Optically-active Vibrations and Effective Charges of Calcite and Magnesite[1)]

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A rigid-ion model analysis was made for the optically-active crystal vibrations of calcite ($CaCO_3$) and magnesite ($MgCO_3$) with reference to the previous vibrational treatments. The effects of the effective charge distribution on the TO–LO splittings of the lattice modes were examined on the proposed distribution model, and the effective charges have been found: $Z_{Ca}=1.21$, $Z_C=0.20$, and $Z_O=-0.47$ in calcite, and $Z_{Mg}=1.28$, $Z_C=0.21$, and $Z_O=-0.50$ in magnesite, all in electron units. The force fields and effective charges determined in the present study reproduce satisfactorily the observed transverse and longitudinal frequencies of the optically-active lattice vibrations.

The vibrational spectra of calcite and magnesite have been studied by many investigators[2—14)] in connection with those of the isomorphic crystals with the calcite structure. In this work, our attention will be confined to the optically-active vibrations of calcite and magnesite; the vibrations will be analyzed on the basis of the rigid-ion model.[15)] In the rigid-ion formulation, account is taken only of the long-range Coulomb interactions of vibrationally-induced dipoles as those of rigid point dipoles; any contribution originating in the distortion of the electronic distribution is implicitly neglected. The model has been extensively applied to the vibrational analysis of relatively simple crystals[16,17)] and has been found to give less good results for the explanation of phonon-dispersion relations[18)] than the more elaborate models.[19,20)] We will, however, apply the model to the vibrational analysis of the calcite-type crystals, since only a small number of unknown parameters are introduced in taking the Coulomb interactions, and since a fairly good agreement can be obtained at least between the calculated and observed optically-active vibration frequencies.[21)]

Method of Calculation

Crystal Structure. Calcium carbonate and magnesium carbonate crystallize in a calcite structure. The primitive unit cell is trigonal, and two formula units are present in it. The space group is D_{3d}^6–$R\bar{3}c$, and the cell constants[22)] of calcite and magnesite are $a_{rh}=6.375$ Å and $\alpha=46°5'$, and $a_{rh}=5.675$ Å and $\alpha=48°11'$ respectively. In the calcite-type lattices, each metal atom is coordinated by six oxygen atoms of different carbonate groups, and each such atom is bound to two metal atoms, as is illustrated in Fig. 1.

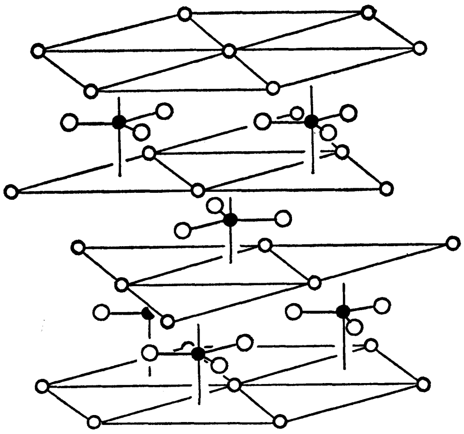

Fig. 1. Crystal structure.
○, Ca or Mg; ●, C; ○, O,

Normal Coordinate Treatment. A dynamical matrix is composed of two constituents:[15)]

$$\boldsymbol{D}=\boldsymbol{D}^s+\boldsymbol{D}^c,$$

where $\boldsymbol{D}^s$ and $\boldsymbol{D}^c$ are the short-range non-Coulomb and the long-range Coulomb interaction parts respectively; $\boldsymbol{D}^c=\boldsymbol{ZCZ}$, where $\boldsymbol{C}$ represents the long-range Coulomb interactions and $\boldsymbol{Z}$ is a diagonal matrix, the elements of which are effective charges.

Short-range Part: An application of the *GF*-matrix method[23)] to the analysis of optically-active crystal vibrations was previously reported by Shimanouchi *et al.*[24)] In the present study, a modified Urey-Bradley force field[25)] was applied to the intramolecular vibrations of carbonate groups, the correction terms of which were the bond interaction term, *p*, and the angle interaction term, *n*. On the other hand, a central force field was used for the lattice vibrations,

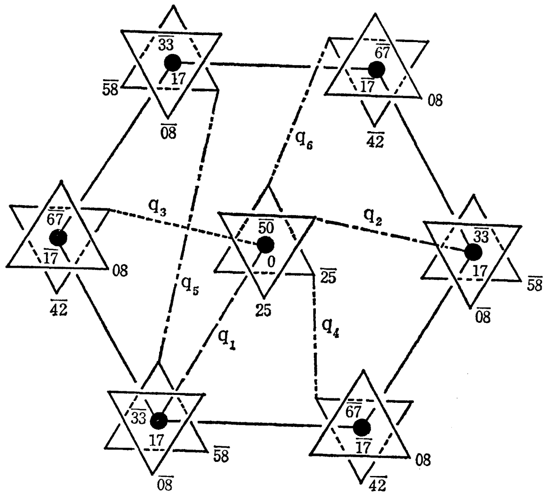

Fig. 2. Short-range interactions, projected on a plane perpendicular to the z axis of the hexagonal cell. The heights of atoms or carbonate groups are expressed in units of $100/c_0$.
(——), Ca or Mg···C; (······), C···O; (—·—), Ca or Mg···O; (—··—), O···O,

