

A Lattice Dynamical Investigation of Raman and Infrared Wavenumbers of Mn_2SiO_4

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Abstract— Wilson's GF matrix method has been applied for the investigation of optical phonons of Mn_2SiO_4 in orthorhombic phase having space group Pbnm using normal coordinate analysis. The calculation of zone center phonons have been made with fifteen stretching and ten bending force constants. The calculated values of Raman and infrared wavenumbers are in good agreement with the experimental values. The contribution of each force constant towards the zone centre phonons has been determined in terms of potential energy distribution.

Keywords— Phonon spectra; lattice dynamics; force constant; potential energy distribution.

I. INTRODUCTION

Olivine, $(Mg,Fe)_2SiO_4$, is the major rock-forming mineral in the Earth's upper mantle [1]. The family of olivine compounds, including forsterite (Mg_2SiO_4), fayalite (Fe_2SiO_4), tephroite (Mn_2SiO_4) and solid solutions between them, play a significant role in geosciences since olivines are the most common silicate phases in the Earth's mantle. Manganese orthosilicate, Mn_2SiO_4 , the mineral tephroite, has been the subject of structural, crystal, chemical and thermodynamical study because of its petrological and geophysical importance [2]. Apart from its importance in Earth sciences, this family of olivines is potentially significant from technological point of view [3-4]. Silicate olivines show predominant occurrence in igneous rock and have been used as an important composition in some refractory materials, grit blasting materials, ceramic pigments, additives in cement concrete, flux and slag conditioner in the steel industry [5-6], and so on.

The study of phonon properties of these minerals is crucial for understanding the phenomenon of phase transition in such compounds. The complete information of the macroscopic behavior of the minerals can be best obtained from a detailed knowledge of microscopic nature and this relation is best made via their vibrational spectra. However, the experimental task required for studying the lattice dynamical behavior and properties of minerals is exigent because of the technical difficulties involved in reproducing the temperature and pressure conditions that are relevant to the Earth's interior and in carrying out controlled experiments at such conditions. Therefore, the theoretical prediction of vibrational properties through accurate modeling is the only feasible solution. It is well known that many interatomic force dependent properties of solids can be described very

successfully through harmonic models. Hence, in the present work, the lattice dynamical investigation of Mn_2SiO_4 olivine has been undertaken within the harmonic approximation.

Previous studies reveal that Mg_2SiO_4 and Fe_2SiO_4 olivines have been a subject of thorough study to investigate the lattice dynamical properties both experimentally and theoretically [7-9], but few studies have been conducted to investigate the spectral activity in Mn_2SiO_4 . However, none of the observations [10-11] could assign all the observed Raman and infrared modes in Mn_2SiO_4 . Also to our knowledge, no theoretical calculation of optical phonons has been made in the orthorhombic phase of Mn_2SiO_4 . Hence, in this paper a short range force constant model has been applied to investigate the optical phonons using normal coordinate analysis involving fifteen stretching and ten bending force constants. The theoretically obtained wavenumbers are in very good agreement with the experimental ones. Also, an effort is also made to assign experimental wavenumbers to their respective optical phonon modes. The potential energy distribution (PED) has also been investigated for determining the significance of contribution from each force constant towards the Raman and infrared wavenumbers.

II. THEORY

Mn_2SiO_4 , the mineral tephroite, crystallizes in the orthorhombic olivine structure with space group Pbnm (no 62) and D_{2h} symmetry with four formula units. The structure is composed of an almost hexagonally close packed array of oxygen ions. One eighth of the tetrahedral sites are occupied by silicon ions and one half of the octahedral positions are filled with manganese ions. The Mn octahedra have common edges and form chains along the c-axis. Mn ions occupy two crystallographically non-equivalent octahedral positions with different site symmetries, M1 and M2 (as given in Fig 1) with M1 having 4a site and M2 occupying 4c site. The oxygen ions occupy three distinct positions i.e. O1, O2 and O3. Si, O1 and O2 reside at 4c and O3 ions occupy 8d site. The crystal structure consists of SiO_4 tetrahedra linked by the divalent manganese cations in six fold oxygen anion coordination. Thus there are twenty eight atoms in primitive cell resulting in eighty four vibrational modes. The detailed analysis of total number of modes at zone centre ($k=0$) is:

