Coulomb Interactions and Optically-active Vibrations of Calcite-type Carbonates[1)]

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(Received December 22, 1975)

Polarizable-ion model calculations are made for optically-active vibrations of five carbonates with calcite structures: calcite, magnesite, dolomite, rhodochrosite, and smithsonite. The fit to the experimental TO-LO splittings of the internal modes is found to be greatly improved by the introduction of ionic polarizabilities. It is also ascertained that the electronic polarizabilities of constituent atoms must be regarded as anisotropic in order to interpret the optical anisotropy. The resulting force constants for non-bonded oxygen-oxygen interactions can give the correct orders of magnitude for the Lennard-Jones potential constants.

This paper is complementary to a preceding paper,[2)] denoted as Paper I hereafter, on the lattice dynamics of sodium nitrate. There we described a method of polarizable-ion (PI) model calculations[3)] for partially ionic crystals, together with an illustrative example. The object of the present paper is to report the results of a systematic application of the PI model to several important carbonates with a calcite structure, *viz.*, $CaCO_3$, $MgCO_3$, $CaMg(CO_3)_2$, $MnCO_3$, and $ZnCO_3$, and also to test the adequacy of the force field in Paper I.

The structure and symmetry properties of calcite-type crystals have been described on several occasions,[4)] the structure being rhombohedral with 10 atoms in the primitive cell. As is shown in Fig. 1, the space groups of dolomite and the others[5,6)] are $R\bar{3}$ and $R\bar{3}c$ respectively. Our lattice dynamical interest in carbonate crystals is a result especially of the fact that their chemical bonds are fairly intermediate between those of ionic and covalent crystals: both the splittings of the transverse optic (TO) and longitudinal optic (LO) branches and the internal vibrations of quite high frequencies bear little resemblance to typical ionic and/or covalent crystals.

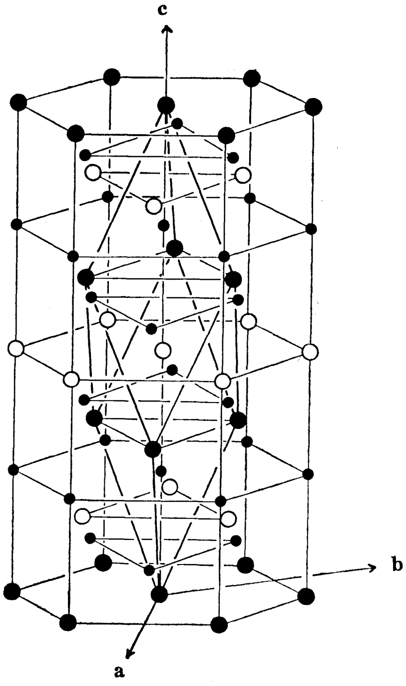

Fig. 1. Crystal structure of calcite-type carbonates. ○, ●: Metal, •: Carbonate.

In the vibration treatments, the estimation of the non-Coulomb contribution of carbonate groups to the potential energy is feassible by the use of a modified Urey-Bradley force field. On the other hand, the contribution due to the partially ionic nature of the bindings is characterized by using the method of lattice dynamics developed for simple crystals.[3)] One of the simplest models to take the Coulomb interactions explicitly may be the rigid-ion (RI) model[3,7)] with short-range forces. The present author and his coworkers have analyzed the optically-active vibrations of carbonate crystals[8,9)] on the basis of the RI model. It is concluded that the calculated TO-LO separations of the intermolecular vibration modes are fairly comparable with the experimental results, but that those of the intramolecular modes do not agree with the observed separations. Then we introduce a model where the effects of the electronic polarizabilities[3,10,11)] can be appropriately taken into account. The shell model[10)] may be one of the most elaborate models for such a purpose; it has been successfully used in the analysis of phonon dispersion relations and of specific heats of simple crystals. As for the shell model, however, we sometimes find it difficult to determine the unmanageable number of Coulomb parameters uniquely. Thus, the PI model of Born and Huang[3)] has been employed; this model is used with a certain extension in an attempt to incorporate the anisotropy of the electronic polarizability. The effects of the distortion of electronic distributions on the crystal vibrations can be rigorously estimated by the model; however, higher-order multipole effects are implicitly neglected, for we believe them to be much less important. In order to evaluate the Coulomb components of the dynamical matrix,[3)] we take the constituent atoms to be point ions of unknown charges and electronic polarizabilities; then those which can best explain the observed Coulomb interactions are determined to be the effective ionic charges and electronic polarizabilities.

