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Force Field and Elastic Constant of Corundum*

By

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with 11 Tables and 5 Text-figures

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ABSTRACT: Basing on ascription of the infrared spectra of corundum at 637, 583, 571, 436, 400 and 387 cm^{-1} given by BARKER and of Raman spectra of ruby at 751, 642, 578, 450, 432, 417 and 375 cm^{-1} obtained by KRISHNAN and on the modified formula of UREY-BRADLEY force field, the values for the normal frequency of corundum have been estimated. The data for the elastic constant derived from those for the force constant have been in good harmony with those obtained megascopically from the practical observation, being connected more sensitively with the bending and repulsive forces than with the stretching force. This view has also been comfirmed by evaluating variation in the internal coordinate in relation to the elastic stress. The values for the constants related to the stretching force and elasticity in the cases of corundum, rutile and quartz have been compared with one another.

CONTENTS

I. INTRODUCTION

In the infrared absorption data given for corundum and ruby by COBLENTZ (1908), STRONG (1937), PARODI (1937), KRISHNAN (1948) and MITSUISHI *et al.* (1962) etc. have there been a sort of ambiguity and disagreement with one another. The reliable data, however, have been proposed by BARKER (1963) as a result of the experiment concerning re-examination of the previous figures, being ascribed to A_{Iu}, A_{1u} and E_u on the basis of factor group analysis suggested by BHAGAVANTAM *et al.* (1939). On the other hand, the Raman spectra attained for corundum and ruby by KRISHNAN (1948) are those related to A_{1g} and E_g with certain deviation caused by the effects of Fermi resonance and presence of Cr_2O_3 spectra.

In this paper, the normal coordinate treatment was made in order to determine assignment of various vibrations and the force field in corundum. For an exact evaluation of the frequency it is necessary to scrutinize the forces controlling all of the

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atoms, if possible. Even in the simple case of cubic symmetry a large number of the force constants are to be subjected to inspection. Because of complication of the constants ascribed to low symmetry in the present specimens some modifications proposed by SHIMANOUCHI have been added to the constants of UREY-BRADLEY force field. Three correction terms h_1, h_2 and k other than six kinds of the force constant given by the authors alluded to above have been taken into consideration as follows:

K_1 for the stretching force of Al–O bond with 1.845Å in length,
K_2 for to that with 1.990Å in length,
H_1 for deformation of O–Al–O angle,
H_2 for that of Al–O–Al angle,
F_1 for the repulsive force between non-bonded O…O distance,
F_2 for that between non-bonded Al…Al distance,
h_1 for the interaction constant between two adjacent angles around Al atom,
h_2 for that around O atom, and
k for that between two adjacent bonds.

It is generally difficult to estimate the complicated forces of the inorganic crystals due to their strength of bonds and ionic character. However, it is the purpose of the present work to refer to the normal coordinate treatment of corundum and to reach the reasonable conclusion for the force field in comparison of the elastic constant deduced from SHIRO's method (1967) with the observed values.

II. STRUCTURE AND FACTOR GROUP ANALYSIS

Corundum, α-Al_2O_3, belongs to the rhombohedral holohedral class D_{3d}^6 and bears the unit cell with $a=5.120\pm0.010$Å and $\alpha=55°17'$, containing four Al atoms and six O atoms in such disposition as:

Al atoms: $(1/2-w,\ 1/2-w,\ 1/2-w)$, $(w+1/2,\ w+1/2,\ w+1/2)$,
$(w,\ w,\ w)$, $(\bar{w},\ \bar{w},\ \bar{w})$
O atoms: $(1/2,\ 1/2-u,\ u+1/2)$, $(1/2-u,\ u+1/2,\ 1/2)$, $(u+2/1,\ 2/1,\ 2/1-u)$
$(u,\ 0,\ u)$, $(0,\ u,\ \bar{u})$, $(u,\ \bar{u},\ 0)$
where $w=0.1050\pm0.0010$Å
$u=0.303\pm0.003$Å (*cf.* PAULING and HENDRICKS, 1925 and WYCKOFF, 1964)

The unit cell of corundum is illustrated in the figure 1 revealing the content of four Al atoms and six O atoms with the elements of symmetry such as identity, two sixfold axes of rotatory reflection, three threefold axes, three glide mirror planes and center, and the groups of atoms combined with one another through symmetry operations are listed in the table 1.

The result obtained for the factor group analysis of corundum by the present authors with reference to BHAGAVANTAM's method are indicated in the table 2, wherein thirty kinds of vibration are discriminated, two for A_{1g} and five for E_g are attributable to Raman active vibrations and two for A_{2u} and four for E_u to infrared active vibrations.

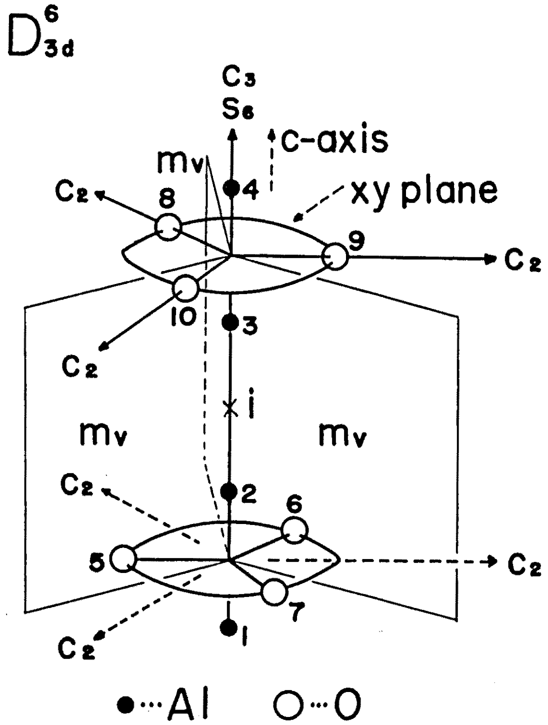

FIG. 1. Schematic illustration of atoms in corundum.

