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Lattice dynamics of molecular calcite crystals

R. K. Singh and N. K. Gaur
School of Physics, Bhopal University, Bhopal-462026 and Centre for Science and Technology Development Studies, Bhopal-462016, India

S. L. Chaplot
Nuclear Physics Division, Bhabha Atomic Research Centre, Bombay-400085, India

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The lattice dynamics of molecular crystals ($CaCO_3$, $MgCO_3$, and $ZnCO_3$) has been investigated for the first time by means of the rigid-molecular-ion model developed by employing the external mode formalism and the interaction potential operative between nonbonded atoms. The phonon dispersion curves computed from this model are, generally, in good agreement with their available experimental data measured with the technique of inelastic neutron scattering. The values of the eigenvectors are also reported. The calculated values of the cohesive energy for $CaCO_3$, $MgCO_3$, and $ZnCO_3$ show good agreement with the thermochemical data. The scope of further extension of the present model has also been discussed.

I. INTRODUCTION

A survey of literature reveals that the analysis of the neutron-spectroscopically-measured phonon dispersion curves (PDC's), by means of phenomenological models, has become almost a routine operation for ionic crystals[1] having high symmetry and a small number of atoms per unit cell. However, very scant attention has been paid to more complex systems like molecular crystals which contain molecular-formula units (or clusters) as regular components in their unit cells. Earlier, a few theoretical[2–5] and experimental[6–10] investigations were carried out to describe the lattice dynamics of molecular crystals. In the case of calcite crystals, despite the detailed experimental investigations of the lattice vibrations[11–13] and Raman spectra,[14,15] no complete theoretical model was developed until Cowley and Pant[12] applied a rigid-shell model (RSM) to $CaCO_3$ and Singh and Chaplot[16] used a rigid-molecular-ion model[4] (RMIM) for $NaNO_3$. This RMIM has also been successfully applied to a variety of complex crystals, namely, $(NH_4)_2CuCl_4 \cdot 2H_2O$,[17] $K_2CuCl_4 \cdot 2H_2O$,[17] NH_4Cl,[18] $LiKSO_4$,[19] and others.[18,20,21]

Looking to its remarkable success in the case of several complex molecular crystals, we thought it pertinent to apply this RMIM to describe the lattice dynamics of molecular crystals of calcite structure. Thus, the chief aim of this paper is to predict the external modes of vibrations in the phonon dispersion curves (PDC's) of $CaCO_3$, $MgCO_3$, and $ZnCO_3$, which are typical crystals of the calcite family. Besides this prediction, we have computed the eigenvectors along the symmetry direction [qqq] and the cohesive energy for understanding their interaction mechanism. The novelty in our approach lies in the fact that we have obtained the model parameters (effective charges and radii of ions) on the basis of some physicochemcial considerations and have not taken recourse to the least-square fitting as adopted by Cowley and Pant[12] for predicting the measured PDC's of $CaCO_3$ using RSM. In

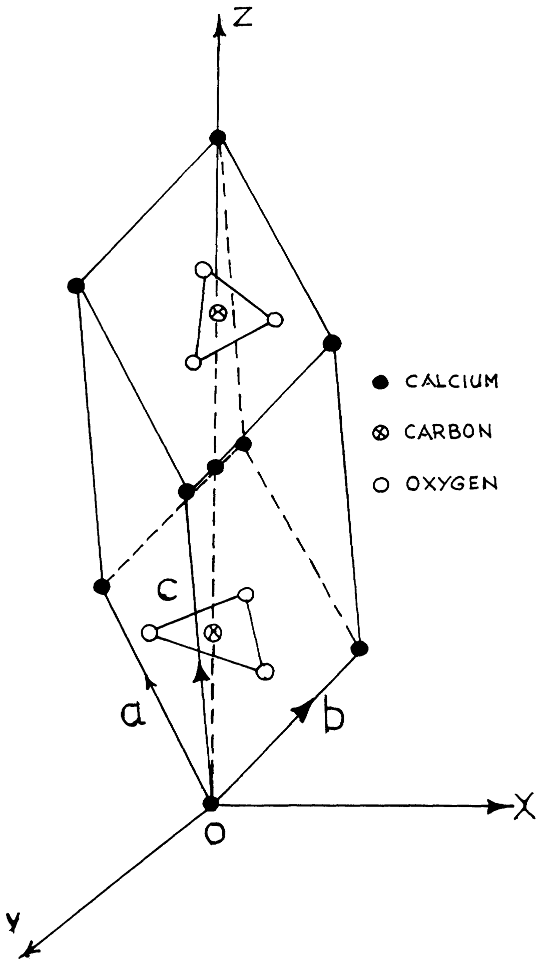

FIG. 1. The calcite crystal structure.

