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Optically-active Vibrations and Elastic Constants of Calcite and Aragonite[1)]

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Treatments of the normal coordinate and the elastic constant were undertaken for two calcium carbonate crystals. By the use of the least-squares technique, we obtained sets of the force constants which reproduce satisfactorily both the observed vibrational frequencies and the macroscopic elastic constants. The intermolecular interactions, the elastic strains of the internal coordinates, and the nature of the splitting of the normal frequencies in these crystals were briefly discussed.

The vibrational spectra of molecular crystals and ionic crystals have been studied by many investigators. Some of them have performed normal coordinate analyses, and the force fields of many crystals have been determined. Recently more rigorous treatments of the lattice dynamics, such as those based on the rigid-ion model[2)] or on the shell model,[3)] have been made for relatively simple crystal systems mainly by physicists.[4)] Presumably the impracticability of these treatments arises in part from the difficulties in the reasonable estimation of the potential parameters. The results of these treatments are quite suggestive for the analysis of the crystal vibration in a complex crystal system, though the application of the above models to actual complex crystals is difficult at the present time.

Generally, in contrast to the treatment of isolated free molecules, many restrictions which are characteristic of the solid state make it difficult to determine the force fields from only the vibrational spectra. These restrictions are caused by the experimental limitations, the complicated crystal structures, the strong intra- or inter-molecular interactions, and so on. The short-range interaction, intramolecular or intermolecular, is considered to dominate the crystal vibration and the elastic deformation, at least in molecular crystals or in predominantly covalent crystals. Therefore, it is necessary, for the determination of the force fields in the successional models, to ascertain the fundamental short-range force fields.

The present investigations of the short-range force fields of two calcium carbonates, and of sodium nitrate and sodium nitrite in the low-temperature ferroelectric phase[1)] were undertaken not only in order to check the reasonability of the vibrational force fields, but also to determine those force fields which interpret both the observed vibrational frequencies and the elastic constants.

Methods of Calculation

Crystal Structure. According to the X-ray diffraction analyses,[5,6)] the Bravais unit cells of calcite and aragonite belong to the rhombohedral space group D_{3d}^{6}—R$\bar{3}$c, with Z=2, and the orthorhombic D_{2h}^{16}—Pmcn, with Z=4 respectively. The cell constants are $a_{rh}=6.3753$ Å and $\alpha=46°4.6'$ in calcite and $a=4.9614$ Å, $b=7.9671$ Å, and $c=5.7404$ Å in aragonite. Figures 1 and 2 show the structures of calcite and aragonite respectively. The structure of calcite may be regarded as a sodium chloride arrangement distorted by the introduction of disk-shaped carbonate groups. Each calcium atom is coordinated by six oxygen atoms, each belonging to a different carbonate group, and such oxygen atom is bound to two calcium atoms. On the other hand, the orthorhombic structure of aragonite is related to that of nickel arsenide. Each calcium atom is now surrounded by nine neighbors, each of which is, in its turn, bound to three calcium atoms.

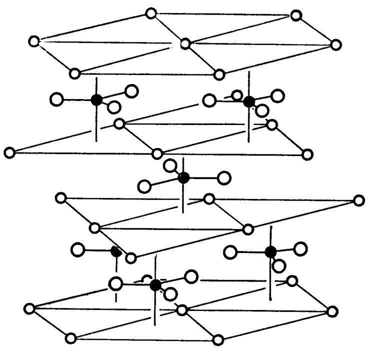

Fig. 1. Crystal structure of calcite.
●: carbon, ○: calcium, ◯: oxygen.

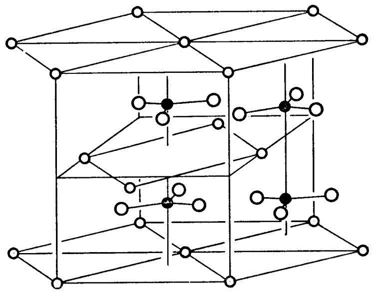

Fig. 2. Crystal structure of aragonite.
●: carbon, ○: calcium, ◯: oxygen.

Normal Coordinate Treatment. The application of the *GF*-matrix method[7)] to the analysis of optically-active crystal vibrations was reported previously by Shimanouchi, Tsuboi, and Miyazawa.[8)] The modified Urey-Bradley force field[9)] was applied to the intramolecular vibrations in carbonate groups, the correction terms of which were the bond interaction term, p, for the adjacent C–O bond pairs and the angle interaction term, n, for the adjacent O–C–O angle pairs in a single carbonate group. On the other hand, the central force field, which is based on the two-body interaction, was used for the intermolecular vibrations.

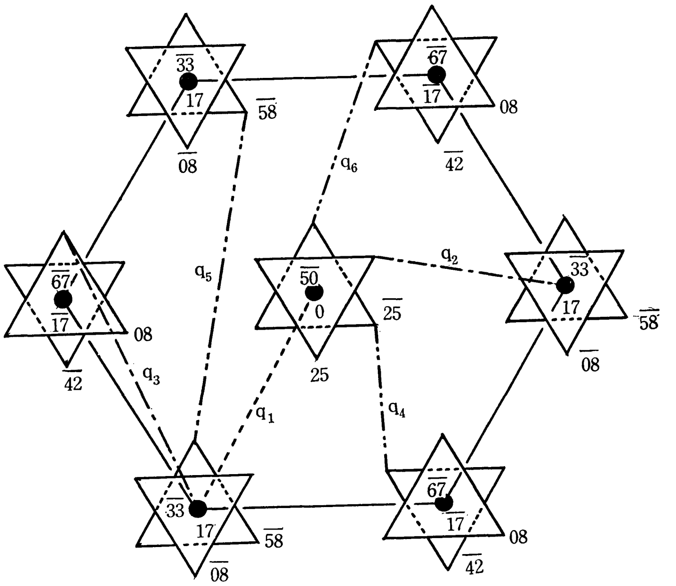

Fig. 3. Short-range interactions in calcite viewed along the z axis of the hexagonal cell. The heights of atoms or carbonate groups are expressed in units of $100/c_0$.
----, calcium···carbon; ———, calcium···oxygen; ————, oxygen···oxygen.

