Study of lattice dynamics of Fe$_2$SiO$_4$- and Mg$_2$SiO$_4$-spinels

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Abstract. Fe$_2$SiO$_4$ is an end member of Mg-rich (Mg, Fe)$_2$SiO$_4$ which is believed to be a major mineral of the Earth’s transition zone [1, 2]. The presence of iron has a pronounced effect on elastic and thermodynamic properties of rock-forming minerals. These properties play crucial role in the interpretation of the geophysical data and thus have a large influence on our knowledge of the earth’s interior. An understanding of the elastic properties of silicate will be further helpful to the interpretation of seismological data, in particular the variation in the depth range of transition zone of earth’s interior. The spinel form of magnesium-iron orthosilicate, (Mg, Fe)$_2$SiO$_4$, is believed to be one of the most abundant minerals in the mantle’s transition zone and is found to be stable in ambient conditions and therefore, a detailed study of zone centre phonons of this stable phase of orthosilicates (Mg, Fe)$_2$SiO$_4$ is of high interest. Hence, in the present study, the zone centre phonons of antiferromagnetic Fe$_2$SiO$_4$-spinel and Mg$_2$SiO$_4$-spinel have been studied by using short range force constant model involving interatomic interactions upto first three neighbours. The zone centre phonons of Fe$_2$SiO$_4$ is compared with that of Mg$_2$SiO$_4$ in order to study the effect of the cation exchange on the dynamic and thermodynamic properties of (Mg, Fe)$_2$SiO$_4$-spinel. The calculated results are compared and analyzed with exiting experimental results.

1. Introduction
The spinel form of magnesium-iron orthosilicate, (Mg, Fe)$_2$SiO$_4$ is the most abundant mineral in the Earth upper mantle and is believed to have dominant influence on crucial geophysical processes in this part of the Earth [1,2]. The olivine-spinel phase transition and crystal structure of silicate spinel have been extensively investigated for understanding possible phase transformations and crystal chemistry of the orthosilicate. Detailed characterization of this mineral and its end members, Mg$_2$SiO$_4$ and Fe$_2$SiO$_4$, is, therefore, crucial for future understanding of the main Earth processes. (Mg,Fe)$_2$SiO$_4$ is known to exists in three phases: (i) low-pressure $\alpha$ orthorhombic (olivine), (ii) moderate-pressure $\beta$ orthorhombic (wadsleyite), and (iii) high-pressure $\gamma$ cubic (ringwoodite) [3] So far, several experimental [4] and theoretical [5,6] studies have been reported concerning the structural, dynamical, and thermodynamical properties of Mg$_2$SiO$_4$, crystallizing in all three {$\alpha$,$\beta$,$\gamma$} phases. Whereas, Fe$_2$SiO$_4$ is known to exist only in two stable phases ($\alpha$ fayalite and $\gamma$ spinel) represents much more challenging material as it belongs to the group of transition metal orthosilicates, additionally possessing nonvanishing magnetic moment [7].

The knowledge of the properties of all phases of (Mg,Fe)$_2$SiO$_4$ is of great importance for earth sciences, since it determines crucial geophysical properties of the earth’s interior such as possible phase transitions and thermodynamics of the rock forming minerals. These properties play crucial role in the interpretation of the geophysical data, and thus have a large influence on our knowledge of the earth’s interior. However, it is very difficult and expensive to reproduce the pressure conditions of the deep regions of the earth in the laboratory and it is more difficult to perform precise measurements in such conditions. The fundamental link between microscopic (atomistic) behaviour of minerals and macroscopic properties can be made through the lattice dynamics of the minerals which is determined by interatomic interactions, and this in turn determine the basic thermodynamic properties of the minerals. In comparison to the Fe$_2$SiO$_4$ fayalite, its high-pressure-spinel phase is a much less studied
system. Therefore, in the present investigation the interatomic interaction and zone center phonons of high-pressure-spinel phase of Fe$_2$SiO$_4$ has been studied by using an angular force constant model [8]. We compare them with those obtained for Mg$_2$SiO$_4$-spinel in order to understand the influence of cation exchange on lattice dynamics and thermodynamics in the ringwoodite (Fe,Mg)$_2$SiO$_4$.

2. Crystal structure
Spinel phase of (Mg,Fe)$_2$SiO$_4$ is cubic and exists in a γ-spinel structure that belongs to space group Fd3m (O$_h^7$) [9]. This cubic structure consists of isolated SiO$_4$ tetrahedra, with Mg/Fe atoms occupying the interstitial sites between SiO$_4$ groups. The primitive cell has 2 formula units including 14 atoms (figure 1), so there are 42 normal modes for each point in the Brillouin zone, among which 3 are acoustic and 39 are optical modes. The optical modes at the BZ centre may be divided by symmetry as

$$\Gamma = A_{1g} + 2A_{2u} + E_g + 2E_u + T_{1g} + 4T_{1u} + 2T_{2u} + 3T_{2g}.$$ 

Here subscripts g and u denote symmetric and antisymmetric modes with respect to the centre of inversion, while R and IR represent Raman and infrared active modes. All E modes are doubly degenerate, and all T modes are ternary degenerate. A$_{1g}$, E$_g$, and all T$_{2g}$ modes are Raman active, while all T$_{1u}$ modes are infrared active.