TABLE I. Unit-cell size and atomic positions of calcite crystals (Ref. 22).

Crystals	a_0 (Å)	α	u	Atomic positions	
$CaCO_3$	6.361	46°6′	0.2593	Ca, Mg, or Zn	$\pm(\frac{1}{4},\frac{1}{4},\frac{1}{4})$
				C	$(0,0,0);(\frac{1}{2},\frac{1}{2},\frac{1}{2})$
				C	$(u,\bar{u},0);(\bar{u},0,u);(0,u,\bar{u});$ $(\frac{1}{2}-u,u+\frac{1}{2},\frac{1}{2});$ $(u+\frac{1}{2},\frac{1}{2},\frac{1}{2}-u);$ $(\frac{1}{2},\frac{1}{2}-u,u+\frac{1}{2})$
$MgCO_3$	5.675	48°12′	0.28		
$ZnCO_3$	5.683	48°20′	0.28		

the present computatons, we have taken the rhombohedral symmetry with two molecular formula units per unit cell. The symmetry and structure of such calcite crystals has been described below. Our results on PDC's are, generally, in good agreement with their experimental data available only in the case of $CaCO_3$ at room temperature along **Λ** direction. In other cases, our results at present are only of academic interest and will be deferred until the report of measured data on them. Our results on cohesive energy and eigenvectors for these solids seem to be appropriate.

The contents of the present paper are organized as follows. The structure and symmetry of calcite crystals are presented in Sec. II. A description of the interatomic interaction and corresponding lattice dynamical model is given in Sec. III. Finally, the computed results have been presented in Sec. IV and discussed in the last section.

II. CALCITE STRUCTURE AND SYMMETRY

The calcite crystal structure has been given by Wyckoff[22] and its details are reported elsewhere by Cowley[23] and Rao *et al.*[24] The composition of these crystals is RMX_3, which is isomorphous with NaCl like the arrangement of R^+ and $MX_3{}^-$ ions distorted by the spatial requirements of its complex anions. These crystals have associated space group $R\bar{3}C(D_{3d}^6)$. The calcium (or magnesium or zinc) and carbon atoms lie on the unique threefold axis such that the former ones are positioned at (0,0,0) and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the latter ones at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$ as indicated in Fig. 1. The three oxygen atoms of each carbonate group are arranged symmetrically about the carbon atoms in planes normal to the threefold axis. Each oxygen atom lies on a twofold axis. Successive carbonates are rotated 60° relative to each other

These calcites have rhombohedral symmetry with bimolecular unit cell of dimensions (a_0,α) as given by Wyckoff and listed in Table I. Using these data we have obtained the atomic coordinates (x,y,z) listed in Table II for $CaCO_3$, $MgCO_3$, and $ZnCO_3$. Some of these crystals suffer structural phase transition as is obvious from the fact that the calcium carbonate ($CaCO_3$) exhibits rhombohedral structure at 18 °C and orthorhombic at 26 °C.

TABLE II. Atomic coordinates of calcite crystals.

Crystal	Atom type	Fractional atomic coordinates x	y	z
$CaCO_3$	Ca	0.0	0.0	0.0
	Ca	0.5	0.5	0.5
	C	0.25	0.25	0.25
	O	0.5093	−0.0093	0.250
	O	−0.0093	−0.250	0.5093
	O	0.250	0.5093	−0.0093
	C	−0.25	−0.25	−0.25
	O	−0.5093	0.0093	−0.250
	O	0.0093	−0.250	−0.5093
	O	−0.250	−0.5093	0.0093
$MgCO_3$ and $ZnCO_3$	Mg (or Zn)	0.0	0.0	0.0
	Mg (or Zn)	0.5	0.5	0.5
	C	0.25	0.25	0.25
	O	0.510	−0.010	0.250
	O	−0.010	0.250	0.510
	O	0.250	0.510	−0.010
	C	−0.25	−0.25	−0.25
	O	−0.510	0.010	−0.250
	O	0.010	−0.250	−0.510
	O	−0.250	−0.510	0.010

A group-theoretical study of lattice vibrations in this space group is reported by Rao *et al.*[24] This has been used in classifying the phonon modes.

III. FORMALISM OF RMIM

The rigid-molecular-ion model (RMIM), employed in the present investigation, was originally developed by Rao *et al.*[4] for the lattice dynamics of complex molecular crystal (KNO_3) using the so-called external mode formalism.[3] The relevant expressions for the interaction potential and the dynamical matrix corresponding to RMIM are given below.