TABLE 1. INTERNAL COORDINATES IN CALCITE AND MAGNESITE

Coord.[a]	F. C.[b]	Distance (Å)	
		Calcite	Magnesite
R	K(C–O)	1.294	1.286
θ	H(O–C–O)	(120°)	(120°)
	F(O···O)		
ϕ[c]	$\alpha(CO_3)$		
	p[d]		
	n[d]		
q_1	f_1(M···C)[e]	3.213	2.953
q_2	f_2(M···O)[e]	2.353	2.102
q_3	f_3(C···O)	3.406	3.019
q_4	f_4(O···O)	3.189	2.849
q_5	f_5(O···O)	3.249	2.924
q_6	f_6(O···O)	3.406	3.019

a) Notations are the same to Fig. 2. b) Force constants. c) Out-of-plane angle deformation coordinate. d) Correction terms. See text. e) M: Ca or Mg.

where only the pairs that lie within 3.5 Å were taken into consideration as effective short-range terms. As is shown in Fig. 2, there are six kinds of pairs in these crystals; the interatomic distances are given in Table 1.

Long-range Coulomb Part: In ionic crystals, the long-range Coulomb interactions are considered to play an important role in the splitting of a longitudinal mode frequency, ν_l, from the transverse ν_t. The Coulomb interaction part, $\boldsymbol{D}^c$, was calculated with the expression established by Born and Huang,[15] where the magnitude of the wave vector must be set at zero for the optically-active vibrations. In the Born and Huang expression, the $\boldsymbol{Q}$ term is a tensor of the second rank, the elements of which are called "the dipole lattice sum." The evaluation of the sum has been discussed in several places;[15,26,27] the actual calculations were performed by the use of the computer program PEG0.[28]

In contrast with simple crystals, some additional charge parameters must be introduced into these crystals, since the distribution of the effective charges in the unit cell is not known in advance. As is shown in Fig. 3, we have assumed the charge distribution on the carbonate groups under electrically neutral conditions.

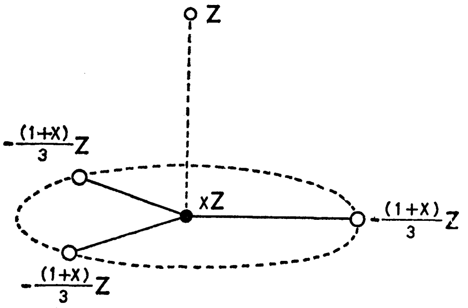

Fig. 3. Charge distribution.
○, O; ○, Ca or Mg; ●, C; Z, magnitude of effective charge in electron units; x, charge distribution parameter.

In the same manner as with short-range force constants,[29] one of the Coulomb parameters, *i.e.*, Z, can be refined by the least-squares method, since the Coulomb part has a common factor, Z^2, for a fixed distribution parameter, x.

The actual calculations were carried out on the TOSBAC 3400 TOPS 14 electronic computer at the Computing Center of Hiroshima University.

TABLE 2. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1})[a]

Sym.	Calcite				Magnesite			
	ν_t^{obsd}	ν_l^{obsd}	ν_t^{calcd}	ν_l^{calcd}	ν_t^{obsd}	ν_l^{obsd}	ν_t^{calcd}	ν_l^{calcd}
A_{1g}	1086		1086		1096		1095	
A_{1u}	—		1088		—		1101	
	—		255		—		345	
A_{2g}	—		884		—		906	
	—		254		—		349	
	—		192		—		315	
A_{2u}	872	890	874	885	876	911	881	899
	303	387	321	375	362	459	363	458
	92	136	93	133	230	281	236	268
E_g	1434		1424		1460		1451	
	712		714		735		745	
	284		262		332		332	
	156		165		212		213	
E_u	1407	1549	1424	1429	1436	1599	1451	1459
	712	715	712	713	747	783	743	745
	297	381	296	357	356	475	353	464
	223	239	226	234	301	315	310	314
	102	123	101	123	225	241	226	239

a) Observed frequencies are taken from Refs. 4, 5, and 11. ν_t, transverse frequency; ν_l, longitudinal frequency.