TABLE 1. ATOMIC GROUPS IN RELATION to SYMMETRY OPERATION

Symmetry operation	Atomic Groups
E	....
$2S_6$	(1, 4) (2, 3) (5, 8, 6, 9, 7, 10) (1, 4) (2, 3) (5, 10, 7, 9, 6, 8,)
$2C_3$	(1) (2) (3) (4) (5, 6, 7) (10, 8, 9) (1) (2) (3) (4) (5, 7, 6) (10, 9, 8)
i	(1, 4) (2, 3) (5, 9) (6, 10) (7, 8)
$3\sigma_v$	(1, 3) (2, 4) (5, 9) (6, 8) (7, 10) (1, 3) (2, 4) (5, 8) (6, 10) (7, 9) (1, 3) (2, 4) (5, 10) (6, 9) (7, 8)
$3C_2$	(5) (9) (1, 2) (3, 4) (6, 7) (10, 8) (6) (10) (1, 2) (3, 4) (5, 7) (8, 9) (7) (8) (1, 2) (3, 4) (5, 6) (10, 9)

Table 2. Factor Group Analysis of Corundum

D_{3d}	E	$2S_6$	$2C_3$	i	$3\sigma_v$	$3C_2$	N	T	T′	R′	n	Activity
A_{1g}	1	1	1	1	1	1	2	0	0	0	0	Raman
A_{1u}	1	−1	1	−1	−1	1	2	0	0	0	2	
A_{2g}	1	1	1	1	−1	−1	3	0	1	1	1	
A_{2u}	1	−1	1	−1	1	−1	3	1	0	1	1	infrared
E_g	2	−1	−1	2	0	0	5	0	1	1	3	Raman
E_u	2	1	−1	−2	0	0	5	1	0	1	3	infrared

III. Modes of Symmetry

The results of group analysis clearly suggest that thirty kinds of vibrations are classified into those belonging to six point groups, and the coordinate of *k*th vibration Q_k, an equilibrated position, is defined as displacement of atoms from the origin as follows:

$$Q_k=\sum_i a_{ik}x_j+\sum_i b_{ik}y_i+\sum_i c_{ik}z_i$$

where x_i, y_i and z_i are the coordinate of the *i*th atom and a_{ik}, b_{ik} and c_{ik} are its respecitve amplitude along the directions x, y and z.

The symmetry coordinates for the non-degenerate modes are easily exhibited through the factor group analysis, as shown in the figure 2. Those for the degenerate class are also revealed in relation to orthogonality along x, y and z, as given in the figure 3. In the illustrations of the symmetry modes, Z-axis taken trigonally, X-axis perpendicular to the former through O atom and Y-axis were placed to dispose the system in the right-handed arrangement.

Be it so, corundum includes four Al atoms and six O atoms in a unit cell and Q is expressed linearly as:

$$Q=\sum_1^{10}a_ix_i+\sum_1^{10}b_iy_i+\sum_1^{10}c_iz_i$$

where (+) x_i points to the intersection of three twofold axes on the xy plane, (+) z_i represents the upward one normal to the xy plane, and (+) y_i connects with the right-handed motion in the direction perpendicular to X and Y axes.

In view of these relationships, the symmetry coordinates of respective classes are summarised as follows:

A_{1g}

$$Q_1=-z_1+z_2-z_3+z_4$$

$$Q_2=-2\,(x_5-x_9)\;+\;(x_6+x_7-x_8+x_{10})$$

A_{1u}

$$Q_3=z_1-z_2-z_3+z_4$$

$$Q_4=-2\,(x_5+x_9)\;+\;(x_6+x_7+x_8+x_{10})\;+\;3\,(x_6-x_7+x_8-x_{10})$$

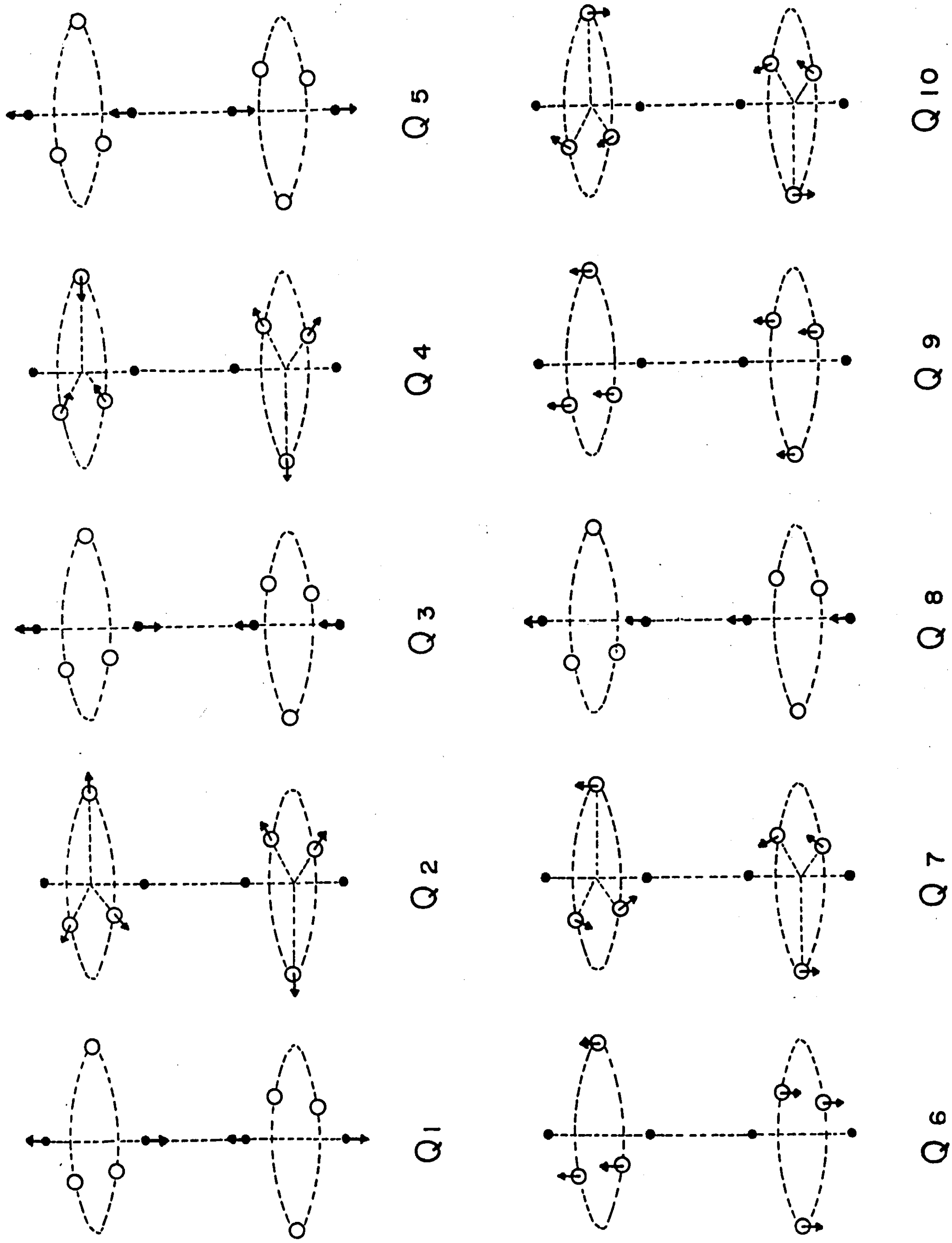

FIG. 2. Modes of Symmetry.

