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# Theoretical determination of the Raman spectra of single-crystal forsterite ($Mg_2SiO_4$)

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## ABSTRACT

Density functional perturbation theory is used to calculate the Raman spectrum of forsterite ($Mg_2SiO_4$). In addition to the fundamental mode frequencies and atomic displacements, the scattering intensities are computed from first principles for the first time. Six independent single-crystal Raman spectra are measured for synthetic forsterite, and good agreement is found between calculation and experiment over a range of nearly six orders of magnitude of scattered intensity. Calculated atomic displacements of these fundamental Raman modes generally agree closely with the results of previous lattice dynamics studies. Modes with frequencies above 500 $cm^{-1}$ consist primarily of motions internal to the $SiO_4$ tetrahedra, while those below 500 $cm^{-1}$ are dominated by Mg2 displacements mixed with $SiO_4$ translations and rotations. The considerably larger Raman amplitudes for modes above 500 $cm^{-1}$ appear to be due to displacements within the highly polarizable oxygen environments surrounded by covalently bonded $Si^{4+}$ and ionically bonded $Mg^{2+}$. With regard to calculated frequencies, the theory underestimates frequencies by as much as 8 $cm^{-1}$ for modes over 500 $cm^{-1}$, while it generally overestimates frequencies by as much as 17 $cm^{-1}$ for modes below 500 $cm^{-1}$. An equivalent set of Raman spectra were measured for the Fe end-member of the olivine solid-solution series, fayalite ($Fe_2SiO_4$), and compared to the results for forsterite.

**Keywords:** Raman spectroscopy, fayalite, forsterite, density functional theory