A. Intermolecular potential

According to Rao *et al.*,[4] the molecular crystal potential energy ϕ is written as

$$\phi=\frac{1}{2}\sum_{\substack{l,k\\ k\in K}}\sum_{\substack{l',k'\\ k'\in K'}}{}' \frac{1}{4\pi\epsilon_0}\frac{Z_{Kk}Z_{K'k'}e^2}{|\mathbf{r}(lKk;l'K'k')|} + A\exp\left|\frac{-13.6\,|\mathbf{r}(lKk;l'K'k')|}{1.1(R_{Kk}+R_{K'k'})}\right| , \tag{1}$$

where the first and second terms represent the long-range Coulomb and the short-range Born-Mayer-type repulsive energy, respectively. For convenience, these interactions in RMIM have been considered to be pairwise and operative between the atoms of different molecules and we have ignored them between atoms within a molecule. The various symbols have the following meaning: l,l' are the unit cell indices; K,K' are the indices for atomic or molecular vibrating units in unit cells; k,k' are the indices for atoms in molecular units; $k\in K$ implies that the atom k belongs to molecule K; e ($=1.6\times10^{-19}$ C) is the electronic charge; ϵ_0 is the permittivity constant with $\frac{1}{4\pi\epsilon_0}=9.0\times10^9$ Nm^2/C^2; Z_{Kk} and R_{Kk} are the effective charge and radii on the atoms denoted by Kk and they are treated as the model parameters. Following Kitaigorodskii and Mirskaya,[25] we have taken $A=1822.0$ eV/atom.

The instantaneous position vector of atom Kk in the lth unit cell is given by

$$\mathbf{r}(lKk)=\mathbf{r}(l)+\mathbf{r}(Kk)=\mathbf{r}(lK)+\mathbf{r}(k) =\mathbf{r}(l)+\mathbf{r}(K)+\mathbf{r}(k) , \tag{2}$$

with the distance between atoms (lKk) and $(l'K'k')$ as

$$|\mathbf{r}(lKk;l'K'k')|=|\mathbf{r}(l'K'k')-\mathbf{r}(lKk)| . \tag{3}$$

Here, $r(l)$ is the position vector of origin of the lth cell with respect to some crystal origin; $\mathbf{r}(k)$ is the position vector of center of mass of the molecule K with respect to the cell origin; $\mathbf{r}(k)$ is the position vector of the atom Kk with respect to the center of mass of molecule K. During lattice vibrations, it is more convenient to express the position vectors as

$$\mathbf{r}(lKk)=\mathbf{X}(lKk)+\mathbf{u}(lKk) , \tag{4}$$

in terms of the respective equilibrium position vectors $\mathbf{X}(lKk)$ and the displacements $\mathbf{u}(lKk)$.

B. Dynamical matrix in the external mode formalism

In calcite crystals (MCO_3), we shall regard the metallic (M) and carbonate (CO_3) ions as the atomic or molecular units designated by (lK) and/or, $(l'K')$. In the framework of adiabatic and harmonic approximations,[26] the crystal potential can be expressed in terms of translational (u^t) and rotational (u^r) displacements of the atomic and molecular units as[3]

$$\phi=\phi_0+\sum_{l,K\alpha i}\phi_\alpha^i(lK)u_\alpha^i(lK) +\tfrac{1}{2}\sum_{l,K\alpha i}\sum_{l',K',\beta j}\phi_{\alpha\beta}^{ij}(lK;l'K')u_\alpha^i(lK)u_\beta^j(l'K') , \tag{5}$$

where α and β are the Cartesian components x, y, and z; i and j refer to the translation (t) and/or rotation (r); $u_\alpha^i(l,K)$ is the displacement of the Kth unit in the lth unit cell. The remaining symbols are defined as[3]

$$\phi_\alpha^i(l,K)=\left.\frac{\partial\phi[\,|\mathbf{r}(lK;l'K')|\,]}{\partial u_\alpha^i(lK)}\right|_{r=X(lK;l'K')} , \tag{6}$$

$$\phi_{\alpha\beta}^{ij}(lK;l'K')=\left.\frac{\partial^2\phi[\,|\mathbf{r}(lK;l'K')|\,]}{\partial^2u_\alpha^i(lK)u_\beta^j(l'K')}\right|_{r=X(lK;l'K')} . \tag{7}$$