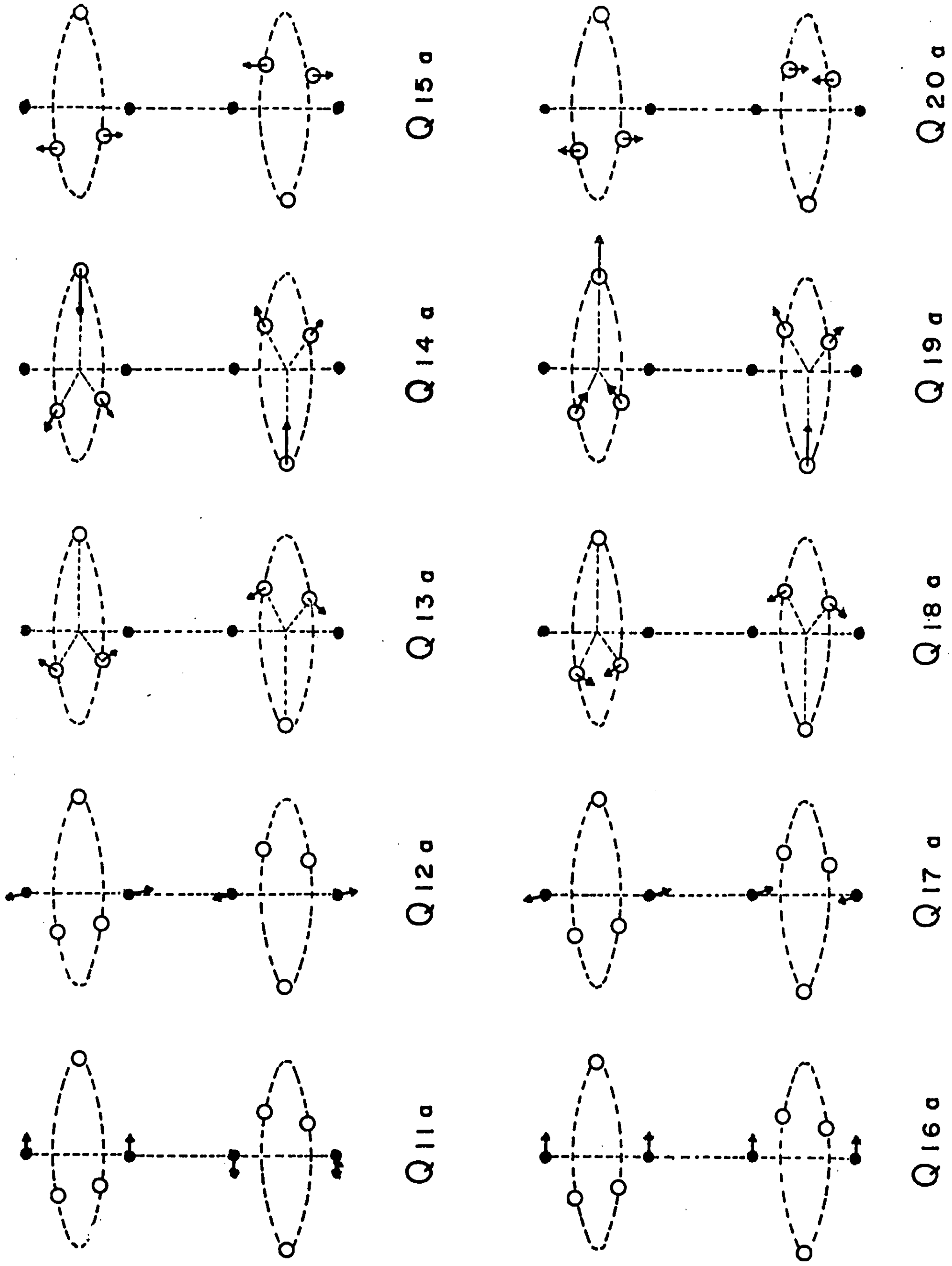

FIG. 3. Modes of Symmetry (continued).

A_{2g}

$Q_5 = -z_1 - z_2 + z_3 + z_4$

$Q_6 = -z_5 - z_6 - z_7 + z_8 + z_9 + z_{10}$

$Q_7 = -2\,(y_5 - y_9) + (y_6 + y_7 - y_8 - y_{10}) - 3\,(x_6 - x_7 + x_8 - x_{10})$

A_{2u}

$Q_8 = z_1 + z_2 + z_3 + z_4$

$Q_9 = z_5 + z_6 + z_7 + z_8 + z_9 + z_{10}$

$Q_{10} = -2\,(y_5 + y_9) + (y_6 + y_7 + y_8 + y_{10}) - 3\,(x_6 - x_7 - x_8 + x_{10})$

E_g

$Q_{11a} = -x_1 - x_2 + x_3 + x_4$

$Q_{12a} = -y_1 + y_2 - y_3 + y_4$

$Q_{13a} = -3\,(x_6 + x_7 - x_8 - x_{10}) - (y_6 - y_7 + y_8 - y_{10})$

$Q_{14a} = 2\,(x_5 - x_9) + (x_6 + x_7 - x_8 - x_{10}) - 3\,(y_6 - y_7 - y_8 - y_{10})$

$Q_{15a} = z_6 - z_7 + z_8 - z_{10}$

$Q_{11b} = y_1 + y_2 - y_3 - y_4$

$Q_{12b} = x_1 - x_2 + x_3 - x_4$

$Q_{13b} = 3\,(y_6 + y_7 - y_8 - y_{10}) + (x_6 - x_7 + x_8 - x_{10})$

$Q_{14b} = -2\,(y_5 - y_9) - (y_6 + y_7 - y_8 - y_{10}) + 3\,(x_6 - x_7 + x_8 - x_{10})$

$Q_{15b} = -2\,(z_5 - z_9) + (z_6 + z_7 - z_8 - z_{10})$

E_u

$Q_{16a} = x_1 + x_2 + x_3 + x_4$

$Q_{17a} = y_1 - y_2 - y_3 + y_4$

$Q_{18a} = -\,(y_6 - y_7 - y_8 + y_{10}) - 3\,(x_6 + x_7 + x_8 + x_{10})$

$Q_{19a} = 2\,(x_5 + x_9) + (x_6 + x_7 + x_8 + x_{10}) - 3\,(y_6 - y_7 - y_8 + y_{10})$