Results and Discussion

In calcite and magnesite, only the E_u and A_{2u} modes are infrared-active. The non-zero dipole moment is induced parallel to the z axis in the A_{2u} modes and normal to the axis in the E_u modes. When the wave vector $\mathbf{y}\rightarrow\mathbf{0}//z$, the A_{2u} modes are identified as the longitudinal modes, and the E_u, as the transverse. On the other hand, when $\mathbf{y}\rightarrow\mathbf{0}\perp z$, the E_u modes are longitudinal and the rest transverse.

Intramolecular Vibration. The intramolecular vibration modes have the following irreducible representations:[3)]

$$\Gamma_n = A_{1g} + A_{1u} + A_{2g} + A_{2u} + 2E_g + 2E_u.$$

The observed[4,5,11)] and calculated vibrational frequencies are compared in Table 2. It is shown that the interactions between the induced dipoles and the macroscopic field appear to exert little effect on the intramolecular modes. Since an out-of-plane angle deformation mode is accompanied by translational motions along the direction perpendicular to the tightly binding plane, the interactions may be fairly well approximated by the present model as compared with those of the other intramolecular modes. In an in-plane vibrational mode, however, the vibrational motions in the tightly binding regions should be actually followed by an intense electronic polarization originating in the distortion of the electronic distribution. Therefore, the polarization due to the electronic interactions between tightly binding atoms is likely to contribute predominantly to the total polarization rather than that due to the long-range electrostatic interactions between rigid dipoles in the above regions. It may be concluded that the rigid-ion approximation is not suitable for the interpretation of the dynamical properties of tightly-bonded systems, *e.g.*, the in-plane intramolecular vibration modes in these crystals. These subjects have been in part discussed by Decius *et al.*,[30–34)] by Ishigame *et al.*,[35)] and by Donoghue *et al.*[36)] No quantitative explanation of the experimental results seems to have been made, though their discussions are quite suggestive. Further study based on some elaborate models will, therefore, be essential in order to obtain a satisfactory agreement with these experimental results.

Lattice Vibration. It can be shown from the factor-group theory[3)] that the optical lattice modes are: $2A_{2g}+2E_g+A_{1u}+2A_{2u}+3E_u$. The observed[11)] and calculated vibration frequencies are listed in Table 2, showing that the calculated frequencies for the lattice modes are in good agreement with the observed frequencies. The reason for this may be that the lattice vibration is considered to be essentially concerned with the relative motions of weakly interacting groups; therefore, the dynamical properties of these systems can be fairly well approximated by the rigid-ion model.

An introduction of the Coulomb interaction terms will change some vibrational modes from the corresponding non-Coulomb interaction modes; it has been found in some critical cases[37)] that the changes are so serious that even the vibrational assignments of the fundamental bands must be modified from those determined from the non-Coulomb point of view. By examining the calculated eigenvectors carefully, it is found that there is not such a significant change in TO modes as in the above critical cases. Small changes, however, are noticeable in the LO modes, especially in the "polar" modes, which give rise to a large polarization. For instance, two polar modes, the modes which have high LO frequencies about 400 cm^{-1} in the A_{2u} and E_u symmetry, are seen to become more translational along the macroscopic field than the corresponding TO modes through additional interactions with the field.

Normal coordinate treatments have been made for calcite[38–41)] on the basis of the short-range interaction models. In addition to these treatments, the long-range Coulomb interactions have been introduced by two groups of workers. First, both the interactions between the vibrationally-induced dipoles and the influence of the electronic distortion have been taken into account in the shell model by Plihal and Schaack.[42)] They regarded a carbonate group as one bulky ion whose charge is located at the center of the group; they analyzed the optically-active vibrations of the three minerals of the calcite structure. Their rigid-ion model corresponds essentially to the present distribution model with $x=-1$; however, the results on these crystals were not given in their paper. If one assumes this charge distribution, any influence of the long-range interactions appears in the translational lattice modes; consequently, the Z-dependency of the lattice vibration is monotonic. In spite of their rather crude approximation, the calculated frequencies are in fair accord with the experimental results. Recently, phonon-dispersion relations were calculated for calcite by Plihal[43)] by using the same model; however, the results have not been compared in detail with the observed results. Secondly, a rigid-ion model analysis was made for calcite by Onomichi.[44)] He took, for the sake of simplicity, only four short-range force constants into consideration; therefore, the agreement with his observed values was seen to be less good. The effective charges attributed to the constituent atoms are read as $Z_{Ca}=1.86$, $Z_O=0.074$, and $Z_C=-2.08$ respectively in electron units; a positive value, though relatively small, was given on the most electrically-negative oxygen atom. The present authors have allowed only a negative charge on oxygen atoms from the chemical point of view.