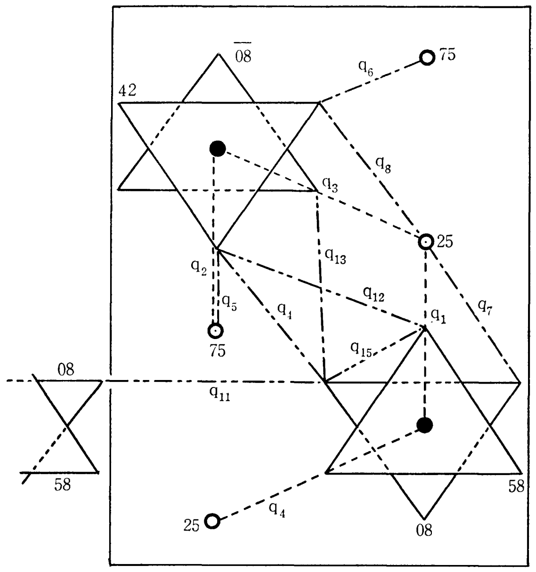

Fig. 4. Short-range interactions in aragonite viewed along the z axis. Other descriptions are the same to Fig. 3.

In this study, only those pairs that lie within 3.5 Å were taken into consideration. As is illustrated in Figs. 3 and 4, there are six different kinds of these pairs in calcite and fifteen in aragonite respectively. The corresponding atomic separations are also listed in Table 3.

In many cases, group theoretical considerations, such as the site-group analysis[10] or the factor-group analysis,[11] have been found to be useful for the analysis of crystal vibrations. The factor-group analysis of these crystals was once performed by Bhagavantam and Venkatarayudu;[11] their results are summarized in Tables 1 and 2. It is obvious from these tables that, of the twenty-seven degrees of freedom for genuine vibrations eight modes are infrared-active, and five, Raman-active, in calcite, and that, of the fifty-seven degrees, twenty-seven are infrared-active, and thirty, Raman-active, in aragonite. The selection rules for the optically-active vibrations are followed under the mutual exclusion rule, since each crystal has a center of symmetry.

Table 1. Factor-group analysis of calcite

D_{3d}^6	E	$2S_6$	$2S_6^2$	S_6^3	$3C_2$	$3\sigma_v$	N_i	T_i	T_i'	R_i'	n_i	IR	Raman
A_{1g}	1	1	1	1	1	1	1	0	0	0	1	f	$\alpha_{xx}=\alpha_{yy}$, α_{zz}
A_{1u}	1	−1	1	−1	1	−1	2	0	1	0	1	f	f
A_{2g}	1	1	1	1	−1	−1	3	0	1	1	1	f	f
A_{2u}	1	−1	1	−1	−1	1	4	1	1	1	1	M_z	f
E_g	2	−1	−1	2	0	0	4	0	1	1	2	f	$\alpha_{xx}=-\alpha_{yy}$, α_{xy}, α_{yz}, α_{zx}
E_u	2	1	−1	−2	0	0	6	1	2	1	2	M_x, M_y	f

f, forbidden; N_i, number of degrees of freedom belonging to the i-th species; T_i, number of over-all translations of Bravais unit cell; T_i', number of translational lattice modes; R_i', number of rotational lattice modes; n_i, number of intramolecular vibrational modes.

Table 2. Factor-group analysis of aragonite

D_{2h}^{16}	E	C_2^c	C_2^b	C_2^a	i	σ_c	σ_b	σ_a	N_i	T_i	T_i'	R_i'	n_i	IR	Raman
A_{1g}	1	1	1	1	1	1	1	1	9	0	4	1	4	f	α_{xx}, α_{yy}, α_{zz}
A_{1u}	1	1	1	1	−1	−1	−1	−1	6	0	2	2	2	f	f
B_{1g}	1	1	−1	−1	1	1	−1	−1	6	0	2	2	2	f	α_{xy}
B_{1u}	1	1	−1	−1	−1	−1	1	1	9	1	3	1	4	M_z	f
B_{2g}	1	−1	1	−1	1	−1	1	−1	6	0	2	2	2	f	α_{zx}
B_{2u}	1	−1	1	−1	−1	1	−1	1	9	1	3	1	4	M_y	f
B_{3g}	1	−1	−1	1	1	−1	−1	1	9	0	4	1	4	f	α_{yz}
B_{3u}	1	−1	−1	1	−1	1	1	−1	6	1	1	2	2	M_x	f

Notations are the same to Table 1.

