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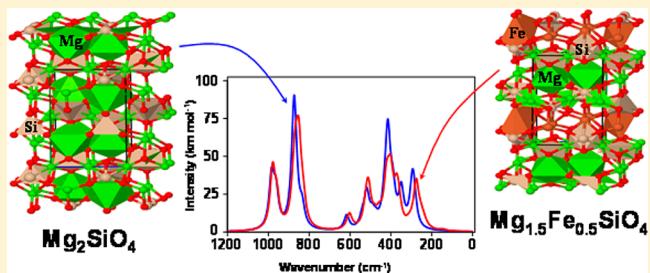
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S Supporting Information

ABSTRACT: B3LYP periodic simulations have been carried out to study some physicochemical properties of the bulk structures and the corresponding nonpolar (010) surfaces of Mg-pure and Fe-containing olivine systems; i.e., Mg_2SiO_4 (Fo) and $Mg_{1.5}Fe_{0.5}SiO_4$ (Fo₇₅). A detailed structural analysis of the (010) Fo and Fo₇₅ surface models shows the presence of coordinatively unsaturated metal cations (Mg^{2+} and Fe^{2+} , respectively) with shorter metal–O distances compared to the bulk ones. Energetic analysis devoted to the Fe^{2+} electronic spin configuration and to the ion position in the surfaces reveals that Fe^{2+} in its quintet state and placed at the outermost positions of the slab constitutes the most stable Fe-containing surface, which is related to the higher stability of high spin states when Fe^{2+} is coordinatively unsaturated. Comparison of the simulated IR and the corresponding reflectance spectra indicates that Fe^{2+} substitution induces an overall bathochromic shift of the spectra due to the larger mass of Fe compared to Mg cation. In contrast, the IR spectra of the surfaces are shifted to upper values and exhibit more bands compared to the corresponding bulk systems due to the shorter metal–O distances given in the coordinatively unsaturated metals and to symmetry reduction which brings nonequivalent motions between the outermost and the internal modes, respectively.



INTRODUCTION

Olivines are silicate solid solutions with general formula $Mg_{2-x}Fe_{(2-2x)}SiO_4$ ($x = 0 - 1$) and are one of the most abundant silicate groups in the Earth's upper mantle. Crystalline olivines present an orthorhombic structure with space group $Pbnm$ and are characterized to have $[SiO_4]^{4-}$ tetrahedra linked by the divalent cations. Their magnesium and iron end members are forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). The interest for investigating olivines is not only due to their prominence as common rock-forming minerals but also because olivinic dust grains are ubiquitously present throughout interstellar and circumstellar media.^{1–3} An important chemical role of cosmic dust particles is, like in heterogeneous catalysis, to accelerate certain astrochemical reactions by orders of magnitude when occurring at their surfaces.^{4,5} The presence of dust grains is especially important for the synthesis of molecules that otherwise would be impossible to form via simple gas-phase reactions, such as H_2 ^{6,7} and H_2O ,⁸ two of the most relevant molecules in the Universe. On Earth, these silicate groups are mostly found in a crystalline state, whereas cosmic olivines are mainly present as amorphous materials,³ although crystalline forms have also been detected.⁹ Both on Earth and in space, crystalline olivines appear to be richer in magnesium than in iron.^{9,10}

Atomic-scale simulations of solid state surfaces are useful techniques to understand their physicochemical properties, as they provide structural atomistic details (e.g., the presence and

nature of surface defects), one-electron properties (e.g., charge distribution, electrostatic potentials, and spin densities) or spectroscopic properties (e.g., vibrational features and infrared signatures). Forsterite surfaces are by far the most studied olivine surfaces with different atomistic simulation techniques;^{11–27} i.e., by means of periodic treatments or cluster model approaches using classical shell-ion model potentials and density functional methods. Moreover, most of these studies include the interaction with $H^{14–18}$ and $H_2O^{19–27}$ to evaluate the adsorption features. The large number of studies on forsterite contrasts with the limited works focused on Fe-containing olivine surfaces, the available theoretical works being limited to the bulk and the (010) surface of fayalite.^{28–31} This lack of theoretical studies is partly due to the large compositional variability in these minerals that can tolerate various isomorphic substitutions and to the fact that the treatment of Fe-containing minerals bears additional difficulties due to the possible presence of strong correlations effects. Therefore, the physicochemical properties of Fe-bearing olivine surfaces (and in a more extent, of Fe-bearing minerals) are