The equations of motion for the present system are given by the translational (or linear) force

$$\begin{aligned}F_\alpha^t(lK)&=m_K\ddot{u}_\alpha^t(lK)\\ &=-\Bigg[\sum_{l',K',\beta}\phi_{\alpha\beta}^{tt}(lK;l'K')u_\beta^t(l'K') +\sum_{l',K'\in\mathrm{II},\beta}\phi_{\alpha\beta}^{tr}(lK;l'K')u_\beta^r(l'K')\Bigg]\end{aligned} \tag{8}$$

on unit (lK) along α direction and the corresponding torque

$$\begin{aligned}F_\beta^r(lK)&=\sum_\beta I_{\alpha\beta}(K)\ddot{u}_\beta^r(lK)\\ &=-\Bigg[\sum_{l',K',\beta}\phi_{\alpha\beta}^{tr}(lK;l'K')u_\beta^t(l'K') +\sum_{l',K'\in\mathrm{II}}\phi_{\alpha\beta}^{rr}(lK;l'K')u_\beta^r(l'K')\Bigg]\end{aligned} \tag{9}$$

on unit (lK) along β direction. Here, $K\in\mathrm{II}$ implies summation over "molecular units" only. m_k is the mass of the atomic or molecular unit given by $\sum_{k\in K}m_K$;$I_{\alpha\beta}(K)$ is the moment of inertia tensor of the molecular unit (K) with its matrix elements[4]

$$I_{\alpha\beta}(K)=\sum_{k\in K}m_K[\,|X(k)|^2\delta_{\alpha\beta}-X_\alpha(K)X_\beta(K)] . \tag{10}$$

Recently, Chaplot *et al.*[27] have made the model calculations, which employ pairwise interaction potential between various atoms on distinct clusters and adjust the potential parameters in such a way that these forces and torques on each cluster vanish in equilibrium. Then the

TABLE III. Potential parameters and cohesive energies of calcite crystals.

Crystals	Ions	Potential parameters Effective radii[a]	 Effective charge	Cohesive energy (kcal/mol)	Unit-cell volume ($\mathring{A}^3$)
$CaCO_3$	Ca^{2+}	1.80 (0.94)[b]	1.58	$\phi_{\rm Coul}=-748$	121.91
	C^{4+}	0.80 (0.77)[b]	0.82	$\phi_{\rm rep}=52$	
	O^{2-}	1.35 (1.46)[b]	-0.80	$\phi_{\rm total}=-696$	
				$\phi_{\rm expt}=(-672)$[c]	
$MgCO_3$	Mg^{2+}	1.50 (1.40)[b]	1.70	$\phi_{\rm Coul}=-891$	93.10
	C^{4+}	0.80 (0.77)[b]	0.70	$\phi_{\rm rep}=58$	
	O^{2-}	1.35 (1.46)[b]	-0.80	$\phi_{\rm total}=-833$	
				$\phi_{\rm expt}=(-746)$[c]	
$ZnCO_3$	Zn^{2+}	1.80 (0.83)[b]	1.75	$\phi_{\rm Coul}=-852$	93.92
	C^{4+}	0.80 (0.77)[b]	0.65	$\phi_{\rm rep}=76$	
	O^{2-}	1.35 (1.46)[b]	-0.80	$\phi_{\rm total}=-776$	
				$\phi_{\rm expt}=(-782)$[c]	

[a] The values enclosed within the parenthesis are reported by Kittel (Ref. 30) and compared with our effective radii (R_{KK}).

[b] Reference 30.

[c] Reference 29.

translational and rotational invariance conditions (sum rules) are automatically fulfilled in them. This, in turn, emphasizes the appropriateness of RMIM for the lattice dynamical studies.

Assuming the wave-like solution of the type

$$u^i_\alpha(lK)=U^i_\alpha(\mathbf{q}/K)\exp\{i[\mathbf{q}\cdot\mathbf{X}(1K)-\omega(\mathbf{q})t]\} \qquad (11)$$

for the equation of motion given by Eqs. (8) and (9) and substituting it in them, we get the following eigenvalue equation (Rao *et al.*[4]):

$$\underline{M}(\mathbf{q})\underline{U}(\mathbf{q})=\omega^2(\mathbf{q})\underline{m}\,\underline{U}(\mathbf{q})\ , \qquad (12)$$

where $\underline{M}(\mathbf{q})$ is the dynamical matrix of order $(3\mu+6\nu)$ with μ and ν representing the number of individual atoms (like Ca) and clusters (like CO_3) in the primitive unit cell. The elements of $\underline{M}(\mathbf{q})$ and $\underline{m}$ are defined as[4]

$$M^{ij}_{\alpha\beta}(\mathbf{q}/KK')=\sum_{l'}\phi^{ij}_{\alpha\beta}(lK;l'K')\exp\{i[\mathbf{q}\cdot\mathbf{X}(lK;l'K')]\} \qquad (13)$$

$$m^{ij}_{\alpha\beta}(KK')=m_K\delta_{\alpha\beta}\delta_{KK'}\delta_{ij}\quad \text{for } i=t\ , \qquad (14a)$$

$$=I_{\alpha\beta}(K)\delta_{KK'}\delta_{ij}\quad \text{for } i=r\ , \qquad (14b)$$

with

$$\mathbf{X}(lK;l'K')=\mathbf{X}(l'K')-\mathbf{X}(lK) \qquad (15)$$

as the equilibrium separation between units (lK) and $(l'K')$.