$$\Gamma_{total} = 11A_g + 11B_{1g} + 7B_{2g} + 7B_{3g} + 10A_u + 10B_{1u} + 14B_{2u} + 14B_{3u}$$

where $B_{1u}+B_{2u}+B_{3u}$ are acoustical modes, $11A_g$, $11B_{1g}$, $7B_{2g}$ and $7B_{3g}$ are Raman active, $9B_{1u}$, $13B_{2u}$ and $13B_{3u}$ are infrared active and $10A_u$ are inactive modes.

Wilson's GF matrix method [12] has been employed to calculate the Raman and infrared wavenumbers by using normal coordinate analysis. In this method the concept of internal coordinates is being introduced which makes the problem more logical. These internal coordinates includes the parameters like bond distances and angles or interatomic distances. The zone centre modes are determined in terms of kinetic and potential energies of the system. The Kinetic energy T is dependent on geometrical arrangement of the atoms and their masses m_{ij} where as the potential energy V which originate due to interactions within the molecule is defined in terms of force constants F_{ij} .

$$T = \frac{1}{2} \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} (G^{-1})_{ij} \dot{S}_i \dot{S}_j$$

$$V = \frac{1}{2} \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} F_{ij} \dot{S}_i \dot{S}_j$$

where G^{-1} stands for the inverse of the G matrix which is describing the kinetic energies in terms of mass-weighted cartesian displacements and $\dot{S} = \frac{dS}{dt}$. The secular equation for calculating the frequencies is given by $|FG - E\lambda| = 0$

Here G is a matrix connected with the vibrational kinetic energy and F is a matrix of force constants to represent potential energy required for each vibration and thus gives an idea of the bond strength. Molecules are constructed in cartesian coordinates and then transformed to internal coordinates with changes in bond distances and bond angles. Both F and G are symmetrical in nature and E is a unit matrix and λ is related to the frequency ν given by $\lambda = 4\pi^2 c^2 \nu^2$.

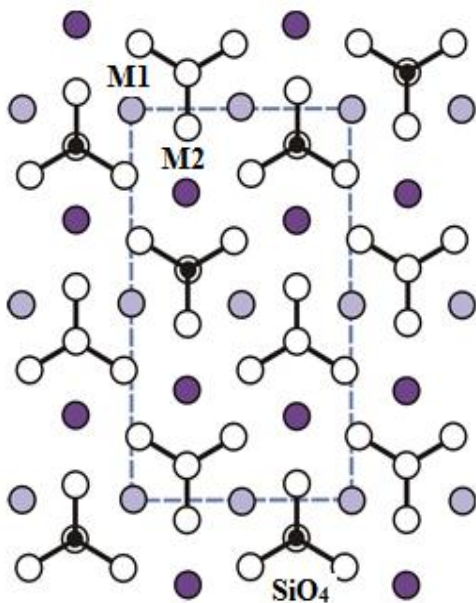


Fig. 1. Unit cell of Mn_2SiO_4 in orthorhombic phase

The present study includes fifteen stretching K_i and ten bending force constants H_i to formulate F matrix. The short range forces are significant upto certain neighbors and their magnitude generally decreases after the second neighbor interaction. The reason for inclusion of bending forces in our calculations is that the stretching forces only are not sufficient to explain transverse vibrations. Short range stretching forces between nearest neighbors Si-O, Mn-O, O-O and bending forces between O-Mn-O and O-Si-O are used in the present analysis. The input parameters used for the study are masses of the atoms, unit cell dimensions [13], symmetry coordinates and available Raman and infrared frequencies [11].

III. RESULTS AND DISCUSSION

The force constants as given in Table I have been optimized and empirically scaled so as to make the vibrational wavenumbers in good agreement with the observed Raman and infrared numbers.