$Q_{20a} = -z_6 + z_7 + z_8 - z_{10}$

$Q_{16b} = -y_1 - y_2 - y_3 - y_4$

$Q_{17b} = -x_1 + x_2 + x_3 - x_4$

$Q_{18b} = -\,(x_6 - x_7 - x_8 + x_{10}) - 3\,(y_6 + y_7 + y_8 + y_{10})$

$Q_{19b} = -2\,(y_5 + y_9) + (y_6 + y_7 + y_8 + y_{10}) - 3\,(x_6 - x_7 - x_8 + x_{10})$

$Q_{20b} = 2(z_5 + z_9) - (z_6 + z_7 + z_8 + z_{10})$

IV. CALCULATION OF FREQUENCY

Assuming that the vibrational, rotational and translational motions may be treated separately and the first may be harmonic motion, the values for the normal vibrational frequency of crystal are given according to LAGRANGE's equation of motion. General coordinates of atoms are here determined in relation to the crystal structure of corundum. So if the kinetic and potential energies are expressed in the term of the coordinates it is also possible to evaluate the value of the normal frequency, although in general the potential field of crystal is still remained unknown. As for the force constants of corundum, it is thus schemed to find an identity of the calculated values with the observed frequencies. Since the fact is however that in the case of complicated structure it is not easy to attain the data of frequency only on the basis of LAGRANGE's equation, the method of WILSON's GF-matrix and the secular equation $|\boldsymbol{GF}-\boldsymbol{E}\lambda|=0$ have been applied to calculation by means of computor. In the secular equation mentioned above, $\boldsymbol{F}_x$, the potential energy matrix expressed in the term of the Cartesian symmetry coordinates, is soluble through substitution of the force constants in

$$\boldsymbol{F}_x=\boldsymbol{U}^\dagger \boldsymbol{B}\boldsymbol{F}_R\boldsymbol{B}^\dagger \boldsymbol{U}$$

where $\boldsymbol{F}_R$ represents the intermolecular potential energy matrix, $\boldsymbol{B}$ derived from the atom coordinate of the crystal is the matrix translatable from the intermolecular coordinate to the cartesian coordinate and $\boldsymbol{U}$ inferred from the symmetry coordinate is the matrix translatable to the symmetry coodinate.

The UREY-BRADLEY potential energy used here is expressed as follows:

$$\begin{aligned}V=&\sum_i[K'_i r_i+\sum_{j(\neq i)}F'_{ij}s_{ij}q_{ij}](\Delta r_i)+\sum_{i>j}[H'_{ij}r_{ij}+\\&F'_{ij}q_{ij}(t_{ij}t_{ji})^{1/2}](r_{ij}\Delta\alpha_{ij})+1/2\sum_i[K_i+\sum_{j(\neq i)}(t^2_{ij}F'_{ij}\\&+s^2_{ij}F_{ij})(\Delta r_i)^2+1/2\sum_{i>j}[H_{ij}-s_{ij}s_{ji}F'_{ij}+t_{ij}t_{ji}F_{ij}]\\&\times(r_{ij})^2(\Delta\alpha_{ij})^2+\sum_{i>j}[-t_{ij}t_{ji}F'_{ij}+s_{ij}t_{ij}F_{ij}](\Delta r_i)(\Delta r_j)\\&+\sum_{i(\neq j)}[t_{ij}s_{ji}F'_{ij}+t_{ji}s_{ij}F_{ij}](r_j/r_i)^{1/2}(\Delta r_i)(r_{ij}\Delta\alpha_{ji})\end{aligned}$$

where

$$s_{ij}=(r_i-r_j\cos\alpha_{ij})/q_{ij}\quad s_{ji}=(r_j-r_i\cos\alpha_{ij})/q_{ij}$$
$$t_{ij}=r_j\sin\alpha_{ij}/q_{ij}\qquad t_{ji}=r_i\sin\alpha_{ij}/q_{ij}$$
$$q^2_{ij}=r^2_i+r^2_j-2\cos\alpha_{ij}r_ir_j \text{ and } r_{ij}=(r_ir_j)^{1/2}$$

Since in this formula the terms of the first order are taken zero under a condition at the equilibrium position, it becomes necessary for attaining $\boldsymbol{F}_R$-matrix only to find the following factors:

$$\begin{aligned}&fr_ir_i=K_i+\sum_{(j\neq i)}(t^2_{ij}F'_{ij}+s^2_{jj}F_{ii})\\&f\alpha_{ij}\alpha_{ij}=(H_{ij}-s_{ij}s_{ji}F'_{ij}+t_{ij}t_{ji}F_{ij})r_ir_j+3h/\sqrt{8}\\&fr_ir_j=-t_{ij}t_{ji}F'_{ij}+s_{ij}s_{ji}F_{ij}\\&fr_i\alpha_{ij}=(t_{ji}s_{ji}F'_{ij}+t_{ji}s_{ij}F_{ij})r_j\\&f\alpha_{ij}\alpha_{ik}=\sqrt{2}h/2\end{aligned}$$

where K is the constant for the stretching force, H that for the bending force, F that for the repulsive force and h the interaction constant between adjacent angles.

Bond length and bond angle of corundum requisite for calculating its potential energy are listed in the table 3. Concerning the values for its normal vibrational frequency, those of Al–O distance were estimated 1.843Å and 1.982Å by the present authors in place of 1.845 ± 0.015Å and 1.990 ± 0.020Å given by PAULING and HENDRICKS (1925), for which the stretching forces K_1 and K_2 were respectively defined. The bending forces H_1 for O–Al–O and H_2 for Al–O–Al as well as the repulsive forces F_1 for O…O and F_2 for Al…Al were considered as UREY-BRADLEY potential. Further the interaction constants h_1 and h_2 between two adjacent angles around Al and O and k between two adjacent bonds were taken as the correction terms.

The kinetic energy matrix G is derivable from $\boldsymbol{G}=\boldsymbol{U}\boldsymbol{M}^{-1}\boldsymbol{U}^\dagger$, where $\boldsymbol{M}$ is the diagonal matrix constituted of the masses of Al atoms and O atoms.