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poorly understood. Understanding these systems is of significant importance because they serve as an important source for electrons in redox reactions in various geochemical environments.^{32–35} Moreover, the change of the Fe oxidation state has a profound impact on the electronic structure of the surfaces of these minerals, such as in their adsorption properties and chemical activity. Several theoretical works have been devoted to understand the redox activity of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ pair in different clays and minerals.^{36–40}

The aim of the present work is to provide, based on ab initio electronic structure calculations, a detailed description of different physicochemical features of the bulk and (010) surfaces (the main cleavage crystallographic plane of forsterite) of Mg_2SiO_4 and $\text{Mg}_{1.5}\text{Fe}_{0.5}\text{SiO}_4$ (25% of Fe^{2+} substitution), this latter being considered as a paradigmatic case for the Fe-containing olivine surfaces. In particular, analysis of the surface structures, electronic properties (electrostatic potentials, spin densities, and Fe^{2+} electronic states), and vibrational (IR spectra) and dielectric (reflectance spectra) properties are presented. Special attention to the differences between Mg-pure and Fe-containing surfaces is also addressed.

COMPUTATIONAL DETAILS

All periodic calculations have been performed with the ab initio CRYSTAL09 code.⁴¹ This code implements the Hartree–Fock and Kohn–Sham self-consistent field method based on localized Gaussian Type Orbitals (GTO) for periodic systems.⁴² Surface models computed by CRYSTAL09 are true 2D systems, at variance to plane wave-based codes, in which the slab is artificially replicated through infinity also in the direction perpendicular to the slab by including a large amount of empty space.

The multielectron wave function is described by linear combination of crystalline orbitals, which in turn are expanded in terms of GTO basis sets. Specifically, oxygen, magnesium, silicon, and iron were described by (8s)-(411sp)-(1d), (8s)-(511sp)-(1d), (8s)-(6311sp)-(1d), and (8s)-(64111sp)-(1d) contractions, respectively; these basis functions were already used in previous works focused on the forsterite^{43–45} and fayalite³⁰ bulk properties.

All the SCF calculations and geometry optimizations were performed with the B3LYP density functional method.^{46,47} Geometry optimizations of the forsterite bulk systems have been performed in $Pbnm$ space symmetry, whereas of the Fe-containing bulk structures and for the surface models in $P1$ group symmetry (no symmetry), in order to ensure the maximum degrees of freedom during the optimization. Both lattice constants and internal coordinates have been simultaneously optimized within the same run, using analytical gradients and upgrading the numerical Hessian with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.^{48–51} Default values of the tolerances that control the Coulomb (6 6 6) and exchange (14) series have been adopted. This means that when the overlap between two atomic orbitals is smaller than 10^{-6} (for Coulomb) and 10^{-14} (for exchange) the integral is either approximated or disregarded.⁴¹ The Hamiltonian matrix has been diagonalized⁵² in 20 reciprocal lattice points (k points) to sample the Brillouin zone, corresponding to a shrinking factor of 6.⁴¹ Open-shell calculations were based on an unrestricted formalism. Electron spin densities on the atoms have been obtained by using the Mulliken population analysis.

Phonon frequencies of the considered systems have been calculated as the eigenvalues obtained by diagonalizing the

mass-weighted Hessian matrix at Γ point (point $k = 0$ in the first Brillouin zone, called the central zone). The mass-weighted Hessian matrix was obtained by numerical differentiation (central-difference formula) of the analytical first energy derivatives, calculated at geometries obtained by displacing, in turn, each of the $3N$ equilibrium nuclear coordinates by a small amount, $u = 0.003 \text{ \AA}$. We refer to this work⁵³ for a complete discussion of the computational conditions and other numerical aspects concerning the calculation of the vibrational frequencies at the Γ point. The value of the infrared intensity for each normal mode was also computed via the dipole moment variation along the normal mode adopting the set of localized Wannier functions.^{54–56}

Reflectance spectra ($R(\nu)$) of 3D-periodic systems can be simulated with CRYSTAL09 by combining different ingredients available in the code: i) calculation of the vibrational modes, their corresponding intensities, and separation of the transverse and longitudinal optical (TO and LO, respectively) modes;^{53,57} ii) calculation of the high frequency dielectric tensor (ϵ_{∞})^{58–61} contributing to the frequency-dependent complex dielectric function ($\epsilon(\nu)$); and iii) calculation of the mass-weighted effective mode Born charges.^{62–64} Reflectance spectra of several crystalline mineral systems have successfully been simulated with CRYSTAL09,^{30,44,45,65–67} and the interested reader can find all details there.

