ANALYSIS OF THE INFRARED ABSORPTION SPECTRUM OF DIOPSIDE

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ABSTRACT

Frequencies of the normal modes of vibration for a long chain $(Si_2O_6)_n$ molecule in both infrared and far infrared absorption spectra of diopside were calculated on the basis of the Urey-Bradley force field and compared with those measured. The wave numbers calculated were found to be in good agreement with those measured. The force constants obtained for the Si_2O_6 molecule were K_R 5.0, K_r 4.5, H_ϕ 0.4, $F_{RR(SiSi)}$ 0.4, $F_{RR(OO)}$ 0.1, F_{rr} 0.1, F_{Rr} 0.05, $F_{\phi R}$ −0.9 and $F_{\phi r}$ −0.9 md/Å.

INTRODUCTION

Infrared absorption spectra of inosilicates have been studied in the wave number regions from 4000 to 650 cm^{-1} by Launer (1952) and from 900 to 400 cm^{-1} by Omori (1964). Saksena (1961) has calculated the wave numbers of the absorption bands from 1250 to 650 cm^{-1} for the inosilicates including diopside, by using three common force constants, such as stretching K_1:5, deformation K_2:4, and K_2/r^2:0.7 md/Å. Omori (1970) has calculated the infrared active frequencies of sulfohalite by using Wilson's GF matrices method (Wilson, Decius, and Cross, 1955) and obtained the force constants.

In the present paper the author has calculated the wave numbers of the infrared active normal modes of vibration for the long chain $(Si_2O_6)_n$ molecule in diopside and has compared them with those measured.

INFRARED ABSORPTION SPECTRUM OF DIOPSIDE

Diopside used for the study was collected by the author in August, 1934, from the Posu phlogopite mine in the Archaean dolomite formation in northeastern Korea. Axial ratio and axial angle of diopside determined by using a two-circle goniometer were $a:b:c = 1.092:1:0.589$ and $\beta = 105° 56'$, respectively (Ito, 1935).

Infrared absorption spectra of diopside were studied by the usual methods (Omori and Kerr, 1964; Omori, 1970), where observations in the wave number regions from 4000 to 400 cm^{-1} and from 500 to 60 cm^{-1} were obtained by infrared spectrophotometers of both Perkin-Elmer Type 125 and Hitachi Type FIS-1. The infrared spectrum obtained is shown in the wave number region from 1500 to 60 cm^{-1} in Figure 1 with peaks of the absorption bands indicated on the spectrum. Both

Dedicated to Paul F. Kerr, Newberry Professor Em. of Columbia University, who has encouraged study of the infrared spectra of minerals.
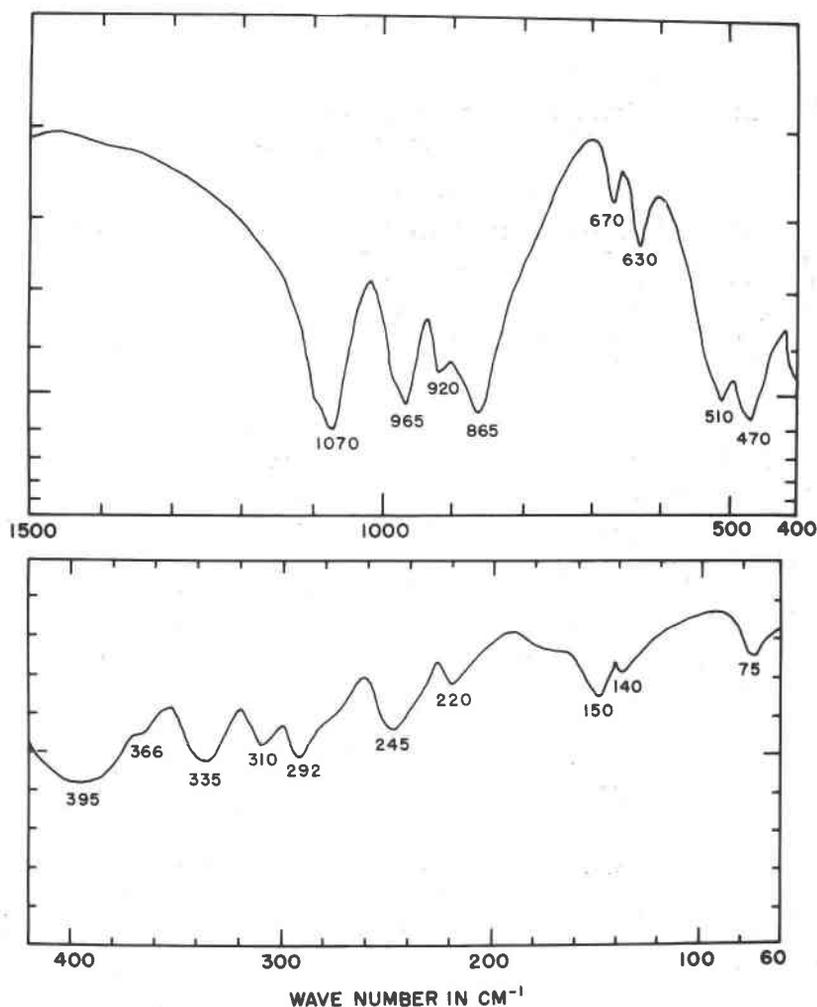
FIG. 1. Infrared absorption spectrum of diopside from the Posu mine, Korea.