TABLE I. INTERATOMIC FORCE CONSTANT VALUES (in $N\ cm^{-1}$)

Force constant	Between atoms	Coordination Number	Distance (Å)/ Angle (degree)	Force constant value
K1	Si-O1	4	1.619	3.812
K2	Si-O3	8	1.639	3.466
K3	Si-O2	4	1.657	3.388
K4	Mn1-O2	8	2.167	0.474
K5	Mn1-O1	8	2.200	0.414
K6	Mn1-O3	8	2.249	0.328
K7	Mn2-O2	4	2.139	0.522
K8	Mn2-O3	8	2.154	0.354
K9	Mn2-O1	4	2.278	0.311
K10	O2-O3	8	2.580	0.638
K11	O1-O3	8	2.753	0.305
K12	O1-O3	8	3.154	0.203
K13	O2-O3	8	3.031	0.172
K14	O2-O3	8	3.358	0.153
K15	O2-O3	8	3.585	0.146
H1	O2-Si-O3	8	103.03	0.423
H2	O3-Si-O3	4	105.53	0.524
H3	O1-Si-O2	4	113.11	0.272
H4	O1-Si-O3	8	115.32	0.179
H5	O3-Mn2-O3	8	87.64	0.156
H6	O3-Mn2-O3	4	115.59	0.182
H7	O1-Mn2-O3	8	90.70	0.156
H8	O3-Mn2-O3	4	68.47	0.484
H9	O2-Mn1-O3	4	108.51	0.212
H10	O1-Mn1-O3	8	84.71	0.159

With the force constants taken as input, the eigen value equation involving 84×84 matrix was solved. It is obvious from Table I that the stretching force constants for Si-O i.e. K1, K2 and K3 show a systematic variation with interatomic distance. The value of K1 is the highest among all corresponding to the smallest interatomic distance Si-O1 in comparison, the results of previous experimental [11] studies are listed in Table II along

with the present calculated results. There is a good agreement between the theory and experimental results thus establishing the validity of present calculations. The potential energy distribution for each normal mode in Mn_2SiO_4 is also investigated and the two dominant contributions from force constant are given in the results. The assignment of specific modes have been made observing the atomic displacements in the eigen vectors.

TABLE II. CALCULATED AND EXPERIMENTAL RAMAN ACTIVE WAVENUMBERS (in cm^{-1}) FOR Mn_2SiO_4

Mode	Expt [11]	Present result	Two dominant contribution as per PED
A_g	935	944	K1-40%, K2-29%
	840	853	K3-57%, K2-24%
	808	812	K1-40%, K2-11%
	575	565	H1-33%, K10-13%
	515	511	H2-48%, K13-9%
	389	408	H3-23%, K13-13%
	291	318	H6-19%, K8-12%
	256	283	K13-21%, K9-15%
	244	247	K8-30%, K10-15%
	167	182	H7-27%, K7-24%
B_{1g}	124	129	K7-21%, K8-15%
	-	942	K1-41%, K2-30%
	-	858	K3-52%, K2-27%
	820	819	K1-39%, K3-16%
	588	560	H1-31%, K10-14%
	546	530	H2-50%, K13-8%
	393	403	H3-31%, H4-15%
	307	312	K7-18%, H6-15%
	288	273	K9-18%, H8-10%
	271	253	H8-21%, K13-12%
B_{2g}	203	192	H7-28%, H6-14%
	155	168	K7-31%, H7-12%
	-	882	K2-82%, K11-3%
	553	550	H1-43%, K10-24%
	401	427	H4-37%, K12-17%
	319	338	H5-29%, K8-19%
	274	288	K13-21%, K12-13%
	188	186	K8-37%, K9-30%
	119	123	H11-20%, K14-12%
	B_{3g}	892	866
555		548	H1-45%, K10-24%
378		395	H4-36%, K11-21%
304		318	H7-26%, K8-28%
276		279	K9-29%, K13-14%
223		226	K8-20%, K15-13%
137		165	H5-25%, K14-20%