Method of Calculation

The method has been described in detail in Paper I; here we shall merely quote the results relevant to the present work. From the Born and Huang theory,[3)] a dynamical matrix is constructed from four constituents:

$$\mathbf{D} = \overline{\mathbf{M}}(\mathbf{F}^{\mathrm{N}}+\mathbf{F}^{\mathrm{C}}+\mathbf{F}^{\mathrm{I}}+\mathbf{F}^{\mathrm{M}})\overline{\mathbf{M}},$$

where $\overline{\mathbf{M}}_{\alpha\beta\mathrm{kk}'}=\delta_{\alpha\beta}\delta_{\mathrm{kk}'}m_{\mathrm{k}}^{-1/2}$, where α and $\beta=x$, y or z, and where m_{k} and δ are the mass of the k-th kind of atom and the usual Kronecker delta symbol respectively. The first term arises from short-range non-Coulomb interactions; both the central force interactions of non-bonded atom pairs within 3.5 Å and the non-central force interactions of carbonate groups are taken into consideration. A complete description of them has been given elsewhere,[8,9] denoted by Papers II, and the notations of these papers are used here. The second and third terms are due to rigid-ion and induced-dipole interactions respectively. In the long-wavelength limit, the terms are thus far independent of the direction of the wave propagation. The last term is the macroscopic field part and is dependent on the direction.

Now, to proceed with the actual calculations we require the numerical values of the ionic charges and electronic polarizabilities of the constituent atoms. Unlike simple crystals, the situation is complicated here by the fact that the distribution of the ionic charges is not known in advance. Two disposable parameters, x and Z, have been introduced in order to represent the distribution under electrically neutral conditions: $Z_{\mathrm{Metal}}=Z$, $Z_{\mathrm{c}}=xZ$, and $Z_{\mathrm{o}}=-(1+x)Z/3$. Furthermore, the ratio of Z_{Ca} to Z_{Mg} for dolomite was taken to be that of the Szigeti charges,[12] since the results do not depend on the ratio.[9] The electronic polarizability can be easily incorporated in tensor form by generalizing the Born and Huang expressions.[3] In order to reduce the number of disposable parameters, it is assumed that the off-diagonal elements of the polarizability tensors are negligibly small. It is then shown from the crystal symmetry that only two of the diagonal elements are independent, *i.e.*, $\alpha_{11}(\mathrm{k})=\alpha_{22}(\mathrm{k})$ $(=\alpha_{\perp}(\mathrm{k}))\neq\alpha_{33}(\mathrm{k})(=\alpha_{/\!/}(\mathrm{k}))$. The electronic polarizabilities of the constituent atoms were recalculated in order to take the anisotropy into account by using this expression:

$$\boldsymbol{\varepsilon}_{\infty} = \mathbf{I} + 4\pi v^{-1}\boldsymbol{\rho},$$

where $\boldsymbol{\varepsilon}_{\infty}$ is the macroscopic dielectric susceptibility tensor at a frequency higher than where the lattice vibration will contribute. $I_{\alpha\beta}=\delta_{\alpha\beta}$, v is the unit cell volume, and

$$\rho_{\alpha\beta} = \textstyle\sum_{\mathrm{kk}'}\{(\mathbf{I}'-\mathbf{A}\mathbf{Q})^{-1}\mathbf{A}\}_{\alpha\beta\mathrm{kk}'}.$$

In this expression, $I'_{\alpha\beta\mathrm{kk}'}=\delta_{\alpha\beta\mathrm{kk}'}$, $A_{\alpha\beta\mathrm{kk}'}=\alpha_{\alpha\beta}(\mathrm{k})\delta_{\mathrm{kk}'}$, $\boldsymbol{\alpha}(\mathrm{k})$ is the polarizability tensor of the k-th kind of atom, and $\mathbf{Q}$ denotes the Coulomb coefficient matrix. In practice, it has been found that the electronic polarizabilities of the metal atoms are fairly small as compared with those of carbonate groups[13] and that the frequencies given by the model are insensitive to the polarizabilities.[2] The polarizabilities were thus regarded as isotropic and set equal to the values determined by the other methods[13-16] in the final calculations.