Table 3. Force constants (mdyn/Å) of calcite and aragonite

Calcite			Aragonite		
Force constant		Distance[a]	Force constant		Distance[a]
K(C-O)	5.520	1.290	K(C-O)	5.669	1.282
H(OCO)[b]	0.340		H(OCO)[b]	0.340	
F(O O)[b]	1.720		H(O O)[b]	1.720	
$\alpha(\mathrm{CO_3})$[c]	0.797		$\alpha(\mathrm{CO_3})$[c]	0.738	
p	0.052		p	-0.125	
n[c]	0.021		n[c]	0.016	
f_1(Ca C)	0.103	3.185	f_1(Ca C)	0.288	2.904
			f_2(Ca C)	0.074	2.937
			f_3(Ca C)	0.030	3.249
			f_4(Ca C)	0.020	3.415
f_2(Ca O)	0.425	2.333	f_5(Ca O)	0.251	2.419
			f_6(Ca O)	0.096	2.445
			f_7(Ca O)	0.040	2.550
			f_8(Ca O)	0.060	2.520
f_3(C O)[b]	0.000	3.392	f_9(Ca O)	0.040	2.653
			f_{10}(C C)	0.123	2.877
			f_{11}(O O)	0.316	2.744
			f_{12}(O O)	0.224	3.065
f_4(O O)	0.080	3.185	f_{13}(O O)	0.132	2.983
f_5(O O)	0.040	3.203	f_{14}(O O)	0.086	3.075
f_6(O O)	0.028	3.392	f_{15}(O O)	0.069	3.149

a) Unit of distances is in Å. b) Fixed force constants.
c) Units of n and α are in mdyn·Å.

Treatment of the Elastic Constant. When a crystal is subjected to homogeneous deformation, the elastic constant of the crystal can be calculated in accordance with the method established by Shiro.[12] The course of the calculation is outlined below. In the first place, by the use of the resulting matrices of the preceding section, *i.e.*, $\boldsymbol{F}_0{}^{\mathrm{R}}$ and $\boldsymbol{B}_\rho$, and of the external strain matrix, $\boldsymbol{D}$, the (6×6) elastic constant matrix is derived as:

$$\boldsymbol{C}=1/v\tilde{\boldsymbol{H}}\boldsymbol{F}_0{}^{\mathrm{R}}\boldsymbol{H}, \tag{1}$$

where a tilde denotes a transposed matrix, where v is the unit cell volume, and where

$$\boldsymbol{H} = (\boldsymbol{E}-\boldsymbol{B}_\rho(\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_0{}^{\mathrm{R}}\boldsymbol{B}_\rho)^{-1}\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_0{}^{\mathrm{R}})\boldsymbol{D}. \tag{2}$$

The Jacobian matrix with respect to the elastic constant, $(\partial C_i/\partial K_h)$, and the contribution of the h-thp otential term to the i-th elastic constant, $(PED)_{ih}$, are also given:

$$J_{ih}{}^{\mathrm{E}} = (\partial C_i/\partial K_h) = 1/v(\tilde{\boldsymbol{H}}\boldsymbol{A}_h\boldsymbol{H})_{ii}, \tag{3}$$

$$(\mathrm{PED})_{ih} = J_{ih}{}^{\mathrm{E}}K_h/C_i, \tag{4}$$

respectively, where $\boldsymbol{A}_h$ is the coefficient matrix of the k-th term in the potential energy matrix. Furthermore, the change in the internal coordinates due to the elastic stress, $\varDelta\boldsymbol{S}$ is calculated as:

$$\varDelta\boldsymbol{R}_0 = \boldsymbol{H}\boldsymbol{C}^{-1}\varDelta\boldsymbol{S}. \tag{5}$$

The change, $\varDelta\boldsymbol{R}_0$, is found to be useful for the analysis of the elastic strains.

Refinement of the Force Constant. The Jacobians with respect to the optically-active vibrations, $\boldsymbol{J}^\lambda$, and to the elastic constants, $\boldsymbol{J}^{\mathrm{E}}$, are derived independently from the treatments of the preceding sections. The force constants of the force fields were refined by the least-squares method:

$$\varDelta\boldsymbol{K} = (\tilde{\boldsymbol{J}}^\lambda\boldsymbol{W}_\lambda\boldsymbol{J}^\lambda+\tilde{\boldsymbol{J}}^{\mathrm{E}}\boldsymbol{W}_{\mathrm{E}}\boldsymbol{J}^{\mathrm{E}})^{-1} \times(\tilde{\boldsymbol{J}}^\lambda\boldsymbol{W}_\lambda\varDelta\lambda+\tilde{\boldsymbol{J}}^{\mathrm{E}}\boldsymbol{W}_{\mathrm{E}}\varDelta\boldsymbol{C}), \tag{6}$$

where $\boldsymbol{W}^\lambda$ and $\boldsymbol{W}^{\mathrm{E}}$ are diagonal weight matrices for the observed vibrational frequencies and elastic constants respectively, where $\varDelta\lambda$ is a deviation column matrix of the calculated frequencies from the corresponding observed ones, and where $\varDelta\boldsymbol{C}$ is that of the elastic constants.

Results and Discussion

Optically-active Vibrations. The vibrational spectra of calcite and aragonite have been reported by several authors.[13–19] However, it seems likely that the observed resonance frequencies will deviate slightly from the corresponding eigenfrequencies[20] when one come to think of the ionic properties of the two crystals. In our normal coordinate treatments, we postulated an equilibrium crystal field, *i.e.*, any dynamical effects are frozen out, since only the short-range interactions were taken into consideration. Consequently, the eigenfrequencies in the idealized equilibrium field should generally deviate from those in the actual dynamical lattices. We have, however, regarded the observed resonance frequencies as the eigenfrequencies without any correction, because the appropriate estimation of the shifts is impracticable, especially for a complex crystal system. Provided that the shifts are brought about through interactions among the vibrating dipoles, the observed frequencies of the g-symmetric vibrations are found to be approximately equal to those in the equilibrium crystal field.[21] Therefore, we have given some priority to the g-symmetric vibrations over the u-symmetric ones in the course of the refinement of the force constants in calcite.