![Figure 1. Crystal structure of Mg$_2$SiO$_4$-spinel](image)

3. Interatomic interaction
The determination of the strengths of the interatomic interaction in these orthosilicates is important from the point of view of their thermo dynamical properties. One of the few procedures suitable are the interatomic force constant investigations. Therefore, in the present investigation a de Launey angular force constant (DAF) model [8] has been applied for the calculation of the interatomic interaction of (γ-spinel). In this model, the relative displacement of the reference atom and one of its neighbours is considered. The restoring force on the reference atom is taken to be proportional to the component of the relative displacement perpendicular to a line joining the two atoms. In the present analysis, the short range force constants between the first three neighbours $\alpha_1$, $\alpha_2$, $\alpha_3$ (central) for the interatomic interactions for Si-O, Mg(Fe)-O, and Mg(Fe)-Mg(Fe) are evaluated by fitting the measured zone-center phonon frequencies [5,7,10-11] to the corresponding analytical expressions for A$_{1g}$, E$_g$, and $\Sigma T_{1u}$ obtained in Ref. 12 by solving a dynamical matrix of order (42x42) at k = 0 for a compound with an ideal spinel structure. The force constants, thus calculated are listed in Table 1. It is obvious from the table 1 that the short range Si-O forces of the SiO$_4$ tetrahedra are larger than other interatomic forces in both orthosilicates. The interatomic interactions between Si-O is covalent in nature may be the reason of dominance over the other interactions. The rattling of cations is the reason for this kind of interactions in minerals [13]. There is almost negligible change (0.9%) in force
constant involving Si-O atoms whereas 10% and 7% changes in the values of force constants involving (Fe/Mg-O) and (Fe/Mg-Fe/Mg) respectively.

Table 1. Short-range force constants (in K dyne cm$^{-1}$)

| Force constant | Mg$_2$SiO$_4$ | Fe$_2$SiO$_4$ |
|----------------|--------------|--------------|
| $\alpha_1$ [Si-O] | 10.05 | 9.96 |
| $\alpha_2$ [Mg(Fe)-O] | 2.14 | 2.35 |
| $\alpha_3$ [Mg(Fe)-Mg(Fe)] | 0.57 | 0.48 |

4. Zone centre phonons

The short range force constants thus calculated are taken as input parameters to compute zone-centre (ZC) phonon frequencies for (Mg/Fe)$_2$SiO$_4$. The calculated ZC phonons along with other results [5,7,10-11] are given in table 2. In the case of the spinel with a cubic Fd3m symmetry, there are three independent displacements, one for each non-equivalent atom (Mg/Fe, Si, and O).

Table 2. Calculated and measured and other calculated [7,10-12] zone-center (ZC) phonon frequencies (in cm$^{-1}$) for Mg$_2$SiO$_4$ and Fe$_2$SiO$_4$

| Species | Mg$_2$SiO$_4$ | Fe$_2$SiO$_4$ |
|---------|---------------|---------------|
|         | Present       | Present       | M. Derzsi et al. |
|         | calculation   | calculation   | [7] |
| $A_{1g}$ | 133           | 133           | 130 |
| $E_g$   | 59            | 59            | 59  |
| $T_{2g}(1)$ | 145       | 126           | 144 |
| $T_{2g}(2)$ | 82       | 95            | 78  |
| $T_{2g}(3)$ | 37       | 48            | 37  |
| $T_{1u}(1)$ | 146       | 132           | 145 |
| $T_{1u}(2)$ | 74        | 87            | 66  |
| $T_{1u}(3)$ | 66        | 71            | 50  |
| $T_{1u}(4)$ | 45        | 56            | 28  |
| $A_{2u}(1)$ | 133       | 126           | 131 |
| $A_{2u}(2)$ | 78        | 89            | 48  |
| $E_u(1)$ | 84            | 83            | 84  |
| $E_u(2)$ | 61            | 56            | 32  |
| $T_{1g}$ | 59            | 55            | 59  |
| $T_{2d}(1)$ | 74        | 65            | 73  |
| $T_{2d}(2)$ | 47        | 35            | 23  |

The eigen vector calculations suggest that Oxygen and silicon ions contribute to majority of the phonon modes. Oxygen ions contribute to the majority of high energetic modes. Table 2 suggests that Raman-active modes of $A_{1g}$ symmetry and $E_g$ symmetry are in excellent agreement with observed results [7,10-11] in these silicates. The eigenvector calculations predict that $A_{1g}$ and $E_g$ vibrations involve only oxide ion displacements. The $F_{2g}(2)$ and $F_{2g}(3)$ phonons are characterized by large oxygen and very small silicon displacements, but the lowest energy $F_{2g}(1)$ phonons derive predominantly from a vibration of the Si sublattice. The contribution of silicon atoms to other than Si-O stretching modes is very small. The phonon modes with the largest energy ($T_{1u}$) involve predominantly (Mg/Fe) vibrations. Comparing the zone center phonon energies of both spinel structures (table 2), it is clear that substitution of all Mg atoms by Fe atoms causes a lowering of all phonon modes. It is found that Raman modes are almost same in two spinels because these modes are due to either Si or O ion vibrations. But there is mark able decrease in magnitudes of infrared active modes [$A_{2u}(2)$, $E_u(2)$ and $T_{2u}(2)$] of Fe$_2$SiO$_4$ than that of Mg$_2$SiO$_4$. The most of these modes is due to the vibrations of (Fe/Mg). It is due to larger mass of iron compare to magnesium and is in agreement with other results [7].
calculated Raman modes are in agreement with experiment [10] whereas, there is a deviation in infrared active modes. The consideration of more interatomic interaction may improve the results.

5. Conclusions
The interatomic interaction (Si-O) is found to be dominating over other interatomic interactions. The rattling of cations may be the cause for this dominance. A comparison of ZC phonons with theory and other calculations shows the agreement of the results. The substitution of magnesium (Mg) by iron (Fe) is mainly influencing some of the infrared active modes. The lowering of phonon modes caused by the replacement of Mg by Fe may lead to change in bulk modulus and hence significant enhancement of entropy and heat capacity.

6. References

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