TABLE 3. BOND LENGTH AND BOND ANGLE OF CORUNDUM

			e. g.	Number
Bond length	R_1	Al-O (1.845Å)	1 – 8	12
	R_2	Al-O (1.990Å)	1 – 5	12
Bond angle	α_1	O-Al-O (77°58′)	5 – 1 – 6	12
	α_2	O-Al-O (85°56′)	5 – 1 – 9	12
	α_3	O-Al-O (90°50′)	5 – 1 – 8	12
	α_4	O-Al-O (102°34′)	8 – 1 – 9	12
	ϕ_1	Al-O-Al (86°50′)	1 – 5 – 2	6
	ϕ_2	Al-O-Al (94°03′)	1 – 5 – 4	12
	ϕ_3	Al-O-Al (118°58′)	3 – 5 – 4	6
	ϕ_4	Al-O-Al (131°51′)	1 – 5 – 3	12

Through solving the secular equation from a set of the assumed force constants the numbers of frequency were evaluated, while the combination of unknown values for the force constant such as K_1, K_2, H_1, H_2, F_1, F_2, h_1, h_2 and k were determined according to the Jacobian matrix (*cf.* Table 4) giving the change of the characteristic

TABLE 4. JACOBIAN MATRIX* OF CORUNDUM ($\Delta\lambda_i/\Delta K_h$)

	K_1	K_2	H_1	H_2	F_1	F_2	h_1	h_2	k
A_{1g}	0.067	0.033	0.228	0.343	0.508	0.024	0.064	0.097	−0.075
	0.052	0.021	0.289	0.180	0.030	0.279	0.193	0.025	−0.044
A_{1u}	0.061	0.035	0.323	0.350	0.602	0.024	0.002	0.101	0.286
	0.058	0.019	0.281	0.318	0.030	0.457	0.185	−0.022	0.229
A_{2g}	0.054	0.057	0.492	0.247	0.727	0.008	−0.045	0.072	0.332
	0.017	0.042	0.466	0.352	0.387	0.028	−0.043	0.102	−0.047
	0·041	0.015	0.328	0.080	0.042	0.168	0.196	0.023	−0.044
A_{2u}	0.112	0.046	0.605	0.423	0.063	0.025	0.405	0.123	−0.130
	0.000	0.067	0.084	0.417	0.302	0.025	0.004	0.121	0.073
E_g	0.035	0.076	0.391	0.332	0.633	0.012	0.070	0.092	−0.123
	0.003	0.081	0.321	0.309	0.082	0.261	0.159	0.005	−0.048
	0.016	0.049	0.311	0.275	0.048	0.268	0.198	0.018	−0.032
	0.083	0.001	0.350	0.270	0.220	0.087	−0.007	0.072	−0.107
	0.046	0.009	0.134	0.351	0.123	0.064	−0.005	0.101	−0.110
E_u	0.033	0.087	0.697	0.693	0.138	0.046	0.419	0.200	−0.128
	0.069	0.037	0.577	0.370	0.435	0.026	−0.030	0.106	−0.147
	0.043	0.029	0.316	0.122	0.039	0.198	0.204	0.017	−0.014
	0.038	0.062	0.120	0.220	0.167	0.012	−0.006	0.063	−0.276
Unit	Å/mdsec^2	//	//	//	//	//	1/mdÅsec^2	//	Å/mdsec^2

*Jacobian matrix represents the change of the ith characteristic value due to that of the hth force constant.

value λ_i due to the change of the force constant ($\Delta\lambda_i/\Delta K_h$).

Repetitions of trial- and error-method for manipulations based on the normal coordinate were carried out to aim coincidence of the calculated values for frequency with those observed with use of Jacobian matrix. From the values obtained for the force constant, those for the elastic constant were derived in comparison with those observed megascopically. When 751 cm^{-1} is inferred to pertain to A_{1g}, it results in that the values for the constant concerned with the stretching or bending force become negative whereas this seems physically unreasonable and the data for the elastic constant calculated from those for the force constant are different from the observed data. So it may be that 751 cm^{-1} is resulted from impurity or combination band. The observed and calculated values for frequency in the case of Set I are listed in the table 5, wherein

Table 5. The Observed* and Calculated Values for Frequency of Corundum (cm^{-1})

	Set I		Set II	
	Obsd.	Calcd.	Obsd.	Calcd.
A_{1g}	578	555	578	567
		264	432	405
A_{2u}	583	555	583	602
	400	389	400	416
E_g	642	643	642	644
	450	520	450	465
	432	453	417	435
	417	382	375	413
	375	317		277
E_u	637	635	637	614
	571	568	571	547
	436	405	436	430
	385	366	385	373

* Barker, A.S. (1963)…………infrared spectra
Krishnan, R.S. (1948)………Raman spectra

Table 6. Force Constant oe Corundum

	Set I	Set II	Dimension
K_1 (Al-O)	1.0	0.5	md/Å
K_2 (Al-O)	0.7	0.4	〃
H_1 (O-Al-O)	0.2	0.08	〃
H_2 (Al-O-Al)	0.12	0.05	〃
F_1 (O……O)	0.05	0.25	〃
F_2 (Al…Al)	0	−0.05	〃
h_1 (O-Al-O, O-Al-O)	−0.25	0.25	md·Å
h_2 (Al-O-Al, Al-O-Al)	−0.3	−0.3	〃
k (Al-O, Al-O)	0.05	0.02	md/Å

the data other than 578 cm^{-1} for A_{1g} are not observable because of the lower values and the others are ascribed to those given by KRISHNAN and BARKER. The data for the force constant determined in each case are shown in the table 6. The data obtained for the Set II are also contained in the table 5, wherein 578 cm^{-1} and 432 cm^{-1} are assignable to A_{1g}, although the latter is combined with E_g by KRISHNAN probably owing to confusion derived from the Fermi resonance. The lowest value of E_g in frequency is considered to have not been found because of its weakness but the others assigned by KRISHNAN and BARKER are of course mentioned in the table.

Inspection of the data obtained clearly suggests that the calculated values of frequency in the Set I were less agreeable with the observed data than those arranged in the Set II, and discordance is most remarkable in the case of E_g, resulting in that the values of the force constant in the Set II would be reasonable for corundum. These results will be checked through scrutiny of the values for the elastic constant in the following section.

V. MODES OF VIBRATION

The modes of fundamental vibration determined already by the preceding calculation are also obtainable in the case of solving the secular equation through L-matrix revealing the relation of certain wave numbers to the modes of symmetry (*cf.*Figs. 2 and 3), as given in the table 7 and drawn quantitatively in the figures 4 and 5.