Ramdas'[13] and Tsuboi's data[14] were adopted as the observed frequencies for the intramolecular vibrations of the carbonate groups and for the (intermolecular) lattice vibrations respectively. In the case of aragonite, though few data are available, Couture's data,[13] which were obtained from the depolarization study of Raman scattering, are noteworthy. Hence, only Couture's data were taken as the observed data, the remaining data[16–19] other than Couture's amounted to no more than supplimentary references.

Intramolecular Vibration of the Carbonate Groups: Carbonate groups in calcite occupy a site, the symmetry of which is $\mathrm{D_3}$, while it is $\mathrm{C_s}$ in aragonite. Because of the lowering of the site symmetry, more numbers of the optically-active frequencies are to be observed in aragonite than in calcite. The intramolecular vibrations in these crystals may, in principle, be explained in terms of the force field of an isolated free carbonate group, since the observed intramolecular frequencies of these crystals show much similarity. The results on force constants are shown in Table 3. The observed and calculated frequencies in calcite and aragonite are also compared in Tables 4 and 5 respectively. It

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) OF CALCITE

Sym.		Obsd.[a]	Calcd.	Assignment	Sym.		Obsd.[a]	Calcd.	Assignment
A_{1g}	ν_{11}	1086	1086	CO str.	A_{1u}	ν_{41}		1089	CO str.
						ν_{42}		211	Ca trans(z).
A_{2g}	ν_{21}		890	CO_3 out-of-plane def.					
	ν_{22}		287	CO_3 trans(z).	A_{2u}	ν_{51}	885	884	CO_3 out-of-plane def.
	ν_{23}		197	CO_3 rot(z).		ν_{52}	290	334	Ca, CO_3 trans(z).
						ν_{53}	110	120	CO_3 rot(z).
E_g	ν_{31}	1434	1428	CO str.					
	ν_{32}	712	710	OCO def.	E_u	ν_{61}	1484	1428	CO str.
	ν_{33}	284	266	CO_3 rot(x, y).		ν_{62}	706	711	OCO def.
	ν_{34}	156	169	CO_3 trans(x, y).		ν_{63}	320	312	CO_3 rot(x, y).
						ν_{64}	230	224	Ca trans(x, y).
						ν_{65}	110	113	Ca, CO_3 trans(x, y).

a) See Refs. 13 and 14.

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) OF ARAGONITE

Sym.		Obsd.[a]	Calcd.	Assignment	Sym.		Obsd.[b]	Calcd.	Assignment
A_{1g}	ν_{11}	1464	1468	CO str.	A_{1u}	ν_{51}		1456	CO str.
	ν_{12}	1086	1090	CO str.		ν_{52}		685	OCO def.
	ν_{13}	854	853	CO_3 out-of-plane def.		ν_{53}		222	CO_3 rot(y).
	ν_{14}	707	717	OCO def.		ν_{54}		140	Ca, CO_3 trans(x).
	ν_{15}	287	275	CO_3 rot(x).		ν_{55}		105	CO_3 rot(z).
	ν_{16}	191	208	CO_3 trans(y).		ν_{56}		99	Ca trans(x).
	ν_{17}	143	146	Ca, CO_3 trans(z).					
	ν_{18}		121	Ca trans(y).	B_{1u}	ν_{61}		1468	CO str.
	ν_{19}	105	99	Ca trans(z).		ν_{62}	1084	1079	CO str.
						ν_{63}	857	851	CO_3 out-of-plane def.
B_{1g}	ν_{21}	1415	1457	CO str.		ν_{64}	712	708	OCO def.
	ν_{22}	716	717	OCO def.		ν_{65}	294	254	CO_3 rot(x).
	ν_{23}		248	CO_3 rot(y).		ν_{66}	200	185	Ca, CO_3 trans(y).
	ν_{24}		197	CO_3 rot(z).		ν_{67}		152	Ca trans(y), (z).
	ν_{25}	154	138	Ca, CO_3 trans(x).		ν_{68}	114	131	Ca trans(y).
	ν_{26}	114	97	Ca trans(y).					
					B_{2u}	ν_{71}	1480	1467	CO str.
B_{2g}	ν_{31}	1415	1457	CO str.		ν_{72}	1082	1084	CO str.
	ν_{32}	702	711	OCO def.		ν_{73}	877	890	CO_3 out-of-plane def.
	ν_{33}	263	247	CO_3 rot(z).		ν_{74}	706	711	OCO def.
	ν_{34}	250	162	CO_3 rot(y).		ν_{75}	274	272	Ca, CO_3 trans(z).
	ν_{35}	208	147	Ca, CO_3 trans(x).		ν_{76}	200	208	CO_3 rot(x).
	ν_{36}	183	73	Ca, CO_3 trans(x).		ν_{77}		169	Ca, CO_3 trans(y).
						ν_{78}	100	87	Ca, CO_3 trans(z).
B_{3g}	ν_{41}	1466	1470	CO str.					
	ν_{42}	1086	1084	CO str.	B_{3u}	ν_{81}	1480	1456	CO str.
	ν_{43}	854	890	CO_3 out-of-plane def.		ν_{82}	712	691	OCO def.
	ν_{44}	703	718	OCO def.		ν_{83}	274	163	CO_3 rot(y).
	ν_{45}	276	273	CO_3 trans(z).		ν_{84}	200	137	Ca, CO_3 trans(x).
	ν_{46}	222	235	CO_3 trans(y).		ν_{85}	118	123	CO_3 rot(z).
	ν_{47}	193	201	CO_3 rot(x).					
	ν_{48}	113	128	Ca trans(y).					
	ν_{49}	105	117	Ca trans(z).					

a) See Ref. 15. b) See Ref. 11.

is obvious from these tables that the large splittings of the frequencies between g-symmetric and u-symmetric C–O stretching vibrations cannot be explained on the basis of the short-range interaction model. Not only the coupling of the motion of the carbonate groups, but also the interaction between the vibrating dipoles would cause these large splittings. These consideration have been made by Haas and Ketelaar,[21] Decius,[22] and Ishigame *et al.*[23] Their results are quite suggestive, but they give only qualitative explanations for complicated crystal systems. These models will actually be applied in our subsequent papers.