wave numbers of the bands measured and calculated are shown with the absorptions measured and the assignments obtained in Table 1.

The space group of diopside is $C2/c = C_{2h}^6$ (Warren and Bragg, 1928) and the Bravais unit cell consists of twenty atoms, $2(MgCaSi_2O_6)$. The result of the factor group analysis shows that each twenty vibrations belonging to A_u and B_u species are expected to appear in the infrared spectrum, where the former couples to become six vibrations. Thus, the total eighteen vibrations calculated are similar to the numbers of the absorption bands observed.

TABLE 1. WAVE NUMBERS, ABSORBANCES, AND ASSIGNMENTS
OF THE ABSORPTION BANDS OF DIOPSIDE

Wave numbers measured	Absorbances measured	Wave numbers calculated	Assignments
1070 cm^{-1}	0.60	1101 cm^{-1}	Si–O(br) stretching (S_3)
965	0.52	969	Si–O(br) stretching (S_{11})
920	0.45	936	Si–O(nbr) stretching (S_4)
865	0.55	849	Si–O(nbr) stretching (S_{16})
670	0.18	—	—
630	0.23	609	O(nbr)–Si–O(nbr) bending (S_5)
510	0.51	}486	Chain deformation [O(nbr)–Mg–O(nbr) bending]
470	0.57		
395	—	415	Chain deformation [O(nbr)–Ca–O(nbr) bending]
366	—	—	—
335	—	348	O(nbr)–Si–O(nbr) wagging (S_{12})
310	—	305	O(nbr)–Si–O(nbr) rocking (S_{17})
292	—	261	Si–O(br)–Si bending (S_{18})
245	—	248	Si–O(br)–Si bending (S_{13})
220	—	{195 {189	Chain deformation [O(nbr)–Mg–O(nbr) stretching] [O(nbr)–Ca–O(nbr) stretching]
150	—	—	—
140	—	—	—
75	—	—	—

INTERNAL COORDINATES

The $(Si_2O_6)_n$ chain in diopside runs parallel to the c-axis in a slightly zigzag way, whose two non-bridging oxygens (O(nbr)) strongly repulse each other. Thus, the angle O(nbr)-Si-O(nbr) is 115–118°, which is wider than the similar angle 109.4° of the tetrahedral SiO$_4$ molecule. And the distance between two non-bridging oxygens is 2.725–2.773 Å, which is also larger than that of 2.535–2.614 Å between the non-bridging and the bridging oxygens.

But, it was assumed for ease of calculation that the form of each SiO$_4$ is tetrahedral and that its two forms on opposite sides combine by bridging oxygens, after Saksena (1961) whose Si$_2$O$_6$ chain is shown in Figure 2.