For nontrivial solutions of wave amplitudes, the eigenvalue equation (12) leads to the following dynamical equation

$$|\,\underline{M}(\mathbf{q})-\omega^2(\mathbf{q})\underline{m}\,|=0 \qquad (16)$$

which can be solved to obtain the eigenvalues, $\omega_j^2(\mathbf{q})$ $(j=1,\ldots,3\mu+6\nu)$, for different values of $\underline{M}(\mathbf{q})$ calcu-

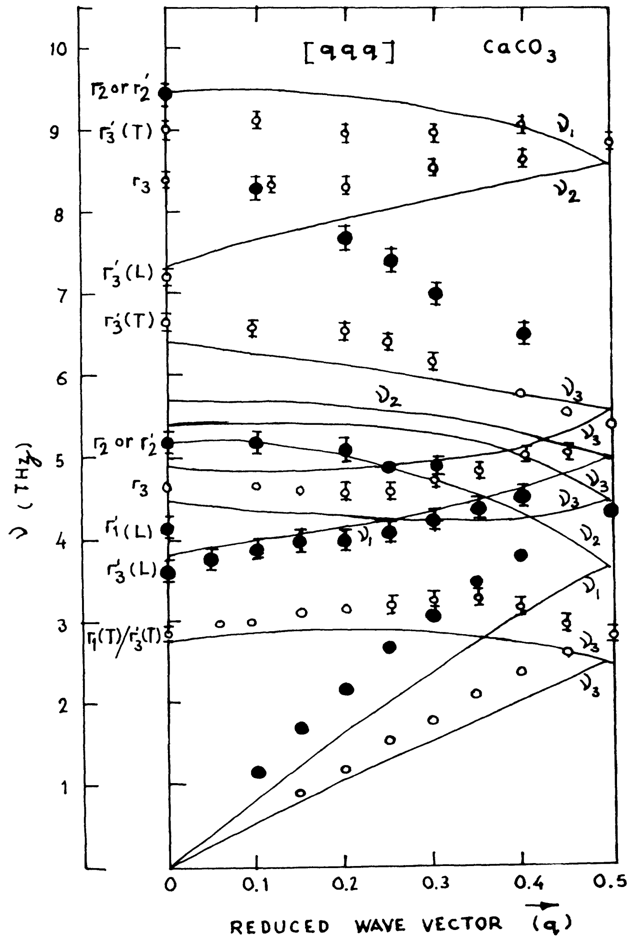

FIG. 2. Phonon dispersion curve for $CaCO_3$ obtained from RMIM. The open and solid circles represent the experimental points taken from Cowley and Pant (Ref. 12).

lated for each wave vector (**q**) from the interaction potential expressed by Eq. (1). The contribution to this dynamical matrix from Coulomb and short-range repulsive energy can be obtained from the methods devised by Venkatraman and Sahni[3] and Rao *et al.*,[4] respectively.

IV. COMPUTATIONS AND RESULTS

The dynamical matrix represented by Eq. (12) can be evaluated from the knowledge of model parameters, namely the effective charges (Z_{Kk}) and radii (R_{Kk}), which can be determined from the criterion that force on "atoms" and forces and torques on "molecules" in their equilibrium configuration vanish. Thus, the constraints on the crystal potential are

$$\left.\frac{\partial\phi}{\partial u_\alpha^i(lK)}\right|_0 = 0 \text{ or } \phi_\alpha^t(lK)=0 \text{ and } \phi_\alpha^r(lK)=0 \qquad (17)$$

and

$$\sum_{Kk} Z_{Kk} = 0 \qquad (18)$$

with ϕ as the same potential as defined by Eq. (1). Once a proper set of parameters is obtained, the dynamical matrix contributions from the Coulomb[3] and short-range forces[4] can be evaluated. A computer program DISPR developed by one of us[28] has been used to determine the model parameters and the dynamical matrix elements, and for calculating the PDC's along [qqq] directions. The value of these model parameters are listed in Table III. The PDC's obtained from these parameters are depicted in Figs. 2, 3, and 4 for $CaCO_3$, $MgCO_3$, and $ZnCO_3$, respectively. The frequencies ν_1 and ν_2 meet at the zone boundary and the pairs of the frequencies ν_3 meet at the zone boundary as is obvious from Figs. 2–4. This conjunction of pairs of branches at the zone boundary is due to the lattice symmetry in calcite crystals belonging to the same space group.[24]

We have also calculated the cohesive energies for these crystals and compared them with the available measured data.[29] The values of the cohesive energies and their contributions from the long-range Coulomb and the short-range repulsive interactions are presented in Table III.