Force Constants and Effective Charges. The short-range force constants and the effective charges are shown in Table 3. In the present study, account is taken separately of the long-range Coulomb interactions, and all of the short-range force constants need not have positive values; therefore, the physical meaning of the force constants is considered to be different from that in the previous short-range force models.

In performing the optimization procedures, some force constants were changed appreciably with the distribution models; however, the magnitude term, Z, was found to fall mostly into the range from 1.0 to 1.3, regardless of the distribution. Though the calculated TO–LO splittings seem to depend critically on the Z

TABLE 3. SHORT-RANGE FORCE CONSTANTS (mdyn/Å) AND EFFECTIVE CHARGES (electron unit)

F. C.[a]	Calcite	S. D.[b]	Magnesite	S. D.[b]
K	5.647	0.008	5.758	0.035
H	0.340	0.000	0.340	0.015
F	1.720	0.001	1.720	0.013
α	0.444	0.003	0.447	0.002
p	−0.012[c]		−0.092	0.019
n[d]	0.043	0.000	0.032	0.016
f_1	0.030[c]		0.091[c]	
f_2	0.605	0.005	0.642	0.003
f_3	0.000[c]		0.000[c]	
f_4	0.074[c]		0.168	0.009
f_5	−0.016	0.001	0.081	0.002
f_6	−0.021	0.002	0.056	0.001
Z_M[e]	1.21	0.08	1.28	0.01
Z_C	0.20		0.21	
Z_O	−0.47		−0.50	

a) Notations are the same as those in Table 1. b) Standard deviation. c) Fixed force constants. d) Unit of n in mdyn·Å. e) Effective charge of metal atom.

term rather than on the x term, the x-dependency of the calculated splittings changes slightly from model to model[21] through the oxygen-oxygen interactions.

A careful comparizon of the calculated and found frequencies has given a fairly good agreement for $x=1/6$, though the lattice-mode frequencies are not so sensitive to the distribution parameter, x, in the range from -1.0 to 0.75 as to the Z parameter. Those distribution models which have values of x larger than unity were seen to give poorer results. The effective charge of the cation in magnesite is larger than that in calcite; the order of magnitude is consistent with the expectation based on the experimental TO–LO separations, and also with that of the effective charges determined for oxide crystals.[45]

In general, effective charges which interpret the sums of the observed TO–LO splittings may, in principle, be estimated for each infrared-active symmetry species by this relation:[17]

$$\sum\omega_l^2 - \sum\omega_t^2 = \mathrm{Trace}\{\boldsymbol{D}_l-\boldsymbol{D}_t\},$$

where ω and $\boldsymbol{D}$ are the circular frequency of the vibration and the dynamical matrix respectively, where the subscripts l and t specify longitudinal and transverse properties respectively, and where the summations are extended over the infrared-active modes. All the charges obtained by using the relation are, however, considered not to be reasonable: for instance, when the frequencies are distributed separately with wide gaps, the TO–LO splittings of the lower frequency modes are essentially neglected in the course of calculation. In these crystals, the charges which may explain appropriately the observed TO–LO separations of the modes around 1400 cm^{-1} were calculated to be extraordinary values about 5 in electron units; with these values, it is quite difficult to explain the TO–LO splittings of the lattice modes. The reason may be that the intense electronic polarization can hardly be reproduced by the point-dipole approximation, as has been mentioned above. However, its utility can best be appreciated by reference to the limitations of the rigid-ion model. Since the contribution of the lattice modes can be estimated fairly well, appropriate change parameters can be obtained when the lattice-mode frequencies are used.

A recent neutron inelastic scattering study will now be discussed briefly. Cowley and Pant[46] performed a simple shell-model analysis of the phonon-dispersion relations for the lowest-ten external branches and for the wave vectors along the optic axis; they obtained the following effective charges: $Z_{Ca}=2.3$, $Z_C=0.27$, and $Z_O=-0.87$, all in electron units. The value of Z_{Ca} is the largest of all the values[42,44] reported thus far. It is not clear at present whether the discrepancy among them depends on the electronic polarizability or on the choice of parameters. Since the intramolecular modes of vibration are influenced by the electronic polarizability [30–34] as well as the lattice modes, the effects of the Coulomb interactions must be estimated so as to reproduce simultaneously both types of vibration. Special attention should also be given to the fact that the two vibrational frequencies of the optically-inactive modes were determined to be 309 cm^{-1} and 172 cm^{-1}.

The charge distribution on molecules or groups has been estimated from the cohesive energies of crystals[47] or from the electronegativities[48,49] of constituent atoms. Those obtained are, however, considered to be static by nature; consequently, they need not always coincide with the present dynamically-effective charges. Even in these studies, the resulting distributions are seen to differ considerably with either investigators or methods.

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