RESULTS AND DISCUSSION

For the sake of brevity, the forsterite (Mg_2SiO_4)-related systems will be hereafter referred to as Fo and the Fe-containing ($\text{Mg}_{1.5}\text{Fe}_{0.5}\text{SiO}_4$) ones as Fo_{75} . This section is organized as follows. First, results related to the structures and to some energy-related features of both the bulk systems and the (010) surfaces of Fo and Fo_{75} are shown. Then, analyses of the electrostatic potential maps of the very same surfaces and of the spin density distribution of the Fo_{75} are provided. Subsequently, the simulated infrared and reflectance spectra of these systems are shown, paying special emphasis to the changes given by the presence of Fe.

Structure and Energy-Related Features. The bulk crystal structure of Fo and Fo_{75} is very similar (see Figure 1). They are made up of distorted SiO_4 tetrahedra and $\text{MgO}_6/\text{FeO}_6$ octahedra, in which the tetrahedra and the octahedra share the vertices. Half of the available octahedral voids are occupied by the divalent cations. In Fo there are two symmetry-independent Mg atoms, named Mg1 and Mg2.⁶⁸ The Mg1-centered octahedra share edges forming rods parallel to the crystallographic c axis, and the Mg2 octahedra are laterally linked to these rods through the corresponding edges. A substitution of half of Mg2 by Fe yields the $\text{Fo}_{75}^{\text{M}2}$ structure (see Figure 1b), whereas half of Mg1 by Fe yields the $\text{Fo}_{75}^{\text{M}1}$ one (see Figure 1c). It is worth mentioning that different studies^{69–71} indicate that the Fe-containing solid solutions are more stable in the high-spin state than in the low-spin one at normal conditions, and accordingly the bulk $\text{Fo}_{75}^{\text{M}2}$ and $\text{Fo}_{75}^{\text{M}1}$ systems have been computed in this high-spin state (i.e., each Fe^{2+} cation (d^6) in a quintet electronic state).

The optimized structural parameters of the bulk structure of Fo (Table 1) are in good agreement with experiments. As already reported,⁴³ calculated cell parameters are slightly overestimated (giving a volume variation of 2.2%) and the experimental Si–O and Mg–O distances are well reproduced, the largest differences being given in the Mg2–O distances (0.024 Å larger, at the most). The calculated equilibrium

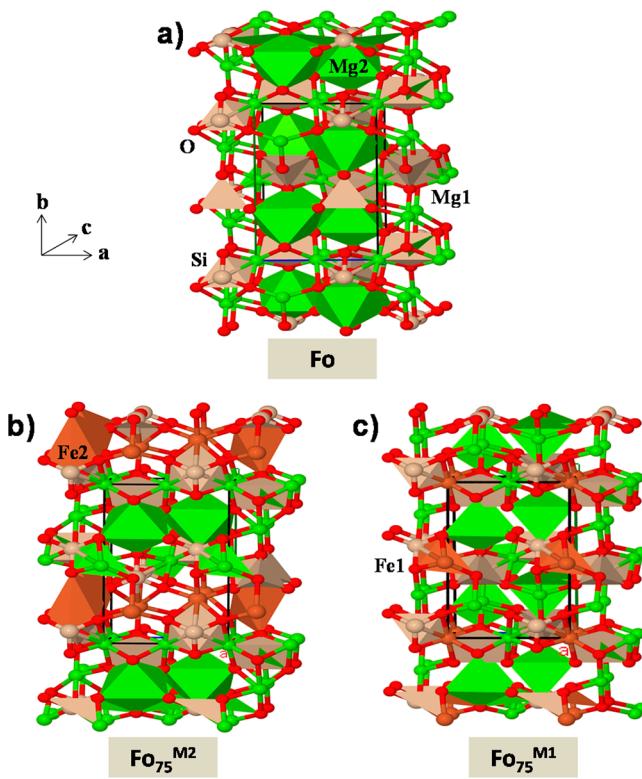


Figure 1. View (along the c crystallographic axis) of the crystal structure of forsterite (Fo, a) and $\text{Mg}_{1.5}\text{Fe}_{0.5}\text{SiO}_4$, in which Fe^{2+} occupies the M2 position ($\text{Fo}_{75}^{\text{M}2}$, b) and the M1 position ($\text{Fo}_{75}^{\text{M}1}$, c).