VI. ELASTIC CONSTANT

As described previously by SHIRO (1967), the matrix for the elastic constant is symmetric and the related elements are counted twenty one. But only six elements independent of the symmetry D_3 in corundum are alined as follows.

$$\begin{pmatrix} C_{11} & & & & & \\ C_{12} & C_{11} & & & & \\ C_{13} & C_{13} & C_{33} & & & \text{symmetric} \\ C_{14} & -C_{14} & 0 & C_{44} & & \\ 0 & 0 & 0 & 0 & C_{44} & \\ 0 & 0 & 0 & 0 & 0 & 2(C_{11}-C_{12}) \end{pmatrix}$$

According to the method reported by SHIRO, the values for the elastic constant have been calculated concerning of the sets of the force constant described above. The result derived as well as the observed values at the room temperature reported by BERNSTEIN are at the same time shown in the table 8. It is evident that the values of the Set II are more agreeable with those obtained than in the case of those for the Set I and are same as those obtained by treatment for the normal coordinate. It is here to be noted that the values of the elastic constant are sensitively dependent on the change of some bands of the force constant. Inspection of the table 9 manifests that increase in the values for

TABLE 7. L-MATRIX OF CORUNDUM

Spec.	Calcd. Freq.(cm^{-1})	Symmetry coordinate				
A_{1g}		Q_1	Q_2			
	567	0.001	$\underline{0.250}$			
	405	$\underline{0.193}$	−0.002			
A_{1u}		Q_3	Q_4			
	597	0.009	$\underline{0.250}$			
	438	$\underline{0.192}$	−0.011			
A_{2g}		Q_5	Q_6	Q_7		
	660	−0.007	$\underline{0.230}$	−0.098		
	479	−0.030	0.095	$\underline{0.228}$		
	407	$\underline{0.190}$	0.024	0.032		
A_{2u}		Q_8	Q_9	Q_{10}		
	602	$\underline{-0.132}$	$\underline{0.182}$	0.004		
	416	0.002	−0.003	$\underline{0.250}$		
E_g		Q_{11}	Q_{12}	Q_{13}	Q_{14}	Q_{15}
	644	−0.011	0.004	$\underline{0.161}$	0.092	$\underline{0.167}$
	465	$\underline{0.169}$	0.000	0.038	$\underline{-0.106}$	0.040
	435	0.012	$\underline{0.187}$	0.028	0.023	−0.045
	413	−0.070	0.043	−0.069	$\underline{-0.160}$	$\underline{0.144}$
	277	0.057	0.017	$\underline{-0.173}$	$\underline{0.130}$	0.100
E_u		Q_{16}	Q_{17}	Q_{18}	Q_{19}	Q_{20}
	614	$\underline{0.123}$	0.008	$\underline{0.176}$	−0.063	−0.047
	547	−0.048	0.012	0.111	$\underline{0.204}$	−0.066
	470	−0.004	$\underline{0.118}$	−0.027	−0.019	−0.041
	373	0.011	0.038	0.062	0.041	$\underline{0.233}$

The numbers underlined represent the fractions of symmetry coordinate related mainly to the vibration system.

the elastic constant is roughly proportional to that in the force constant with order of 0.1md/Å or difference of 0.1md. Å from its values for the Set II is recognizable and that the values for the bending force constant are more sensitive in the case of those for the stretching force constant and those for the bending force constant of O–Al–O, for the repulsive force constant of O…O and for the interaction constant of angles be-

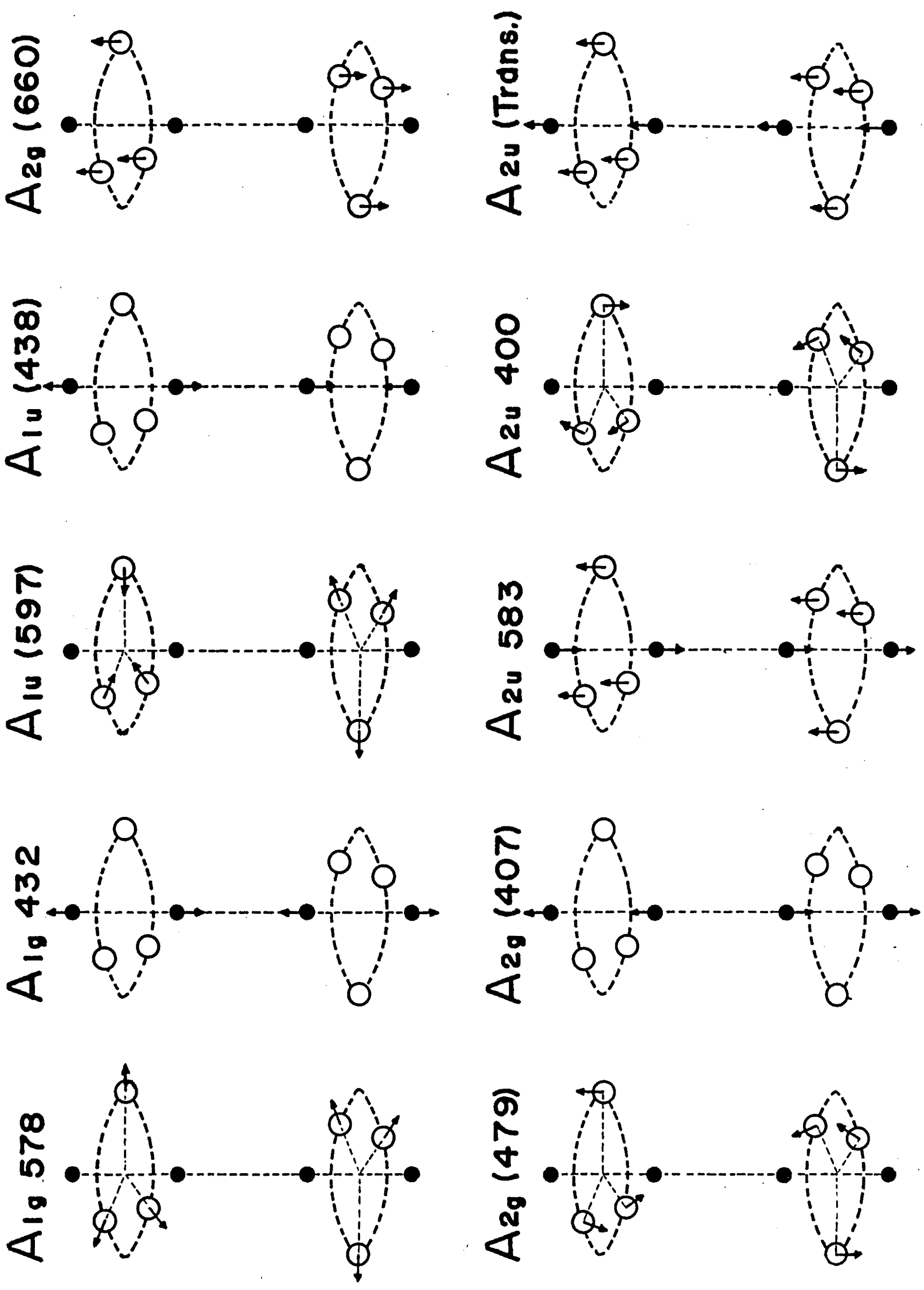

FIG. 4. Modes of Vibration.