The numerical work was performed using a TOSBAC 3400 TOPS 14 electronic computer at the Computing Center of Hiroshima University.

Results and Discussion

Electronic Polarizability. A considerable number of values have been reported for ionic and molecular polarizabilities.[13-16] Almost all of them have, however, been determined for isotropic crystals with simple structures; therefore, they cannot always apply to the present materials. As has been mentioned above, they were used only for less important metal atoms. The resulting electronic polarizabilities of oxygen and carbon atoms are shown in Fig. 2 for calcite, where all of the sets of values on the $\{\alpha_{\perp}(\mathrm{O}),\ \alpha_{\perp}(\mathrm{C})\}$ and $\{\alpha_{/\!/}(\mathrm{O}),\ \alpha_{/\!/}(\mathrm{C})\}$ curves were able to account for the high-frequency dielectric constants corresponding to the two refractive indices,[17,18] $n_{\perp}$ and $n_{/\!/}$ respectively. The determination of the electronic polarizabilities must, therefore, be based on a fit of the calculated to the observed vibrational frequencies.

In the present investigation, the off-diagonal elements of the polarizability tensor were neglected as a first approximation. The validity of the simplifying assumption is unclear at present, although it does predict the correct orders of magnitude for the Coulomb frequency splittings. It seems likely that the influence of the elements, if any, would be appreciable in the case of atoms with a lower site symmetry, such as oxygen atoms in the calcite lattices. Therefore, further work is required to clarify the significance of the off-diagonal elements.

Optically-active Vibrations. From the present calculations, certain frequency splittings in the intramolecular vibrations, *e.g.*, TO-LO and $\mathrm{E_g}$-$\mathrm{E_u}$ splittings,[19-22] were found to be appreciably sensitive to the details of the electronic polarizabilities of oxygen and carbon atoms as well as to the charge distribution within the carbonate groups. The present calculations strongly suggest that the $\mathrm{E_g}$-$\mathrm{E_u}$ splittings of the

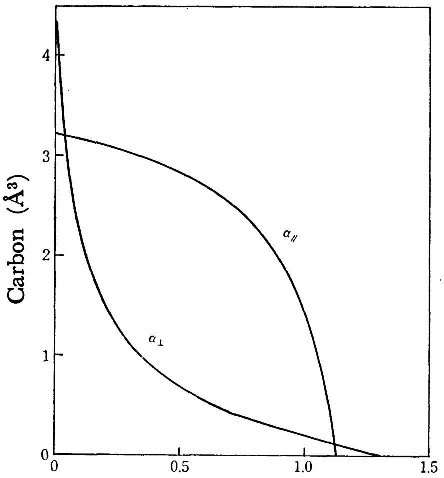

Fig. 2. Electronic polarizabilities of oxygen and carbon atoms for calcite. All of the sets of values on the curves are able to account for the observed high-frequency dielectric constants.
$\alpha_{\perp}$: Perpendicular component.
$\alpha_{/\!/}$: Parallel component.

Table 1. Observed and calculated vibrational frequencies (cm^{-1}) of calcite and magnesite

Sym.	Calcite									Magnesite								
	Observed[a)]			PI Model			RI Model[b)]			Observed[c)]			PI Model			RI Model[b)]		
	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$
A_{1g}	1086			1086			1086			1096			1096			1095		
A_{2g}				883			884						853			906		
	309			282			254						394			349		
	172			177			192						322			315		
A_{1u}				1088			1088						1104			1101		
				257			255						376			345		
A_{2u}	872	890	18	876	887	11	874	885	11	876	911	35	882	905	23	881	899	18
	303	387	84	313	385	72	321	375	54	362	459	97	323	496	173	363	458	95
	92	136	44	100	101	~1	93	133	40	230	281	51	233	265	32	236	268	32
E_g	1434			1438			1424			1460			1459			1451		
	712			708			714			735			736			745		
	284			284			262			332			331			332		
	156			156			165			212			210			213		
E_u	1407	1549	142	1407	1551	144	1424	1429	5	1436	1599	163	1439	1605	167	1451	1459	8
	712	715	3	695	735	41	712	713	~1	747	783	36	745	813	68	743	745	2
	297	381	84	305	345	40	296	357	61	356	475	119	372	464	91	353	464	111
	223	239	16	218	242	24	226	234	8	301	315	14	284	329	45	310	314	4
	102	123	21	106	117	11	101	123	22	221	241	20	222	228	6	226	239	13

TO; Transverse optic mode. LO; Longitudinal optic mode. $\Delta\nu$; TO-LO separation.
a) Refs. 23, 25, and 29. b) Ref. 8. c) Refs. 25 and 41.