The values of eigenvectors, $e^{T/R}$ (T for translational

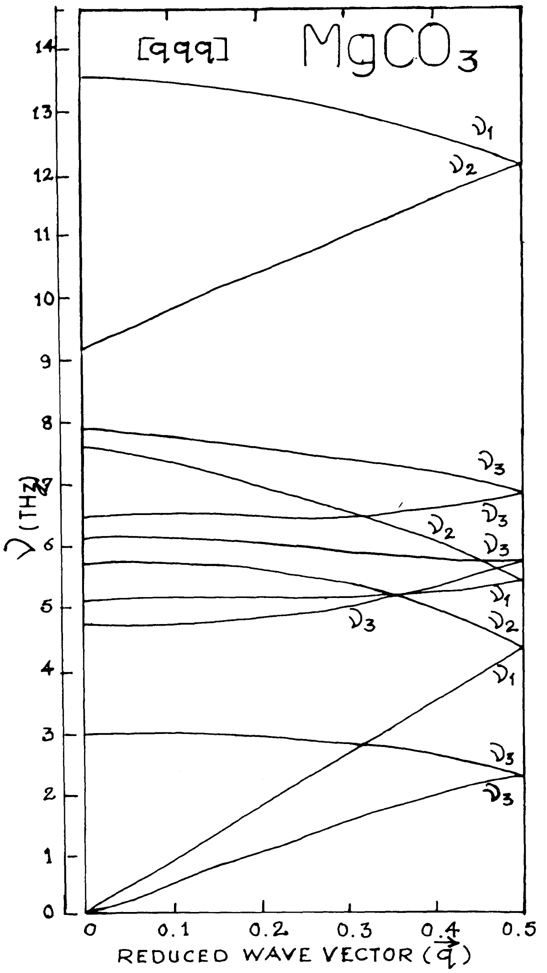

FIG. 3. Phonon dispersion curve of $MgCO_3$ obtained from RMIM.

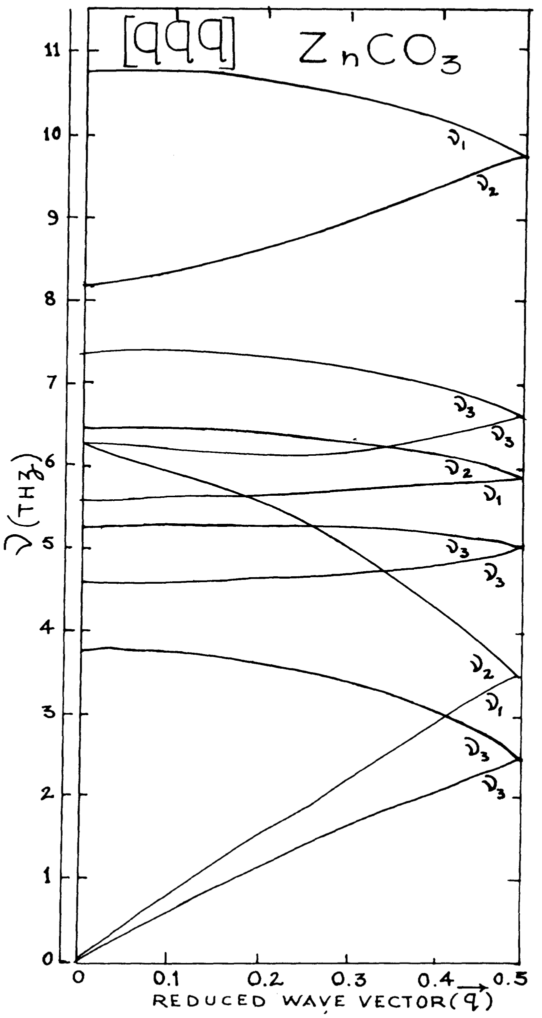

FIG. 4. Phonon dispersion curve of $ZnCO_3$ obtained from RMIM.

TABLE IV. The values of eigenvectors, $e^{T/R}$ (Ca or CO_3), corresponding to the lattice vibration frequencies along [qqq] direction in $CaCO_3$ for $q=0.001$.