In Figure 2, R_1, R_2, R_1', and R_2' denote the equilibrium distances of the Si-O bond in the chain; r_1, r_2, r_1', and r_2' show the equilibrium distances of another Si-O bond; ϕ_1, ϕ_2, ϕ_3, ϕ_4, ϕ_1', ϕ_2', ϕ_3', and ϕ_4' indicate the equilibrium angles O-Si-O for the Si cation; and $\psi_\parallel$, $\psi_\perp$, $\psi_\parallel'$, and $\psi_\perp'$ are the equilibrium angles Si-O-Si for the bridging oxygen in the chain,

FIG. 2. The long chain $(Si_2O_6)_n$ molecule in diopside.

whose suffixes, $\parallel$ and $\perp$, mean that the angles are taken, respectively, in the plane and perpendicular to the plane of the paper.

The g matrix constructed from the internal coordinates and the corresponding f matrix in terms of the general valence force field for the long chain $(SiO_6)_n$ molecule can be indicated similarly by the matrix shown in Table 2.

TABLE 2. THE g AND f MATRIX FOR THE $(Si_2O_6)_n$ MOLECULE IN DIOPSIDE

	R_1	R_2	R_1'	R_2'	r_1	r_2	r_1'	r_2'	φ_1	φ_2	φ_3	φ_4	φ_1'	φ_2'	φ_3'	φ_4'	$\psi_\parallel$	$\psi_\parallel'$	$\psi_\perp$	$\psi_\perp'$
R_1	a_1																			
R_2	c	a_1																		
R_1'	0	d_1	a_1																	
R_2'	d_1	0	c	a_1																
r_1	d_2	0	0	d_2	a_2															
r_2	d_2	0	0	d_2	d_3	a_2														
r_1'	0	d_2	d_2	0	0	0	a_2													
r_2'	0	d_2	d_2	0	0	0	d_3	a_2												
φ_1	h_1	i	0	j_1	h_2	j_2	0	0	b											
φ_2	h_1	i	0	j_1	j_2	h_2	0	0	f_1	b										
φ_3	j_1	0	i	h_1	h_2	j_2	0	0	f_2	e	b		Symmetrical							
φ_4	j_1	0	i	h_1	j_2	h_2	0	0	e	f_2	f_1	b								
φ_1'	i	h_1	j_1	0	0	0	h_2	j_2	g	g	0	0	b							
φ_2'	i	h_1	j_1	0	0	0	j_2	h_2	g	g	0	0	f_1	b						
φ_3'	0	j_1	h_1	i	0	0	h_2	j_2	0	0	g	g	f_2	e	b					
φ_4'	0	j_1	h_1	i	0	0	j_2	h_2	0	0	g	g	e	f_2	f_1	b				
$\psi_\parallel$	k_1	k_1	k_2	k_2	k_3	k_3	k_3	k_3	l_1	l_1	0	0	l_1	l_1	0	0	m			
$\psi_\parallel'$	k_2	k_2	k_1	k_1	k_3	k_3	k_3	k_3	0	0	l_1	l_1	0	0	l_1	l_1	n_1	m		
$\psi_\perp$	k_1	k_1	k_2	k_2	k_4	k_4	k_4	k_4	l_2	l_2	0	0	l_2	l_2	0	0	n_2		m	
$\psi_\perp'$	k_2	k_2	k_1	k_1	k_4	k_4	k_4	k_4	0	0	l_2	l_2	0	0	l_2	l_2	n_2	0	n_1	m

C_{2v} and C_{2h}	I	C_2	i	σ	Active	Numbers of the normal modes of vibration
A_{1g}	1	1	1	1	Raman	2
A_{1u}	1	1	-1	1	Infrared	3
A_{2g}	1	1	1	-1	Raman	1
A_{2u}	1	1	-1	-1	—	2
B_{1g}	1	-1	1	1	Raman	2
B_{1u}	1	-1	-1	1	Infrared	3
B_{2g}	1	-1	1	-1	Raman	2
B_{2u}	1	-1	-1	-1	Infrared	3

Since both silicon and oxygen atoms lie on general positions in the diopside structure, the Si_2O_6 molecule has no symmetry at all. It belongs to the point group C_1. But the simplified chain shown in Figure 2 has the symmetries of both point groups C_{2v} and C_{2h} which refers to pseudo-symmetries introduced to simplify the calculations. In the point group C_{2v} the rotation axis C_2 passes through the Si cation and in the point group C_{2h} it passes through the bridging oxygen anion. Thus, the selection rule obtained is shown in Table 3, where C_2 and σ refer to both point groups C_{2v} and C_{2h}, while i refers to the point group C_{2h}, and the degrees of freedom of the normal modes of vibration for the infrared active A_{1u}, B_{1u}, and B_{2u} species are all three shown in Table 3.