The inferences drawn from the PED are described below: It is quite evident from Table II that the highest frequencies i.e., $944cm^{-1}$, $853cm^{-1}$, $812cm^{-1}$ in A_g mode, $942cm^{-1}$, $858cm^{-1}$, $819cm^{-1}$ in B_{1g} mode, $882cm^{-1}$ in B_{2g} mode and $866cm^{-1}$ in B_{3g} mode has the dominant contribution of Si-O stretching interaction i.e K1, K2 and K3. This result is in confirmation with the inferences drawn by Mouri et al. [10] and Stidham et al. [11]. It has been observed that the M-site cations do not participate in the higher frequency modes. A close look at the reveals that identical results are obtained for the highest infrared wavenumbers in each mode and is attributable mainly due to the Si-O stretching. All the middle order

frequencies lying between $400 cm^{-1}$ to $565 cm^{-1}$ i.e. $565cm^{-1}$, $511cm^{-1}$, $408cm^{-1}$ in A_g mode, $560 cm^{-1}$, $530cm^{-1}$, $403cm^{-1}$ in B_{1g} mode, $550cm^{-1}$, $427cm^{-1}$ in B_{2g} mode and $548cm^{-1}$ and $395cm^{-1}$ in B_{3g} are mainly contributed by O-Si-O bending force constants given by H1, H2, H3 and H4. Thus we find that all the frequencies $> 400 cm^{-1}$ are associated with the internal vibrations within the SiO_4 tetrahedron. The frequencies $< 400 cm^{-1}$ are low frequency modes which have the contribution of multiple force constants (K4 to K15 and H5 to H10). These frequencies are due to Mn-O stretching force and O-O repulsive force among SiO_4 tetrahedra. These modes are external vibrations which involve the rotation and translation of SiO_4 tetrahedra and Mn cations. As per our knowledge no other theoretical data is available to compare the calculated infrared Raman and infrared wavenumbers. A precise determination of infrared wavenumbers is required to further establish the present results.

TABLE III. CALCULATED AND EXPERIMENTAL INFRARED ACTIVE WAVENUMBERS (in cm^{-1}) FOR Mn_2SiO_4

Mode	Expt [11]	Present result	Two dominant contribution as per PED
B_{1u}	875	883	K2-81%, K10-4%
	480	500	H1-46%, K10-26%
	430	437	H4-32%, K11-17%
	350	365	H5-22%, K6-20%
	-	306	K5-31%, H10-26%
	300	283	K5-39%, H10-18%
	240	228	H10-34%, K6-17%
	187	172	H9-31%, K13-19%
	-	129	K6-24%, K5-16%
	B_{2u}	945	931
860		884	K3-51%, K2-20%
816		801	K1-29%, K3-22%
-		564	H1-30%, K10-11%
512		514	H2-40%, H10-13%
454		440	H3-22%, K13-11%
-		373	K12-18%, K6-14%
340		322	H9-31%, H10-19%
276		283	K4-31%, H6-15%
242		236	H8-26%, K7-23%
B_{3u}	-	198	K7-23%, H7-29%
	157	164	K5-25%, H9-14%
	-	100	H8-24%, H5-16%
	950	934	K1-47%, K2-34%
	912	889	K3-53%, K2-20%
	815	792	K1-30%, K2-19%
	562	550	H1-32%, K10-14%
	490	502	H2-42%, K10-11%
	-	444	H3-22%, K13-14%
	-	378	K5-24%, H10-17%
365	341	H10-32%, K7-12%	
297	273	H7-20%, H8-15%	
-	204	K4-33%, H9-24%	
-	188	K6-33%, K5-20%	
177	174	K12-20%, K5-17%	
-	129	K5-22%, K14-15%	

IV. CONCLUSION

Normal coordinate analysis has been performed on Mn_2SiO_4 olivine to calculate the Raman and the infrared wavenumbers with twenty five short range force constants. It was found that the higher order frequencies are mainly contributed SiO_4 tetrahedra while the lower frequencies are dominated by Mn atoms. Eigen vectors associated with Raman and infrared frequencies for tephroite has also been determined. The theoretical results are found to be in good agreement with experimental observed values. The contribution of each force constant has been determined from the potential energy distribution towards the different vibrational modes.

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