			Λ_1			Λ_2					Λ_3		
		(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(4)	(5)	(6)
Eigenvector	axis \ Frequency (THz)	0.01	4.71	9.64	5.21	6.17	6.39	0.01	2.97	4.30	4.61	4.92	5.43
e^T (Ca I)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00	−0.54	0.55	−0.41	0.00
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.10	0.10	−0.16	0.00
	z	0.45	0.01	0.55	−0.00	−0.02	0.71	0.00	0.00	0.00	0.00	0.00	0.00
e^T (Ca II)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.53	0.50	0.44	0.00
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.09	−0.25	−0.04	0.00
	z	0.45	0.01	0.55	−0.00	0.02	−0.71	0.00	0.00	0.00	0.00	0.00	0.00
e^T (CO_3 I)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.55	0.71	0.00	−0.43	−0.01	0.02
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.08	0.06	0.08	0.00
	z	0.55	−0.01	−0.45	0.05	0.71	0.02	0.00	0.00	0.00	0.00	0.00	0.00
e^R (CO_3 I)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.02	0.01	0.03	−0.08	0.71
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.45	−0.01	0.54	0.00
	z	0.00	−0.71	0.01	0.71	−0.05	−0.00	0.00	0.00	0.00	0.00	0.00	0.00
e^T (CO_3 II)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.55	−0.71	0.00	−0.43	0.01	−0.02
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.07	0.06	0.08	0.00
	z	0.55	−0.01	−0.45	−0.05	−0.71	−0.02	0.00	0.00	0.00	0.00	0.00	0.00
e^R (CO_3 II)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.02	−0.03	−0.08	0.08	0.71
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.01	−0.05	0.00
	z	0.00	0.71	−0.01	0.71	−0.05	−0.00	0.00	0.00	0.00	0.00	0.00	0.00

TABLE V. The values of eigenvectors, $e^{T/R}$ (Mg or CO_3), corresponding to the lattice vibration frequencies along [**qqq**] directions in $MgCO_3$ for $q=0.001$.

			Λ_1			Λ_2				Λ_3			
		(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(4)	(5)	(6)
Eigenvector	axis	Frequency (THz) 0.01	5.12	13.53	5.72	7.91	9.24	0.01	2.94	4.67	5.84	7.06	7.13
e^T (Mg I)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	−0.38	0.00	−0.12
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.00	0.41	0.41	0.00	0.55
	z	0.38	−0.04	0.60	0.00	0.00	0.71	0.00	0.00	0.00	0.00	0.00	0.00
e^T (Mg II)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.22	0.38	0.00	−0.12
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.00	0.41	0.41	0.00	−0.55
	z	0.38	−0.04	0.60	0.00	0.00	−0.71	0.00	0.00	0.00	0.00	0.00	0.00
e^T (CO_3 I)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.60	0.70	−0.26	−0.26	−0.11	0.00
	z	0.60	0.03	−0.38	0.22	0.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00
e^R (CO_3 I)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.42
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.11	0.46	−0.34	−0.70	0.00
	z	0.00	0.70	0.05	0.67	−0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00
e^T (CO_3 II)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.60	−0.70	−0.26	−0.26	0.11	0.00
	z	0.60	0.03	−0.38	−0.22	−0.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00
e^R (CO_3 II)	x	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.42
	y	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	−0.46	0.34	−0.70	0.00
	z	0.00	−0.71	−0.05	0.67	−0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00

TABLE VI. The values of eigenvectors, $e^{T/R}$ (Zn or CO_3), corresponding to the lattice vibration frequencies along [qqq] direction in $ZnCO_3$ for $q=0.001$.

Eigenvector	axis		Λ_1			Λ_2			Λ_3					
			(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(4)	(5)	(6)
		Frequency (THz)	0.01	5.62	10.70	6.12	6.36	8.14	0.01	3.71	4.52	4.88	6.28	7.27
e^T (Zn I)	x		0.00	0.00	0.00	0.00	0.00	0.00	0.51	0.00	0.03	0.05	−0.06	0.00
	y		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.70	0.48	0.08	0.00
	z		0.51	−0.02	−0.49	−0.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
e^T (Zn II)	x		0.00	0.00	0.00	0.00	0.00	0.00	0.51	0.00	0.03	−0.05	0.06	0.00
	y		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.70	0.48	0.08	0.00
	z		0.51	−0.02	−0.49	0.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
e^T (CO_3 I)	x		0.00	0.00	0.00	0.00	0.00	0.00	0.49	−0.71	−0.03	0.00	0.00	0.00
	y		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.50	−0.08	0.02
	z		0.49	0.02	0.51	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
e^R (CO_3 I)	x		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	−0.07	0.00	0.00	0.00
	y		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.11	0.70	0.71
	z		0.00	−0.71	0.03	0.00	0.71	−0.04	0.00	0.00	0.00	0.00	0.00	0.00
e^T (CO_3 II)	x		0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.71	−0.03	0.00	0.00	0.00
	y		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	−0.50	−0.08	−0.02
	z		0.49	0.02	0.51	0.00	−0.04	−0.71	0.00	0.00	0.00	0.00	0.00	0.00
e^R (CO_3 II)	x		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.07	0.00	0.00	0.00
	y		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	−0.70	0.71
	z		0.00	0.71	−0.03	0.00	0.71	−0.04	0.00	0.00	0.00	0.00	0.00	0.00