These degrees of freedom are obtained from only the vibrations of a single Si_2O_6 molecule when in fact there are two such groupings in the Bravais unit cell. This immediately doubles the number of chain vibrations active in the infrared from 9 to 18, of which some modes of grouping will be discussed below.

SYMMETRY COORDINATES AND THE ELEMENTS OF THE G AND F MATRICES

A matrix U shown in Table 4 was formed by the coefficients of the symmetry coordinates for the long chain $(Si_2O_6)_n$ molecule. From the matrix multiplications $UgU' = G$ and $UfU' = F$, where the U' matrix is the transpose of the U matrix, and by using Decius' general formulae (Decius, 1948) for obtaining the G matrix elements, and the general equation to represent the potential energy in the Urey-Bradley force field (Shimanouti, 1949), the G and F matrices of the long chain $(Si_2O_6)_n$ molecule in diopside were obtained.

The elements obtained of the G and F matrices for three infrared active species A_{1u}, B_{1u}, and B_{2u} are as follows.

TABLE 4. THE U MATRIX FOR THE LONG CHAIN $(Si_2O_6)_n$ MOLECULE IN DIOPSIDE

		R_1	R_2	R_1'	R_2'	r_1	r_2	r_1'	r_2'	φ_1	φ_2	φ_3	φ_4	φ_1'	φ_2'	φ_3'	φ_4'	$\psi_\parallel$	$\psi_\parallel'$	$\psi_\perp$	$\psi_\perp'$
A_{1g}	S_1	0	0	0	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0	0	0	0	0	0	0	0	0
	S_2	0	0	0	0	0	0	0	0	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	0	0	0	0
A_{1u}	S_3	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{-1}{2}$	$\frac{1}{2}$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	S_4	0	0	0	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{-1}{2}$	0	0	0	0	0	0	0	0	0	0	0	0
	S_5	0	0	0	0	0	0	0	0	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	0	0	0	0
A_{2g}	S_6	0	0	0	0	0	0	0	0	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	0	0	0	0
A_{2u}	S_7	0	0	0	0	0	0	0	0	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	0	0	0	0
	S_8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	0	0
B_{1g}	S_9	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{-1}{2}$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	S_{10}	0	0	0	0	0	0	0	0	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	0	0	0	0
B_{1u}	S_{11}	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{1}{2}$	$\frac{-1}{2}$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	S_{12}	0	0	0	0	0	0	0	0	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	0	0	0	0
	S_{13}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\frac{1}{\sqrt{2}}$	$\frac{-1}{\sqrt{2}}$	0	0
B_{2g}	S_{14}	0	0	0	0	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{1}{2}$	$\frac{-1}{2}$	0	0	0	0	0	0	0	0	0	0	0	0
	S_{15}	0	0	0	0	0	0	0	0	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	0	0	0	0
B_{2u}	S_{16}	0	0	0	0	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{-1}{2}$	$\frac{1}{2}$	0	0	0	0	0	0	0	0	0	0	0	0
	S_{17}	0	0	0	0	0	0	0	0	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	$\frac{-1}{2\sqrt{2}}$	$\frac{1}{2\sqrt{2}}$	0	0	0	0
	S_{18}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$

A_{1u} species:

$$G_{11} = \frac{2}{3}(\mu_{Si} + 2\mu_0) \qquad\qquad G_{22} = \frac{2}{3}\mu_{Si} + \mu_0$$

$$G_{12} = -\frac{2}{3}\mu_{Si} \qquad\qquad G_{23} = -\frac{4}{3}\mu_{Si}\rho$$

$$G_{13} = -\frac{4}{3}\left(\mu_{Si} - \frac{1}{\sqrt{3}}\mu_0\right)\rho \qquad G_{33} = \frac{19}{9}\mu_0\rho^2,$$

where μ_{Si} and μ_0 are the reciprocal mass of the Si and O atoms, respectively, and ρ is the reciprocal length of the Si-O bond.