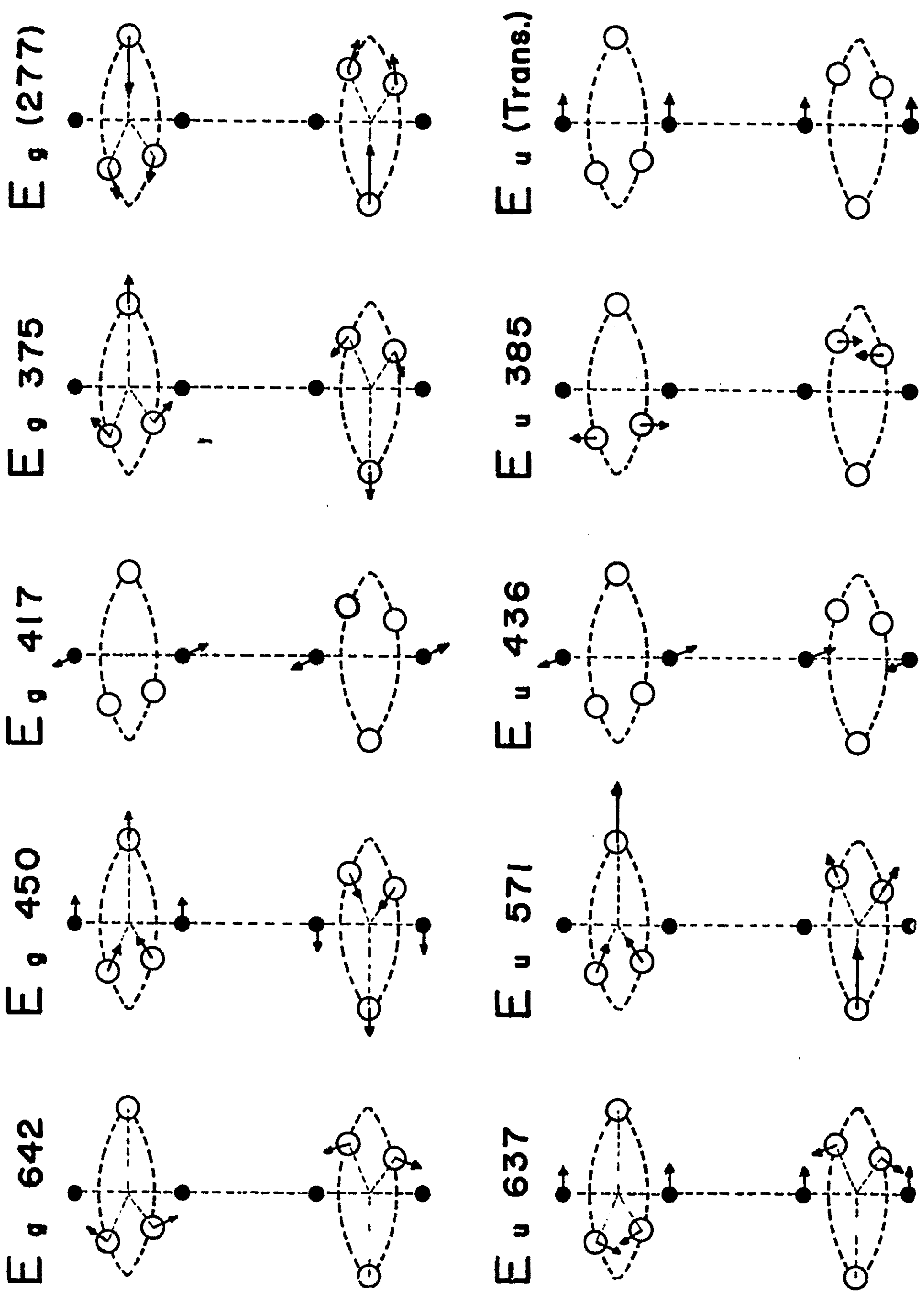

Fig. 5. Modes of Vibration (continued)

TABLE 8. ELASTIC CONSTANT OF CORUNDUM (10^{11}md/Å^2)

	Obsd. *	Calcd.	
		Set I	Set II
C_{11}	49.4	19	39
C_{33}	49.6	17	41
C_{44}	14.5	13	12
C_{12}	15.8	−5	12
C_{13}	11.4	−2	6
C_{14}	-2.3	0	0

* BERNSTEIN, B.T. (1963)

TABLE 9. VARIATION IN ELASTIC CONSTANT DUE TO THAT IN FORCE CONSTANT ($C\alpha\beta/K_h$)

	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}	C_{14}	Dimension
K_1	63	51	26	9	12	4	10^{-2}Å^{-1}
K_2	60	53	50	10	10	−6	//
H_1	761	782	342	−64	−122	−46	//
H_2	486	503	159	−238	−252	51	//
F_1	613	613	175	196	149	−8	//
F_2	317	304	133	54	4	49	//
h_1	554	495	61	220	16	0	10^{-2}Å^{-3}
h_2	70	118	21	−3	−65	−7	//

tween O-Al-O and O-Al-O are also so than those for the bending force constant of Al-O-Al, for the repulsive force constant of Al…Al and for the interaction constant of angles between Al-O-Al and Al-O-Al respectively.

Variation of the internal coordinates concerned with the elastic stress is presented in the table 10, suggesting many interesting informations as follows:

(1) Short bond (Al-O=1.845Å) is more sensitive to stresses S_{xx}, S_{yy} and S_{zz} than in the case of long bond (Al-O=1.990Å).

(2) The changes of the internal coordinates due to the elastic stress are generally small for the larger bond angles.

(3) The internal rotational angles are not changeable with the stress.

(4) The internal symmetry coordinates including A_{1g} are not variable with the stresses S_{yz}, S_{xz} and S_{xy}.

(5) Stress S_{yz} yields more effects on the internal symmetry coordinates than in the cases of the other directions of stress.