and R for rotational components), for $CaCO_3$, $MgCO_3$, and $ZnCO_3$ along x, y, and z axes evaluated by us are reported in Tables IV, V, and VI, respectively. Here, Cartesian x axis is chosen along the direction of vector $\mathbf{a}-\mathbf{b}$, Y axis along $\mathbf{a}+\mathbf{b}+2\mathbf{c}$, and the z axis along $\mathbf{a}+\mathbf{b}+\mathbf{c}$ with **a**, **b**, and **c** as the primitive cell axes of the rhombohedral crystal.

V. DISCUSSIONS AND CONCLUSION

The prediction of PDC's in $CaCO_3$ measured from neutron scattering technique can be considered reasonably good in view of the simplicity of the present RMIM. However, the poor agreement between experimental and our theoretical results corresponding to higher frequencies might be due to the exclusion of van der Waals interaction and electronic polarizability effects.

Cowley and Pant[12] have although obtained slightly better agreement than that of ours for $CaCO_3$ but their results are subject to the fitting procedure and the large number of diposable parameters. Moreover, some of the model parameters in their calculation[12] have attained unrealistic values which is obvious from the positive value of shell-charge parameter (Y_{Ca}) and the overestimated and underestimated values, respectively, for the effective ionic charges Z_{Ca} and Z_C. However, our values of these ionic-charge parameters, reported in Table III, seem to be more realistic.[30] It is also seen from our Table III that our values of effective radii (R_{Kk}), which are the parameters in the nonbonded interatomic potential given by Eq. (1), are not very much different from their experimental values.[30] The agreements in our calculations can be improved further by including the effects of van der Waals interactions which seem to be dominent in $CaCO_3$ as is evident from the negative and positive values of A_2 and B_2 parameters obtained by Cowley and Pant.[12] The PDC's obtained for $MgCO_3$ and $ZnCO_3$ depicted in Figs. 3 and 4 could not be compared with experiments due to lack of experimental data on them.

It is interesting to note that our PDC's for $CaCO_3$, $MgCO_3$, and $ZnCO_3$ have followed the trends more or less similar to those revealed by the measured PDC's of $CaCO_3$. Further comments on our results on them will be restricted until the report of their measured data. The additional virtue of our model is noted from the Tables IV–VI in which we have reported the eigenvectors of $CaCO_3$, $MgCO_3$, and $ZnCO_3$ and found them to show a systematic and reasonably correct trend. The necessity of calculating these eigenvectors is motivated from their importance emphasized by Szigeti *et al.*[31] and Cochran and Pawley.[2]

Besides the description of lattice dynamics of calcite crystals in terms of the eigenvalues and eigenvectors along the Λ direction, we have devoted our efforts to simultaneously describe the lattice statics by calculating the cohesive energy of $CaCO_3$, $MgCO_3$, and $ZnCO_3$. The results reported in Table III are in good agreement with their corresponding thermochemical values.[29] It is also seen that the contributions from the short-range overlap repulsion is less than 10% of the total cohesive energy. This feature is indicative of the fact that the major contribution to cohesion in $CaCO_3$, $MgCO_3$, and $ZnCO_3$ is due to the Coulomb attraction, like that in the ionic crystals alkali halides.[1]

A successful description of lattice dynamics and statics achieved for such complicated systems ($CaCO_3$, $MgCO_3$, and $ZnCO_3$) can be considered remarkable in view of the inherent simplicity of RMIM and its less-parametric nature. A detailed calculation of the phonon dispersion curves along other symmetry directions and allied properties of $CaCO_3$, $MgCO_3$, $ZnCO_3$, and other members of its isomorphic series is in process and results will be published subsequently. The results of the present investigation can be further improved by incorporating the effects of van der Waals interactions and the electronic polarizability.

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