$$F_{11} = K_R - \frac{1}{15}F_{RR(SiSi)} + \frac{7}{10}F_{RR(OO)} \qquad\qquad F_{22} = K_\gamma + F_{\gamma\gamma} + \frac{19}{15}F_{R\gamma}$$

$$+ \frac{19}{15}F_{R\gamma}$$

$$F_{12} = \frac{7}{5} F_{R\gamma} \qquad\qquad\qquad F_{23} = -\frac{3}{5} F_{\phi\gamma} \cdot \gamma$$

$$F_{13} = -\frac{3}{5} F_{\phi R} \cdot \gamma \qquad\qquad F_{33} = \left(H_\phi + \frac{2}{5} F_{R\gamma} \right) \gamma^2,$$

where K, H, and F are the stretching, bending, and repulsive force constants in md/Å, respectively, the suffixes used are shown in Figure 2, and r is the Si-O bond length.

B_{1u} species: B_{2u} species:

$$G_{11} = \frac{4}{3} (\mu_{Si} + \mu_O) \qquad\qquad G_{11} = \frac{4}{3} \mu_{Si} + \mu_O$$

$$G_{12} = \frac{4}{3\sqrt{3}} (\sqrt{3}\, \mu_{Si} - \mu_O)\rho \qquad G_{12} = 4\mu_{Si}\rho$$

$$G_{13} = 0 \qquad\qquad\qquad\qquad G_{13} = 0$$

$$G_{22} = \frac{1}{3}\left(16\mu_{Si} + \frac{8}{3}\mu_O \right)\rho^2 \qquad G_{22} = \left(\frac{16}{3}\mu_{Si} + 2\mu_O \right)\rho^2$$

$$G_{23} = 0 \qquad\qquad\qquad\qquad G_{23} = 0$$

$$G_{33} = \frac{1}{3} (5\mu_{Si} + 8\mu_O)\rho^2 \qquad G_{33} = \frac{1}{3} (7\mu_{Si} + 8\mu_O)\rho^2$$

$$F_{11} = K_R - \frac{7}{10} F_{RR(SiSi)} - \frac{1}{15} F_{RR(OO)} \qquad F_{11} = K\gamma - \frac{1}{15} F_{\gamma\gamma} + \frac{19}{15} F_{R\gamma}$$

$$+ \frac{19}{15} F_{R\gamma}$$

$$F_{12} = \frac{3}{5} F_{\phi R} \cdot \gamma \qquad\qquad\qquad F_{12} = \frac{3}{5} F_{\phi\gamma} \cdot \gamma$$

$$F_{13} = 0 \qquad\qquad\qquad\qquad F_{13} = 0$$

$$F_{22} = \left(H_\phi + \frac{2}{5} F_{R\gamma} \right) \cdot \gamma^2 \qquad F_{22} = \left(H_\phi + \frac{2}{5} F_{R\gamma} \right) \cdot \gamma^2$$

$$F_{23} = 0 \qquad\qquad\qquad\qquad F_{23} = 0$$

$$F_{33} = \frac{2}{5} F_{RR(SiSi)} \cdot \gamma^2 \qquad\qquad F_{33} = \frac{2}{5} F_{RR(SiSi)} \cdot \gamma^2$$

CALCULATION OF THE FREQUENCIES OF THE LONG CHAIN $(Si_2O_6)_n$ MOLECULE IN DIOPSIDE

By using the numerical values of the force constants, such as K_R 5.0, K_r 4.5, H_ϕ 0.4, $F_{RR(SiSi)}$ 0.4, $F_{RR(OO)}$ 0.1, F_{rr} 0.1, F_{Rr} 0.05, $F_{\phi R}$ −0.9, and $F_{\phi r}$ −0.9 md/Å, the numerical values of the F matrices for the infrared active A_{1u}, B_{1u}, and B_{2u} species were obtained.

Then, from the secular equation $\|GF - E\lambda\| = 0$, the wave numbers calculated for the normal modes of vibration were 1101, 936, and 609 cm⁻¹ for the A_{1u} species; 969, 348, and 248 cm⁻¹ for the B_{1u} species; and 849, 305, and 261 cm⁻¹ for the B_{2u} species, all of which are found to be in reasonable agreement with the wave numbers measured and shown in Table 1.