Table 2. Effective charge (electron unit) and electronic polarizability ($Å^3$)

	Magnesite	Dolomite	Calcite		Rhodochrosite	Smithsonite
x	0.25	0.30	0.35	x	0.27	0.30
Z_{Mg}	1.30	1.25		Z_{Mn}	1.19	
Z_{Ca}		1.08	1.11	Z_{Zn}		1.08
Z_C	0.32	0.35	0.39	Z_C	0.32	0.32
Z_O	−0.54	−0.50	−0.50	Z_O	−0.51	−0.47
α(Mg)	0.09	0.09		α(Mn)	0.92	
α(Ca)		1.10	1.10	α(Zn)		0.67
$\alpha_\perp$(C)	1.09	1.03	1.10	$\alpha_\perp$(C)	1.10	1.10
$\alpha_{//}$(C)	1.32	1.25	1.18	$\alpha_{//}$(C)	1.28	1.29
$\alpha_\perp$(O)	0.30	0.30	0.30	$\alpha_\perp$(O)	0.30	0.30
$\alpha_{//}$(O)	1.06	1.06	1.05	$\alpha_{//}$(O)	1.05	1.05
$\varepsilon_\perp^\infty$	2.95	2.82	2.75	$\varepsilon_\perp^\infty$	3.31	3.42
$\varepsilon_{//}^\infty$	2.30	2.25	2.21	$\varepsilon_{//}^\infty$	2.54	2.63

x, charge distribution parameter; //, parallel component; $\perp$, perpendicular component.

CO stretching and OCO angle deformation modes depend very sensitively on the polarizability, $\alpha_\perp$(O) or $\alpha_\perp$(C). If the values about 0.3 $Å^3$ are assigned to the $\alpha_\perp$(O) polarizability, a satisfactorily good agreement can be obtained with the experimental results; therefore, the value was set as 0.3 $Å^3$. On the other hand, it was found that the charge distribution affects the TO-LO separations of the CO stretching modes quite a bit. The distribution parameter was adjusted to explain the experimental separations. For the A_{2u} or A_u modes, the effects of the polarizabilities can be examined only for the TO-LO splitting of the out-of-plane angle deformation modes; the polarizability dependence of the splitting is, however, not so remarkable as that of the E_u modes. It was shown, from a careful analysis of the calculated results, that a polarizability set with $\alpha_{/\!/}(O) \approx 1.05$ $Å^3$ yields a good agreement with the observed splitting. Any choice of isotropic polarizabilities, *i.e.*, $\alpha_\perp(O) = \alpha_{/\!/}(O) = 0.3$ $Å^3$ or 1.05 $Å^3$, was found either to overestimate or to underestimate the experimental results seriously.

Calcite: A large number of experimental studies of the vibrational spectra of calcite have been carried out by means of IR absorption[23,24)] or reflection[25–27)] and of Raman scattering;[23,24,28)] furthermore, the dispersion relations have been in part determined by neutron inelastic scattering.[29)] The observed and calculated frequencies are given in Table 1, together with the results of the RI model calculations for comparison. It is shown that the E -E_u splitting of the CO stretching

Table 3. Observed and calculated vibrational frequencies (cm^{-1}) of dolomite

Sym.	Observed[a]			PI Model			RI Model[b]		
	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$
A_g	1099			1099			1096		
	—			894			900		
	335			339			309		
	—			226			240		
A_u	—	—	—	1099	1100	~1	1098	1098	~0
	879	901	22	879	902	23	883	898	15
	361	429	68	362	446	84	374	436	62
	314	325	11	298	318	20	308	309	~1
	146	193	47	159	159	~0	149	190	41
E_g	1444			1459			1443		
	724			723			729		
	301			308			296		
	178			177			181		
E_u	1435	1580	145	1428	1577	150	1443	1449	6
	728	741	13	713	753	40	729	731	2
	345	439	94	337	412	75	348	418	70
	255	271	16	261	285	24	267	277	10
	150	173	23	155	164	9	152	176	24

The notation is the same as in Table 1. a) Refs. 25 and 43. b) Ref. 9.

modes is fairly comparable with the experimental separation, whereas the splitting of the OCO deformation modes seems to be somewhat overestimated. Recently, Onomichi *et al.*[30] have reported more accurate and reliable spectroscopic data for calcite: 1439 cm^{-1} and 720 cm^{-1} for the E_g modes, and 1411 cm^{-1} and 712 cm^{-1} for the E_u modes. Therefore, the present calculations do not always predict a tendency of the Coulomb shift opposite to that of the experimental data. The optimized set of the Coulomb parameters is listed in Table 2.