For the observed Raman frequency shifts at 1415 cm^{-1} and around 1460 cm^{-1} in aragonite, there are two ways of interpretation. Krishnan[16] regarded only the shift at 1463 cm^{-1} as the fundamental band and assigned the shift at 1415 cm^{-1} to the overtone band of the fundamental band at 707 cm^{-1} on the basis of his second-order Raman scattering study. On the other hand, Krishnamurti[17] considered all these shifts to be fundamental bands. In this study, we have regarded the shift at 1415 cm^{-1} as the fundamental band, with reference to the spectra of carbonate or nitrate crystals.

Lattice Vibration: Normal coordinate treatments of calcite have been performed by Venkateswarlu and Ramaswamy,[24] Tsuboi,[14] Shiro,[25] and Plihal and Schaack;[26] however, no treatment of aragonite has been reported. Though only the short-range interactions were taken into consideration in both Tsuboi's[14] and Shiro's[25] treatments, their results are satisfactory for at least the factor-group vibrations. Assuming an idealized simpler unit cell which contains only four ions, Plihal and Schaack[26] took the long-range Coulomb interaction of vibrating dipoles and the influence of the electronic polarizability of the component ions as well as the short-range interaction; thus they explained fairly well the observed TO–LO splittings of the optically-active lattice vibrations in the calcite-form crystals. A detailed analysis based on the rigid ion model is now in progress; the results will be published in time.

Therefore, we have determined the short-range fields, which reproduce both the observed vibrational frequencies and the elastic constants, and have also improved the previous treatment.[25] Tables 4 and 5 show the observed and calculated frequencies and the tentative assignments of the observed fundamental bands. The contributions of all the potential terms to the calculated vibrational frequencies are also given in Tables 6 and 7. The results of the calculation imply that certain lattice modes in the same symmetry species are fairly well coupled with each other, but that the couplings between an intramolecular mode and lattice modes are negligibly smal, except for the out-of-plane angle deformation modes in carbonate groups. As is shown in Tables 4 and 5, the calculated frequencies of aragonite agree less well with the observed ones than that of calcite, particularly in the B_{2g} and B_{3u} symmetric vibrations. Our resulting force field for calcite is substantially that obtained by Tsuboi.[14] The interatomic force constants will be discussed briefly in a later section.

Elastic Constants. The elastic constants of these crystals have previously been determined [27,28] and tabulated in the "Landolt-Börnstein Phys. Chem. Tables."[29] However, only a few attempts at theoretical calculation have yet been reported. For example, calculations of the two particular constants were performed by Oke[30,31] on the basis of the electrostatic theory of crystal lattices. We have ourselves calculated the elastic constants by the method described above; the calculated elastic constants are compared

TABLE 6. CONTRIBUTION (%) OF POTENTIAL TERMS TO CALCULATED FREQUENCIES FOR CALCITE

Mode	K	H	F	α	p	n	f_1	f_2	f_3	f_4	f_5	f_6
ν_{11}	50	0	46	0	1	0	0	2	0	0	1	0
ν_{41}	50	0	46	0	1	0	0	2	0	0	1	0
ν_{42}	1	0	1	0	0	0	12	86	0	0	0	0
ν_{21}	0	0	0	96	0	0	2	1	0	1	0	0
ν_{22}	0	0	0	1	0	0	3	70	0	4	8	14
ν_{23}	0	0	0	0	0	0	4	4	0	63	23	6
ν_{51}	0	0	0	97	0	0	2	1	0	1	0	0
ν_{52}	0	0	0	0	0	0	5	88	0	0	5	1
ν_{53}	0	0	0	0	0	0	22	1	0	0	67	9
ν_{31}	85	9	6	0	−1	0	1	0	0	0	0	0
ν_{32}	3	30	59	0	0	−1	1	6	0	1	2	0
ν_{33}	0	0	1	0	0	0	2	64	0	25	0	8
ν_{34}	0	0	0	0	0	0	21	32	0	44	0	4
ν_{61}	85	9	6	0	−1	0	1	0	0	0	0	0
ν_{62}	3	29	58	0	0	−1	1	7	0	0	2	1
ν_{63}	0	1	1	0	0	0	13	81	0	0	0	4
ν_{64}	0	1	3	0	0	0	21	73	0	0	0	2
ν_{64}	0	0	0	0	0	0	43	1	0	0	0	55

Notations are the same to Tables 3 and 4.