The assignments shown in Table 1 were obtained from the potential energy distributions calculated as follows, where some couplings were found between the symmetry species.

$$
A_{1u}\text{ species}\quad
\begin{matrix} S_3 \\ S_4 \\ S_5 \end{matrix}
\begin{bmatrix}
0.3096533 & 0.1270491 & 0.1100682 \\
0.0237384 & 0.2136051 & 0.1647751 \\
0.2404991 & 0.1448100 & 0.1688306
\end{bmatrix}
$$

$$
B_{1u}\text{ species}\quad
\begin{matrix} S_{11} \\ S_{12} \\ S_{13} \end{matrix}
\begin{bmatrix}
0.6214200 & 0.0033680 & 0.0000000 \\
0.0227659 & 0.0803109 & 0.0000000 \\
0.0000000 & 0.0000000 & 0.0361599
\end{bmatrix}
$$

$$
B_{2u}\text{ species}\quad
\begin{matrix} S_{16} \\ S_{17} \\ S_{18} \end{matrix}
\begin{bmatrix}
0.5010959 & 0.0000007 & 0.0000000 \\
0.0776029 & 0.0546391 & 0.0000000 \\
0.0000000 & 0.0000000 & 0.0399551
\end{bmatrix}
$$

GROUPING OF THE $(Si_2O_6)_n$ CHAINS

Four Si_2O_6 chains in the unit cell of diopside are combined with each other by the Mg and the Ca cations in coordination groups MgO_6 and CaO_8 interposed in layers parallel to (100). All six oxygens in the MgO_6 coordination group are the non-bridging oxygens.

From the similar calculation for the species F_{1u} of the octahedral molecule by using Wilson's GF matrices (Omori, 1970) the wave numbers calculated for the octahedral MgO_6 coordination group in diopside were 486 and 195 cm⁻¹. The force constants obtained were K 0.8, H 0.1, and F 0.001 md/Å. The wave numbers calculated were similar to those measured, such as the mean value 490 cm⁻¹ between 510 and 470 cm⁻¹, and 220 cm⁻¹, respectively. These modes of vibration are the deformation of the long chain grouped.

As the size of the Ca cation is larger than that of the Mg cation, the Ca cation is surrounded by eight oxygen anions in site 2 of diopside, where four oxygen anions are the non-bridging oxygen and four left over are the bridging oxygen in the Si_2O_6 molecule.

The frequencies were calculated, assuming that the Ca cation is surrounded octahedrally by six non-bridging oxygens, similar to the MgO_6 coordination group.

The wave numbers calculated were 415 and 189 cm^{-1}, which are similar to those measured: 395 and 220 cm^{-1}, respectively. The force constants obtained were K 0.8, H 0.1, and F 0.001 md/Å, which were the same as those obtained for the MgO_6 coordination group. These modes of vibration also belong to the deformation of the long chain Si_2O_6 molecule grouped.

CONCLUSIONS

The frequencies of the long chain $(Si_2O_6)_n$ molecules in diopside were calculated, and the force constants obtained were K_R 5.0, K_r 4.5, H_ϕ 0.4, $F_{RR(SiSi)}$ 0.4, $F_{RR(OO)}$ 0.1, F_{rr} 0.1, F_{Rr} 0.05, $F_{\phi R}$ −0.9, and $F_{\phi r}$ −0.9 md/Å. Both wave numbers measured and calculated were similar as shown in Table 1. The assignments obtained from the potential energy distribution calculated are also shown in Table 1.

The frequencies for the octahedral coordination groups MgO_6 and CaO_6 in diopside, which interpose in the long chains grouped, were calculated, and the common force constants obtained were K 0.8, H 0.1, and F 0.001 md/Å. The wave numbers calculated, whose modes of vibration belong to the deformation of the long chain grouped, were similar to those measured as shown in Table 1.

Although the good agreement between the measured and the calculated frequencies might be attributed to a circular argument, it is believed that the results obtained in diopside are useful for the assignments of the infrared absorption bands for the long chain $(Si_2O_6)_n$ molecule in pyroxene.

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