The vibrational analysis has been performed by many investigators;[22,29–35] however, only a few attempts have been made so far to examine the effects of the Coulomb interactions. Onomichi[36] performed the RI model analysis of the optically-active vibrations; the reproducibility of the observed frequencies seems not to be very good on account of the rough estimate of the disposable parameters. Plihal and Schaack[37,38] have analyzed the intermolecular vibrations based on a shell model; they explained the experimental results fairly well. They regarded the carbonate group as one large ion in order to reduce the shell-model parameters to manageable proportions, and the calcium atom was assumed to be unpolarizable. Of considerable interest is the recent work by Cowley and Pant;[29] the observed frequencies of the optically-inactive A_{2g} modes are in fair accord with the present results (see Table 1). They have determined the shell-model parameters with reference to the dispersion curves for several intermolecular modes. The resulting charge of calcium is read as 2.3 in electron units; this is the largest of the published charges (*viz.*, 1.5,[12] 1.53,[37] and the 1.11 determined presently). There appears to be considerable variation in the charge not only with the calculation models but also with the types of vibration referred to. It should be noted that the present charge can account for both the high- and low-frequency vibrations simultaneously, whereas the published charges were estimated with reference to the low-frequency vibrations only.

The charge distribution within the carbonate ion has been determined from energetic studies of the static lattices. Ladd[39] has recently assigned the following charges: $Z_C=0.31$ and $Z_O=-0.77$ in electron units, where (Z_C+3Z_O) is normalized to the formal ionic charge. The charge distribution seems to be far closer to the present dynamical distribution than that determined previously.[40]

Magnesite and Dolomite: The IR and Raman spectra have been reported by several workers,[25,41–44] but the theoretical analysis of the vibrations has been little attempted in terms of any force models.[8,9,35,37,45] The observed and calculated frequencies of magnesite and dolomite are compared in Tables 1 and 3 respectively. As has been ascertained for calcite, the theoretical frequency splittings of the intramolecular modes are in better agreement with the observed Coulomb splittings than those based on the RI model. The best-fit Coulomb parameters are listed in Table 2. On account of the lowering of the crystal symmetry, the disposable parameters for dolomite number about twice as many as those needed for calcite or magnesite. Accordingly, the initial values of these parameters for fitting-procedures were estimated with reference to both the optimized values on the basis of the RI model[8,9] and those of the PI model for calcite and magnesite. It is obvious, from a close inspection of the effective charges of calcite and magnesite, that a larger dipole moment is induced at each atom site in magnesite

Table 4. Observed and calculated vibrational frequencies (cm^{-1}) of rhodochrosite and smithsonite

Sym.	Rhodochrosite									Smithsonite								
	Observed[a)]			PI Model			RI Model			Observed[a)]			PI Model			RI Model		
	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$	TO	LO	$\Delta\nu$
A_{1g}	1089			1089			1089			1096			1096			1095		
A_{2g}				869			887						878			903		
				339			291						359			304		
				231			255						246			280		
A_{1u}				1092			1093						1099			1100		
				238			230						217			219		
A_{2u}	865	—	—	868	891	23	866	887	21	878	—	—	878	898	20	879	903	24
	285	384	99	271	392	121	293	363	70	287	383	96	285	394	109	294	362	66
	176	—	—	176	181	5	174	211	37	198	—	—	198	198	$\sim$0	193	237	44
E_g	1420			1430			1409			1412			1430			1405		
	722			735			725			733			744			742		
	290			291			288			306			305			300		
	183			183			186			184			184			192		
E_u	1397	1556	159	1392	1550	158	1409	1419	10	1398	1559	161	1393	1551	157	1405	1417	12
	725	725	$\sim$0	710	782	72	724	726	2	743	743	$\sim$0	728	778	50	739	742	3
	285	368	83	306	356	50	278	362	84	287	368	81	306	342	36	275	361	86
	202	—	—	202	242	40	211	227	16	198	—	—	194	230	36	208	231	23
	160	—	—	157	159	2	171	180	9	130	—	—	130	135	5	176	180	4

The notation is the same as in Table 1. a) Refs. 46 and 48.

than in calcite; these features are well reflected in the observed TO-LO separations. The intermediate nature of dolomite between calcite and magnesite is appreciably brought out in the effective charges and short-range force constants; they are either calcite-like or magnesite-like.