TABLE 7. CONTRIBUTION (%) OF POTENTIAL TERMS TO CALCULATED FREQUENCIES FOR ARAGONITE

Mode	K	H	F	α	p	n	f_1	f_2	f_3	f_4	f_5	f_6	f_7	f_8	f_9	f_{10}	f_{11}	f_{12}	f_{13}	f_{14}	f_{15}
ν_{11}	83	8	5	0	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ν_{12}	51	0	46	0	−2	0	0	0	0	0	0	0	0	0	0	0	3	1	0	1	0
ν_{13}	0	0	0	98	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ν_{14}	3	29	58	0	0	−1	1	0	0	0	0	0	0	1	0	0	6	2	0	0	0
ν_{15}	0	0	0	0	0	0	4	0	1	0	30	5	0	2	0	0	0	13	11	2	32
ν_{16}	0	0	0	0	0	0	27	5	0	0	6	0	7	7	1	0	0	24	0	3	19
ν_{17}	0	0	0	0	0	0	20	0	0	3	2	24	6	0	1	0	0	13	5	24	1
ν_{18}	0	0	0	0	0	0	2	0	11	3	32	4	0	3	2	0	0	0	0	2	41
ν_{19}	0	0	0	0	0	0	8	7	1	1	3	19	3	10	3	0	0	28	8	2	7
ν_{21}	84	8	5	0	2	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
ν_{22}	3	30	58	0	0	−1	0	0	0	0	0	0	0	0	1	0	0	4	3	2	0
ν_{23}	0	0	0	0	0	0	0	0	0	0	0	9	0	4	2	0	0	28	14	4	39
ν_{24}	0	0	0	0	0	0	0	3	0	0	0	3	3	0	9	0	0	10	34	2	34
ν_{25}	0	0	1	0	0	0	0	29	0	0	0	1	15	23	7	0	0	9	1	0	14
ν_{26}	0	0	0	0	0	0	0	8	0	15	0	35	0	0	11	0	0	7	9	1	14
ν_{31}	84	8	5	0	2	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
ν_{32}	3	30	59	0	0	−1	0	0	0	0	0	0	0	0	1	0	0	4	3	0	0
ν_{33}	0	0	0	0	0	0	0	2	0	0	0	2	2	3	8	0	0	31	34	8	10
ν_{34}	0	0	1	0	0	0	0	2	0	0	0	12	2	6	1	0	0	9	3	22	41
ν_{35}	0	0	0	0	0	0	0	26	0	5	0	26	2	18	8	0	0	5	1	0	9
ν_{36}	0	1	1	0	0	0	0	5	0	1	0	0	38	0	12	0	0	2	25	6	9
ν_{41}	83	8	5	0	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ν_{42}	51	0	47	0	−2	0	0	0	0	0	0	0	0	0	0	0	3	1	0	0	0
ν_{43}	0	0	0	90	0	0	0	0	0	0	0	0	0	0	0	7	0	0	0	0	1
ν_{44}	3	29	58	0	0	−1	1	0	0	0	0	0	0	1	0	0	6	2	0	0	1
ν_{45}	0	0	0	0	0	0	4	1	1	1	22	4	1	0	0	15	0	0	6	0	44
ν_{46}	0	0	0	0	0	0	12	1	1	0	12	4	2	3	0	2	0	42	7	2	11
ν_{47}	0	0	0	0	0	0	13	0	1	0	10	2	5	0	1	1	0	2	2	38	24
ν_{48}	0	0	0	0	0	0	32	12	0	0	0	1	7	24	0	2	0	5	1	8	6
ν_{49}	0	0	0	0	0	0	0	1	4	4	24	36	0	0	5	3	0	1	6	0	14
ν_{51}	84	8	5	0	2	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
ν_{52}	3	32	63	0	0	−1	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
ν_{53}	0	0	0	0	0	0	0	0	0	0	0	13	2	2	0	0	0	0	0	9	73
ν_{54}	0	0	0	0	0	0	0	27	0	0	0	3	0	1	31	0	0	0	0	21	16
ν_{55}	0	0	0	0	0	0	0	12	0	0	0	1	13	51	2	0	0	0	0	17	2
ν_{56}	0	0	0	0	0	0	0	5	0	14	0	30	16	0	9	0	0	0	0	8	18
ν_{61}	83	8	5	0	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ν_{62}	52	0	47	0	−2	0	0	0	0	0	0	0	0	0	0	0	3	0	0	0	0
ν_{63}	0	0	0	98	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ν_{64}	3	30	59	0	0	−1	1	0	0	0	0	0	0	1	0	0	5	0	0	0	0
ν_{65}	0	0	0	0	0	0	0	0	0	0	31	0	0	0	2	0	0	0	0	15	51
ν_{66}	0	0	0	0	0	0	42	0	2	0	18	2	11	0	1	0	0	0	0	16	7
ν_{67}	0	0	0	0	0	0	13	1	4	5	18	42	1	1	1	1	0	0	0	0	14
ν_{68}	0	0	0	0	0	0	11	16	3	0	4	3	3	34	0	0	0	0	0	17	8
ν_{71}	83	8	5	0	2	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ν_{72}	51	0	46	0	−2	0	0	0	0	0	0	0	0	0	0	0	3	0	0	1	0
ν_{73}	0	0	0	90	0	0	0	0	0	0	0	0	0	0	0	7	0	0	0	0	1
ν_{74}	3	30	59	0	0	−1	1	0	0	0	0	0	0	1	0	0	5	0	0	0	1
ν_{75}	0	0	0	0	0	0	3	0	1	0	19	1	1	0	1	16	0	0	0	10	48
ν_{76}	0	0	0	0	0	0	11	2	1	2	33	18	1	7	1	3	0	0	0	0	20
ν_{77}	1	0	0	0	0	0	43	6	1	0	9	4	13	9	2	0	0	0	0	1	12
ν_{78}	0	0	0	0	0	0	0	3	7	6	4	16	0	6	0	0	0	0	0	3	53
ν_{81}	84	8	5	0	2	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
ν_{82}	3	32	62	0	0	−1	0	0	0	0	0	0	0	0	1	0	0	0	0	2	1
ν_{83}	0	0	0	0	0	0	0	12	0	2	0	38	6	0	9	0	0	0	0	7	25
ν_{84}	0	0	0	0	0	0	0	17	0	3	0	0	5	34	3	0	0	0	0	7	30
ν_{85}	0	0	0	0	0	0	0	6	0	1	0	0	11	4	31	0	0	0	0	1	46

Notations are the same to Tables 3 and 5.

