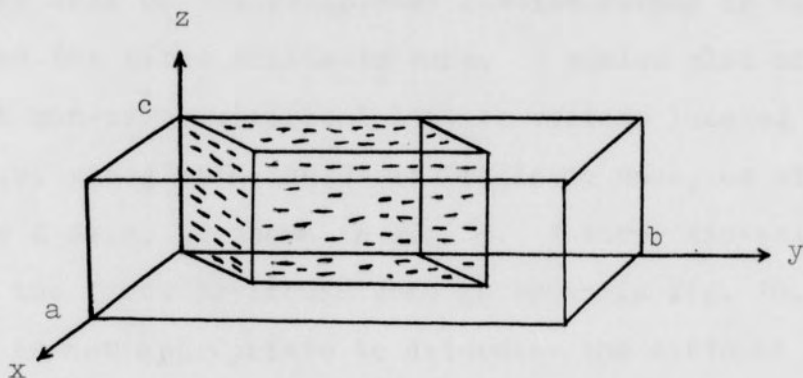$$\underset{\sim}{G} = 2\frac{\pi}{a}(2h - k)\hat{x} + 2\frac{\pi}{b}k\hat{y} + 2\frac{\pi}{c}l\hat{z}. \tag{5}$$

Fig. 8. A primitive cell of gallium. (The shaded area re-
presents the primitive cell.)

The parallelepiped described by $\underset{\sim}{A}$, $\underset{\sim}{B}$, and $\underset{\sim}{C}$ is the primitive cell of the reciprocal lattice. It is more conventional to take the primitive cell of the reciprocal lattice as the smallest volume bounded by the planes normal to each of the shorter non-zero $\underset{\sim}{G}$ vectors at its midpoint. The primitive cell of the reciprocal lattice formed in this way is called the first Brillouin zone. A scaled plot of the shortest non-zero reciprocal lattice vectors located in the X-Y plane, along with the first Brillouin zone, as viewed down the Z axis, is shown in Fig. 9. A three dimensional view of the first Brillouin zone is shown in Fig. 10.

It is now appropriate to determine the distance from the origin of Fig. 9 to the zone boundaries. Figure 11 represents an enlargement of the upper right quadrant of Fig. 9. Point S represents the lattice point located by the reciprocal lattice vector designated $\underset{\sim}{G}_1$. In the reciprocal lattice of Fig. 11 the first Brillouin zone boundary in the x direction is located at the point designated Q. The cosine of the angle theta (Θ) is written as

$$\cos \Theta = \frac{OT}{OS} = \frac{OP}{OR}. \tag{6}$$

Equation (6) then yields

$$OP = \frac{OT}{OS} OR. \tag{7}$$

The tangent of the angle is given by

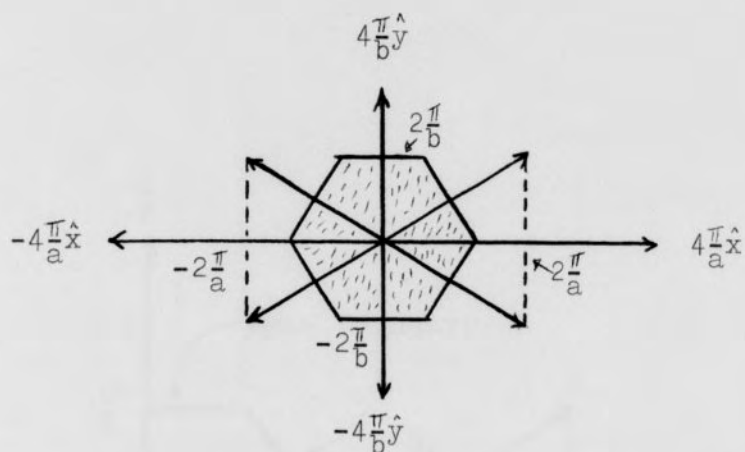$$\tan \Theta = \frac{TS}{OT} = \frac{PQ}{PR}. \tag{8}$$