geometries of $\text{Fo}_{75}^{\text{M}2}$ and $\text{Fo}_{75}^{\text{M}1}$ are also given in Table 1. Cell parameters are larger than those of Fo because of the larger ionic radius of Fe^{2+} than Mg^{2+} (0.78 and 0.72 Å, respectively), and accordingly the volume of the two iron containing systems is larger as well. The presence of Fe (irrespective of its position) slightly affects the Mg–O distances by increasing their values compared to the Fo ones, whereas the Si–O distances are in both systems very similar to those of Fo.

The large variability of oxygen sublattice in Fo results in a complex set of crystal planes. For instance, there are already 7 different planes characterized by the smallest Miller indexes ($\{100\}$, $\{010\}$, $\{001\}$, $\{110\}$, $\{101\}$, $\{011\}$, $\{111\}$ crystal forms) whose modeling is rather difficult, since electro-neutrality should be enforced by rather complex chemical reconstruction. Normally, slab models are modeled by cutting out the bulk crystal at the Mg–O bonds rather than the Si–O

ones to keep the SiO_4 units intact. Moreover, both polar and nonpolar surface slabs can be obtained, depending on the edge layers and the thickness of the slab model. In this work, the nonpolar (010) forsterite surface (hereafter referred as Fo^{surf}) has been studied (shown in Figure 2), since it is the major

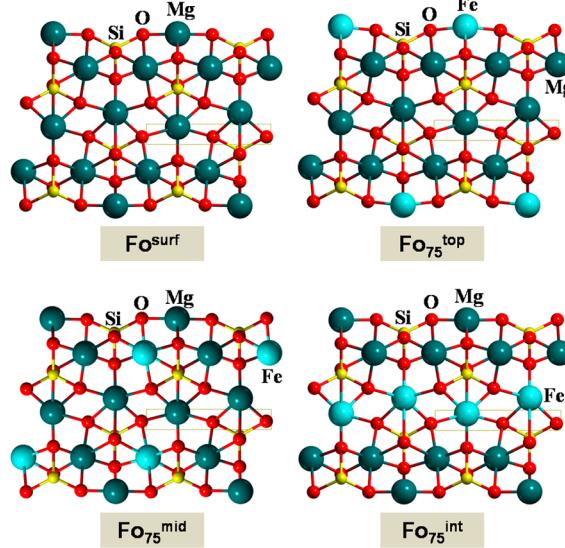


Figure 2. Lateral views of the nonpolar (010) surfaces for forsterite (Fo^{surf}) and for the Fe-containing olivine surfaces ($\text{Fo}_{75}^{\text{top}}$, $\text{Fo}_{75}^{\text{mid}}$, and $\text{Fo}_{75}^{\text{int}}$).

cleavage plane of Fo and, according to previous calculations, the most stable surface in dry conditions.^{11,19,21} This nonpolar surface is terminated by edge-layers containing both M2 magnesium ions and oxygen atoms, in which Mg^{2+} cations are unsaturated centers coordinated by 3 O atoms. The polar (010) surface (not considered in this work) is terminated by a half vacant layer of M1 magnesium ions.¹¹ For the Fe-containing systems, three different slab models have been designed from the two initial bulk structures; i.e., $\text{Fo}_{75}^{\text{top}}$ and the $\text{Fo}_{75}^{\text{int}}$ surfaces from $\text{Fo}_{75}^{\text{M}2}$ and $\text{Fo}_{75}^{\text{mid}}$ from $\text{Fo}_{75}^{\text{M}1}$. $\text{Fo}_{75}^{\text{top}}$ exhibits the Fe^{2+} ions at the outermost positions of the edge-layers of the slab model and, similarly to the analogous Mg^{2+} ions in Fo^{surf} , are coordinatively unsaturated centers. In $\text{Fo}_{75}^{\text{mid}}$, the Fe ions are placed in the midregions of the slab, whereas in $\text{Fo}_{75}^{\text{int}}$ they are in the innermost regions. For these surfaces, the atomic integrated spin density has been evaluated by computing both the quintet, triplet, and singlet states per Fe^{2+} ions. Considering that a unit cell contains two Fe^{2+}