TABLE 8. OBSERVED AND CALCULATED ELASTIC CONSTANTS (10^{10} dyn/cm^2) OF CALCITE AND ARAGONITE

D_{3d}^6	Calcite			D_{2h}^{16}	Aragonite		
	Obsd.[a)]	Calcd.	Sym.		Obsd.[b)]	Calcd.	Sym.
C_{11}	144.0	118.7	A_{1g}, E_g	C_{11}	160.0	165.2	A_{1g}
C_{21}	53.9	49.9	A_{1g}, E_g	C_{21}	37.0	39.1	A_{1g}
C_{31}	51.1	52.8	A_{1g}	C_{22}	89.2	73.4	A_{1g}
C_{33}	84.0	75.5	A_{1g}	C_{31}	1.7	19.8	A_{1g}
C_{41}	−20.5	−20.9	E_g	C_{32}	15.4	24.6	A_{1g}
C_{44}	33.5	33.0	E_g	C_{33}	84.2	89.2	A_{1g}
				C_{44}	41.2	23.2	B_{3g}
				C_{55}	25.6	17.3	B_{2g}
				C_{66}	42.7	24.1	B_{1g}

a) See Ref. 27. b) See Ref. 28.

TABLE 9. CONTRIBUTION (%) OF POTENTIAL TERMS TO CALCULATED ELASTIC CONSTANTS

	Aragonite										Calcite					
	11	21	22	31	32	33	44	55	66		11	21	31	33	41	44
K	2	3	1	1	1	0	0	0	0	K	1	2	1	0	1	0
H	1	−1	0	0	0	0	0	0	0	H	0	−1	0	0	2	1
F	4	1	1	0	0	0	0	0	0	F	2	0	1	0	4	1
α	0	0	0	0	0	0	0	0	0	α	0	0	0	0	0	0
p	0	0	0	0	0	0	0	0	0	p	0	0	0	0	0	0
n	0	0	0	0	0	0	0	0	0	n	0	0	0	0	0	0
f_1	1	5	4	2	2	0	7	0	0	f_1	21	15	16	5	38	26
f_2	5	13	4	12	6	1	4	7	0							
f_3	0	2	2	1	3	0	5	0	0							
f_4	1	3	1	6	3	1	3	9	2							
f_5	0	1	1	5	8	4	4	0	0	f_2	43	75	69	40	43	43
f_6	2	11	7	27	25	8	5	25	4							
f_7	0	2	1	1	1	0	1	1	10							
f_8	1	8	13	5	12	1	10	2	1							
f_9	5	−3	0	6	−1	0	0	6	2	f_3	0	0	0	0	0	0
f_{10}	0	0	0	0	−5	20	0	0	0							
f_{11}	69	−2	0	0	0	0	0	0	0							
f_{12}	0	4	8	−1	−3	0	10	0	16							
f_{13}	5	29	20	2	2	0	0	7	17	f_4	2	−5	5	33	20	23
f_{14}	2	23	28	28	52	9	8	13	37	f_5	26	18	−1	0	−2	0
f_{15}	0	0	7	4	−6	56	42	30	5	f_6	4	−4	9	20	−5	6

Notations are the same to Tables 3 and 8.

with the observed ones in Table 8. It is obvious from these results that a good agreement was obtained for calcite, while only a rough fit was obtained for aragonite. Particularly, the agreement of the elastic constants related to the shear strains, *i.e.*, C_{44}, C_{55}, and C_{66}, is relatively poor in aragonite because of the lack of effective oblique interaction terms compared with those in calcite. The contributions of all the potential terms to the calculated elastic constants are also listed in Table 9. This table shows that the elastic constants have a strong dependence on the following potential terms; f_1, f_2, f_4, and f_5 in calcite, and f_2, f_6, f_8, f_{13}, f_{14}, and f_{15} in aragonite. It is likely that these contributions are partly dependent on the spatial orientation of the internal coordinates. These contributions are considered to be independent of those to the vibrational frequencies, as is shown in Tables 6 and 7; therefore the determination of the interatomic force constants becomes more meaningful.

Interatomic Force Constants. The resulting interatomic force constants are plotted as functions of the interatomic distance in Fig. 5. As this figure illustrates, three steep curves can be drawn through the points of the same pairs, and the distances of their burst upbreaks approximately correspond to the sums of the van der Waals radii or of the Pauling's ionic radii[32)] of the constituent atoms, as shown in Fig. 5: $R_{Ca}+R_O=2.39$ Å, $R_{Ca}+R_C=2.69$ Å, and $2R_O=2.80$ Å. Since these interatomic interaction force constants should be derived from the appropriate interatomic potentials, we began to estimate them with simple Lennard-Jones 6-9 type potentials[33)] determined for some purely ionic crystals and noble gas crystals; however, we thus obtained unreasonable results except