Rhodochrosite and Smithsonite: There have been little vibrational data available for these crystals, and the crystal vibrations have not been analyzed in terms of any force models except in the work by Grandolfo[35] based on a short-range force model. The available data[28,46–48] are, however, barely sufficient to perform the detailed analysis. The observed IR reflectivities[48] were modified by employing the anisotropic refractive indices in the dielectric dispersion formulas: $n_{\perp}=1.818$ and $n_{/\!/}=1.595$ for rhodochrosite and $n_{\perp}=1.849$ and $n_{/\!/}=1.621$ for smithsonite.[17]

The optically-active vibrations of these crystals were analyzed on the basis of both the RI and PI models. The observed and calculated frequencies and the best-fit values of the Coulomb parameters are given in Tables 4 and 2 respectively. Because of the lack of reliable spectroscopic data for these crystals, the present results must be considered to be tentative. Although the physical significance of the values of the adjustable parameters is not clear, a general similarity in the values is found between these crystals and the other crystals investigated here.

Short-range Force Constants. The initial values of the force constants, f_1—f_6, were estimated with reference to those determined by the RI model,[8,9] and then they were refined by a least-squares method. The optimized values are listed in Table 5, where $F'=-0.1F$. The modified Urey-Bradley force field was ascertained to be satisfactory for the intramolecular vibrations of carbonate groups, although the physical meanings of the correction terms of relatively large values remain obscure. It is also found that some force constants between close atom pairs, such as intramolecular constants, are more affected by the ionic polarizabilities than those between distant pairs; an explanation of this can be found in the widely recognized concept that the interactions through the electronic polarizability are more short-range than the electrostatic interactions.

A rough estimation of the Lennard-Jones potential constants for non-bonded oxygen-oxygen interactions was possible from the resulting 17 force constants. The force constants are shown in Fig. 3. If the atoms are assumed to interact with central forces, the Lennard-Jones potential constants, A and B, of the form:[3,49]

$$U(r) = A\,r^{-9} - B\,r^{-6},$$

can be determined by the use of this relation:

$$f(r_0) = [\mathrm{d}^2U/\mathrm{d}r^2]_{r=r_0},$$

where $f(r_0)$ is the force constant at the interatomic distance of r_0. The optimized values for the potential constants were thus calculated to be $A=60\times10^{-82}$ $\mathrm{erg\cdot cm^9}$ and $B=350\times10^{-60}$ $\mathrm{erg\cdot cm^6}$. As Fig. 3 illustrates, the curve I of the carbonates seems to be intermediate between the curves II and III drawn from the self-consistent potential constants of oxides[49] and those of neon with the similar electron configuration to the O^{2-} ion[3] respectively. Figure 3 also indicates that Curve I is similar in the dependence on the interatomic distance to Curve II rather than to Curve III.

Comparison of PI Model with RI Model. The essential correctness of introducing the electronic polarizability is shown by the great improvement in the fit to the experimental Coulomb splittings of the

Table 5. Short-range force constants (mdyn/Å)