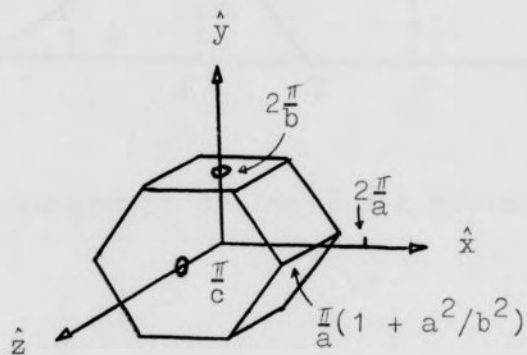Fig. 9. The first Brillouin zone (shaded region) as viewed down the z axis.

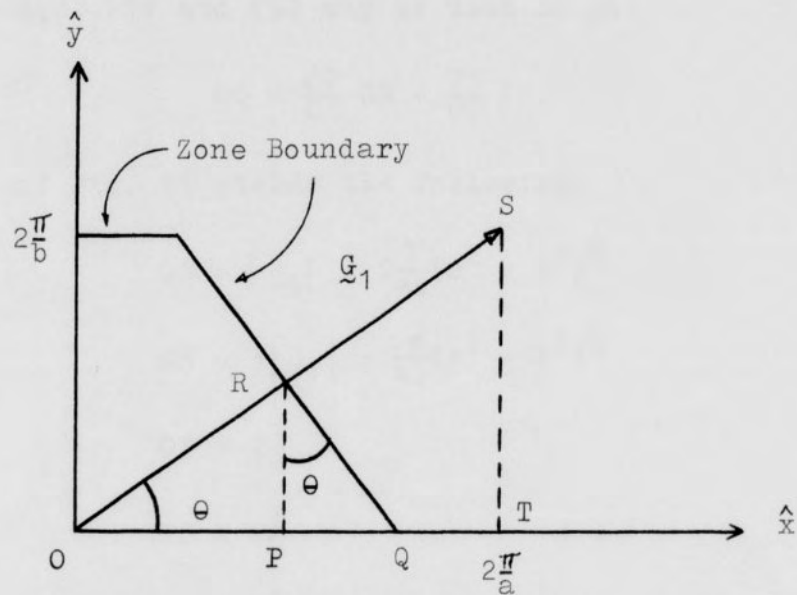Fig. 10. The first Brillouin zone as viewed in three dimensions.

Fig. 11. An enlargement of the first quadrant of Fig. 9.

From Eq. (8) it is observed that

$$PQ = \frac{TS}{OT} PR. \tag{9}$$

Since the zone boundary in the x direction occurs at OQ = OP + PQ, Eqs. (7) and (9) may be used to get

$$OQ = \frac{OT}{OS} OR + \frac{TS}{OT} PR. \tag{10}$$

Analysis of Fig. 11 yields the following:

$$OS = \left| \underline{G}_1 \right| = 2\frac{\pi}{ab}(a^2 + b^2)^{\frac{1}{2}}$$

$$OR = \tfrac{1}{2}\left| \underline{G}_1 \right| = \frac{\pi}{ab}(a^2 + b^2)^{\frac{1}{2}}$$

$$OT = 2\frac{\pi}{a} \tag{11}$$

$$TS = 2\frac{\pi}{b}$$

$$PR = \frac{\pi}{b}.$$

Equations (10) and (11) yield

$$OQ = \frac{\pi}{a}(1 + \frac{a^2}{b^2}). \tag{12}$$

Thus, the first Brillouin zone boundaries in the x direction are located at $\pm\frac{\pi}{a}(1 + a^2/b^2)$. Since Fig. 9 is a scale drawing, one sees that the zone boundaries in the y direction are located at $\pm 2\frac{\pi}{b}$. The zone boundaries in the z direction are shown in Fig. 10 to be located at $\pm\frac{\pi}{c}$.