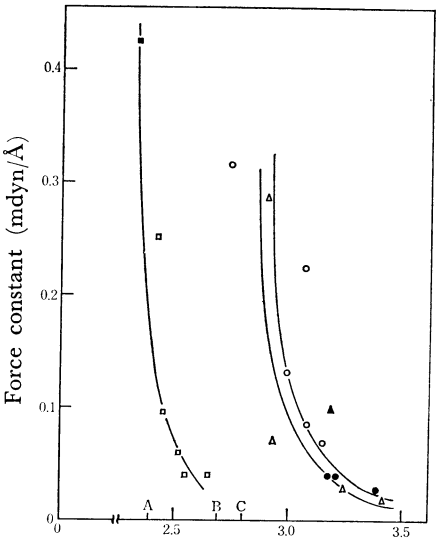

Fig. 5. Interatomic force constants. Closed and open figures indicate those for calcite and aragonite respectively.
△, calcium···carbon; □, calcium···oxygen; ○, oxygen···oxygen; R_C, van der Waals radius of carbon; R_O, van der Waals radius of oxygen; R_{Ca}, Pauling's ionic radius of calcium.
A: $R_{Ca}+R_O$, B: $R_{Ca}+R_C$, C: R_O

for a few cases. We inevitably chose several trial sets of them which reproduced the observed values as well as possible, and then refined by the least-squares method.[12] As is shown in Fig. 5, some plots were found to deviate from the corresponding curves. This must mainly be because of the uncertainty of the experimental frequencies and/or elastic constants, and the incompleteness of the force fields. The former is considered to have an appreciable influence on the force constants in aragonite, while both the observed frequencies and elastic constants were found to be fairly reliable in calcite. The results listed in Tables 6 and 9 suggest that the force constant, f_1, of calcite contributes particularly to certain lattice modes and to all the elastic constants except C_{33}. If this force constant is reduced to the value on the curve, less agreement will be obtained. Therefore, the large deviation of the closed triangle must arise mainly from the incompleteness of the force field. The incompleteness of the force field can be improved by the rigid ion treatment or by the polarizable ion treatment; these treatments are now in progress. As to the open circles in Fig. 5, f_{11} was found to contribute in particular to C_{11} (see Table 9), and f_{12}, to almost all the lattice modes in aragonite. Therefore, the incompleteness must exert an appreciable influence on the force constants, above all, the force constants which are closely related to the lattice vibrations in aragonite.

The force constants obtained would be useful as the initial values of the force constants in the normal coordinate treatments of similar crystals, though it is meaningless to discuss certain fundamental properties of the solid state on the basis of only these data.

Analysis of Elastic Strain. Table 10 shows the change in the internal coordinates due to unit elastic stress in calcite. We can see from this table that the q_5 coordinate is sensitive to the S_{xx} applied stress, the q_3, q_5, and q_6 coordinates, to the S_{zz} stress, and the q_3, q_4, and q_5 coordinates, to the S_{yz} stress. The internal coordinates of calcite, therefore, can be changed by the applied stress along the direction z. For aragonite, Table 11 suggests that the q_4, q_6, q_{14}, and q_{15} coordinates a strong dependence on the appropriate stresses. As well as in calcite, it seems that calcium atoms in aragonite would be easy to displace in the directions to the adjacent carbonate groups, and that the carbonate would be susceptible to certain deformations along the

TABLE 10. CHANGE (Å^3/mdyn) OF INTERNAL COORDINATES DUE TO ELASTIC STRESS IN CALCITE

Coord.[b]	S_{xx}	S_{yy}	S_{zz}	S_{yz}
CO str.	1	1	0	1
OCO def.[a]	−3	3	0	−2
CO_3 out-of-plane[a]	0	0	0	0
q_1	4	42	−1	−70
q_2	10	16	19	58
q_3	27	−65	121	−156
q_4	−18	−46	144	−109
q_5	142	−26	−72	−110
q_6	−36	−74	121	−64

a) Unit of angle coordinates is in Rad·Å^2/mdyn. b) Notations are the same to Fig. 3.

TABLE 11. CHANGE (Å^3/mdyn) OF INTERNAL COORDINATES DUE TO ELASTIC STRESS IN ARAGONITE

Coord.[b]	S_{xx}	S_{yy}	S_{zz}	S_{yz}	S_{zx}	S_{xy}
	A_{1g}	A_{1g}	A_{1g}	B_{3g}	B_{2g}	B_{1g}
CO str.	2	0	0	−1	0	−1
	0	1	0	0	0	0
OCO def.[a]	−4	2	0	−1	−1	−9
	5	−3	0	1	0	0
CO_3 out-of-plane[a]	1	1	0	0	0	0
q_1	4	15	1	−27	0	0
q_2	28	21	12	−41	78	5
q_3	−2	42	7	73	0	0
q_4	22	17	32	63	−164	−55
q_5	2	7	19	23	0	0
q_6	12	27	44	41	−124	−35
q_7	9	16	6	−26	−40	88
q_8	−4	70	9	−73	41	−20
q_9	51	−37	19	2	95	41
q_{10}	3	−18	70	−1	0	0
q_{11}	63	−28	4	0	0	0
q_{12}	−3	31	−10	−37	4	47
q_{13}	12	54	−8	−7	−57	62
q_{14}	1	77	40	−54	−95	114
q_{15}	10	−55	91	52	104	23
	11	−32	93	−54	−122	38
	−6	19	89	−116	5	−14

a) Unit of angle coordinates is in Rad·Å^2/mdyn.
b) Notations are the same to Fig. 4.

z axis. From these considerations, some information will be gained about the phase transitions between polymorphic crystals, though we cannot reach any definite conclusions on the basis of these data only.

Numerical calculations have been carried out on the TOSBAC 3400 MODEL 41 electronic computer at the Computing Center of Hiroshima University. The authors wish to express their gratitude to Professor Michiro Hayashi of Hiroshima University for his encouragement throughout this work, and also to Mr. Masaru Ohsaku and Mr. Tamaki Utida of Hiroshima University for part of numerical computations and their advisable discussions.

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