(6) The internal symmetry coordinate of E_g is alterable with the stresses S_{xx}, S_{yy} and S_{yz}

TABLE 10. VARIATION IN INTERNAL SYMMETRY COORDINATE DUE TO THAT IN ELASTIC STRESS ($R_i/S\alpha\beta$)

				S_{xx}	S_{yy}	S_{zz}	S_{yz}	S_{xz}	S_{xy}	Dimension
A_{1g}	sym.Al-O	R_1	str.	6.7	6.7	6.2	0.	0.	0.	Å^3/mdyn
	sym.Al-O	R_2	str.	0.2	0.2	0.1	0.	0.	0.	〃
	sym.O-Al-O	α_1	bend.	2.2	2.2	−2.4	0.	0.	0.	rad.Å^2/mdyn
	sym.O-Al-O	α_2	bend.	−2.0	−2.0	4.9	0.	0.	0.	〃
	sym.O-Al-O	α_3	bend.	−0.6	−0.6	5.7	0.	0.	0.	〃
	sym.O-Al-O	α_4	bend.	0.7	0.7	−6.7	0.	0.	0.	〃
	sym.Al-O-Al	ϕ_1	bend.	−2.1	−2.1	2.2	0.	0.	0.	〃
	sym.Al-O-Al	ϕ_2	bend.	2.0	2.0	−4.9	0.	0.	0.	〃
	sym.Al-O-Al	ϕ_3	bend.	−1.7	−1.7	1.0	0.	0.	0.	〃
	sym.Al-O-Al	ϕ_4	bend.	0.6	0.6	4.0	0.	0.	0.	〃
	sym. torsion			0.	0.	0.	0.	0.	0.	〃
E_g	deg.Al-O	R_1	str.	4.7	−4.7	0.	−12.0	0.	0.	Å^3/mdyn
	deg.Al-O	R_1	stɹ.	−0.8	0.8	0.	−19.2	0.	0.	〃
	deg.Al-O	R_2	str.	0.7	−0.7	0.	8.7	0.	0.	〃
	deg.Al-O	R_2	str.	1.8	−1.8	0.	3.9	0.	0.	〃
	deg.O-Al-O	α_1	bend.	−0.3	0.3	0.	−3.5	0.	0.	rad.Å^2/mdyn
	deg.O-Al-O	α_1	bend.	−2.3	2.3	0.	3.0	0.	0.	〃
	deg.O-Al-O	α_2	bend.	−5.2	5.2	0.	−0.3	0.	0.	〃
	deg.O-Al-O	α_2	bedd.	−2.8	2.8	0.	−16.8	0.	0.	〃
	deg.O-Al-O	α_3	bend.	1.1	−1.1	0.	−10.9	0.	0.	〃
	deg.O-Al-O	α_3	bend.	−1.8	1.8	0.	−8.2	0.	0.	〃
	deg.O-Al-O	α_4	bend.	2.5	−2.5	0.	9.6	0.	0.	〃
	deg.O-Al-O	α_4	bend.	1.1	−1.1	0.	−14.1	0.	0.	〃
	deg.Al-O-Al	ϕ_1	bend.	−1.2	1.2	0.	−2.7	0.	0.	〃
	deg.Al-O-Al	ϕ_2	bend.	5.3	−5.3	0.	0.3	0.	0.	〃
	deg.Al-O-Al	ϕ_3	bend.	2.8	−2.8	0.	16.8	0.	0.	〃
	deg.Al-O-Al	ϕ_4	bend.	−1.3	1.3	0.	−3.6	0.	0.	〃
	deg.Al-O-Al	ϕ_4	bend.	−1.2	1.2	0.	16.5	0.	0.	〃
	deg.Al-O-Al	ϕ_4	bend.	0.6	−0.6	0.	−3.7	0.	0.	〃
	deg. torsion			0.	0.	0.	0.	0.	0.	〃

VII. CONCLUSIVE REMARKS

The present work mainly deals with a part of investigation concerning the mathematical procedure for analysing the crystal force field by means of infrared spectroscopy in relation to the previous data for microcline (UMEGAKI and IISHI, 1966) and to those for elastic constant (BERNSTEIN, 1963). It has thus become obvious that as a result of the factor group analysis the observed data of absorption are considerably incongruent with those expected numerically from assumption of the UREY-BRADLEY force field. For solving the problem it appears of course indispensable to find all kinds of the reliable data for the forces acting mutually on each atom such as K, Al, Si, O and so forth. In the light of this, the values of the force constant for Al_2O_3 have been estimated as a step to reaching a conclusion applicable to more complicated structure with respect to the infrared absorption data given by BARKER and to the Raman spectra indicated by KRISHNAN.

The UREY-BRADLEY force field including certain modifications for the terms of the angle-interaction potentials h_1 and h_2 together with the bond-interaction potential k is considered sufficient for analysis of corundum structure, giving a clue to interpretation of the values for the vibrational frequency and for the elastic constant. It seems sure that the result attained is of due significance because the quantities obtained microscopically are in good coincidence with those found megascopically. The other fact of importance is that the values for the elastic constant are very sensitive to those for the costants of the bending force, repulsive force and interaction force. It is in general difficult to determine the force constant only in the normal coordinate but relatively easy to confirm the same factor by means of comparison of the data given for the elastic constant and frequency with those observed. This signifies that consideration of the elastic constant is very useful for investigation of the force field of crystals in the normal coordinate treatment.

The data obtained for the stretching force constant and elastic constant of corundum have been arranged for comparison with those of rutile and of quartz (SHIRO, 1967) in the table 11, inspection of which suggests that the values for the elastic constant of cortndum and rutile are about five times that of quartz, while those for the stretching force constant of the latter is about five times larger than those for the former two. It thus seems reasonable that the internal rotation in the case of quartz is very sensitively related to elasticity whereas its angles are hardly variable in corundum and rutile because of their special properties of symmetry.

TABLE 11. ELASTIC CONSTANTS AND THE FORCE CONSSTANTS OF SOME CRYSTALS

	TiO_2[a)]	Al_2O_3[b)]	SiO_2[c)]	Dimension
C_{11}	27.3	49.4	8.7	md/Å^2
C_{33}	48.4	49.6	10.6	〃
C_{44}	12.5	14.5	5.8	〃
C_{12}	17.6	15.8	0.7	〃
C_{13}	14.9	11.4	1.2	〃
C_{14}	0.0	− 2.3	1.8	〃
Force constant $K(X-O)$	1.4 X=Ti	0.5 X=Al	4.5 X=Si	md/Å

a) VERMA, R.K. (1960)
b) BERNSTEIN, B.T. (1963)
c) ATASASOFF, J.V. and HART, P.J. (1941)

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