FC[a]	Pair	Magnesite		Dolomite		Calcite		Pair	Rhodochrosite		Smithsonite	
		Dist.[e]	FC	Dist.[e]	FC	Dist.[e]	FC		Dist.[e]	FC	Dist.[e]	FC
K	C O	1.286	6.141	1.283	6.224	1.294	6.200	C O	1.286	5.761	1.286	5.832
H	OCO		0.908		0.962		0.952	OCO		0.964		0.962
F	O O	2.227	2.386	2.222	2.536	2.241	2.522	O O	2.227	2.554	2.227	2.556
α[b]	CO_3		0.392		0.367		0.325	CO_3		0.358		0.348
p[c]			−1.471		−1.544		−1.427			−1.422		−1.414
n[d]			0.950		1.298		1.220			1.069		1.208
f_1	Mg C	2.953	0.154	3.043	0.069			Mn C	3.051	0.148		
f_1'	Ca C			3.153	0.012	3.213	0.026	Zn C			2.964	0.103
f_2	Mg O	2.102	0.834	2.095	0.806			Mn O	2.916	0.765		
f_2'	Ca O			2.390	0.739	2.353	0.671	Zn O			2.111	0.800
f_3	C O	3.019	0.030	3.133	0.010			C O	3.152	0.011		
f_3'	C O			3.343	−0.005	3.406	0.001	C O			3.026	0.000
f_4	O O	2.849	0.111	3.009	0.080			O O	2.958	0.051		
f_4'	O O			3.086	0.070	3.189	0.064	O O			2.852	0.084
f_5	O O	2.924	0.255	2.916	0.174			O O	3.058	0.110		
f_5'	O O			3.304	0.005	3.249	−0.003	O O			2.943	0.149
f_6	O O	3.019	0.049	3.008	0.068			O O	3.152	0.012		
f_6'	O O			3.454	−0.010	3.406	−0.014	O O			3.026	0.003

a) The notation is the same as in Refs. 8 and 9. b) Out-of-plane angle deformation coordinate. c) Adjacent bond interaction. d) Adjacent angle interaction. Units of n in mdyn·Å. e) Interatomic distance in Å.

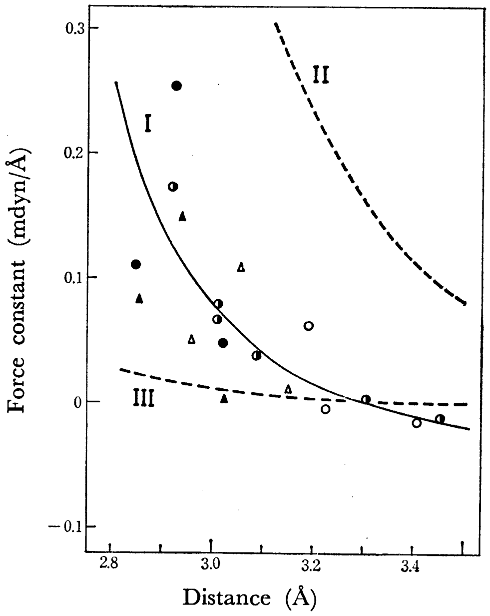

Fig. 3. Force constants for non-bonded oxygen-oxygen interactions. Curves II and III are drawn from the $O^{2-}\cdots O^{2-}$ potential of oxide crystals and Ne···Ne potential, respectively. See text.
○: Calcite, ●: Magnesite, ◑: Dolomite,
△: Rhodochrosite, ▲: Smithsonite.

intramolecular modes. These splittings have been poorly accounted for on the basis of the RI model. With OCO angle deformation modes, the relatively weak absorption intensity makes it difficult to attain accurate and reliable determinations of the TO-LO separations. Consequently, the experimental separations seem to vary considerably with the five carbonates; nearly identical values are assigned to them in the case of CO stretching modes. We cannot, therefore, believe that all the variations arise from the specificity of each modification, although the Coulomb interactions of the angle deformation modes are seemingly reproduced less satisfactorily with the present model. Further experimentation is necessary to examine fully this apparent contradiction to the present results. The observed intermolecular mode frequencies are seen to be satisfactorily explained by both models: certain low-frequency modes are not very well fitted by the PI model, although this lack of fit is probably not significant.

As for the optically-active vibrations, the results of the present and of previous works[2] seem to indicate that the weak Coulomb interactions between moderately separated atoms can be fairly well accounted for by the RI model, and that, however, any strong interactions due to the distortion of electronic distributions can hardly be interpreted at all without the use of a model which takes rigorously ionic polarizations. Moreover, there are a large number of crystalline solids where we are obliged to be content with the oversimplified RI approximation because of the complexity inherent in elaborate models. Under these circumstances, we consider that the present work represents one step in the direction of obtaining a quantitative understanding of the Coulomb interactions in ionic crystals with intricate structures.

The author wishes to express his thanks to Professor Hiromu Murata for his continual encouragement during this work, and to Associate Professor Yuji Shiro for his valuable advice and discussion. Thanks are also due to Messrs. Masaru Ohsaku and Tamaki Utida and Miss Michiko Miura for their kind and helpful discussion and suggestions.

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