Table 1. B3LYP-Optimized and Experimental Bond Distance Range and Cell Parameters (in Å) of the Bulk Structures of Fo, $\text{Fo}_{75}^{\text{M}2}$, and $\text{Fo}_{75}^{\text{M}1}$ ^a

| | Fo | Fo_{exp} | $\text{Fo}_{75}^{\text{M}2}$ | $\text{Fo}_{75}^{\text{M}1}$ |
|--------|-------------|--------------------------|------------------------------|------------------------------|
| Si–O | 1.628–1.673 | 1.616–1.649 | 1.629–1.672 | 1.633–1.674 |
| Mg1–O | 2.073–2.131 | 2.069–2.126 | 2.064–2.148 | 2.096–2.134 |
| Mg2–O | 2.062–2.222 | 2.040–2.166 | 2.070–2.228 | 2.066–2.242 |
| Fe1–O | — | — | — | 2.119–2.226 |
| Fe2–O | — | — | 2.085–2.298 | — |
| a | 4.789 | 4.746 | 4.791 | 4.835 |
| b | 10.253 | 10.18 | 10.369 | 10.320 |
| c | 6.009 | 5.976 | 6.063 | 6.021 |
| volume | 295.10 | 288.73 | 301.28 | 300.46 |

^aThe volume of the bulks (in Å³) is also included.

Table 2. Range of the B3LYP-Optimized Bond Distances of Forsterite (Fo^{surf}) and Fe-Containing Olivine (010) Surfaces ($\text{Fo}_{75}^{\text{top}}$, $\text{Fo}_{75}^{\text{mid}}$, and $\text{Fo}_{75}^{\text{int}}$) for the Different Spin State per Fe^{2+} Ion (Quintet, qt; Triplet, tp; Singlet, sg)^a

| | Si–O | Mg1–O | Mg2–O | Fe1–O | Fe2–O |
|--|----------------------------|------------------|----------------------------|------------------|------------------|
| Fo^{surf} | 1.630–1.703 1.615–1.698 | 2.031–2.196 — | 2.052–2.363 1.868–1.912 | — — | — — |
| $\text{Fo}_{75}^{\text{top}}(\text{qt})$ | 1.631–1.703 1.609–1.688 | 2.040–2.200 — | 2.071–2.247 — | — — | — 1.886–1.999 |
| $\text{Fo}_{75}^{\text{top}}(\text{tp})$ | 1.632–1.703 1.606–1.688 | 2.031–2.201 — | 2.061–2.239 — | — — | — 1.868–1.972 |
| $\text{Fo}_{75}^{\text{top}}(\text{sg})$ | 1.627–1.705 1.607–1.685 | 2.032–2.177 — | 2.070–2.224 — | — — | — 1.876–1.892 |
| $\text{Fo}_{75}^{\text{mid}}(\text{qt})$ | 1.638–1.698 1.624–1.696 | 2.049–2.178 — | 2.055–2.335 1.863–1.912 | 2.062–2.262 — | — — |
| $\text{Fo}_{75}^{\text{mid}}(\text{tp})$ | 1.636–1.704 1.627–1.706 | 2.025–2.188 — | 2.064–2.398 1.851–1.915 | 2.004–2.327 — | — — |
| $\text{Fo}_{75}^{\text{mid}}(\text{sg})$ | 1.632–1.698 1.617–1.698 | 2.029–2.206 — | 2.063–2.314 1.863–1.912 | 2.035–2.173 — | — — |
| $\text{Fo}_{75}^{\text{int}}(\text{qt})$ | 1.628–1.701 1.617–1.701 | 2.026–2.213 — | — 1.874–1.925 | — — | — 2.103–2.471 |
| $\text{Fo}_{75}^{\text{int}}(\text{tp})$ | 1.631–1.703 1.615–1.704 | 2.042–2.184 — | — 1.873–1.918 | — — | — 2.023–2.419 |
| $\text{Fo}_{75}^{\text{int}}(\text{sg})$ | 1.632–1.699 1.611–1.699 | 2.031–2.174 — | — 1.864–1.906 | — — | — 2.070–2.155 |

^aValues in italics correspond to distances involving atoms present at the outermost positions of the edge-layers.

cations, the overall spin multiplicity for the unit cell is, therefore, nonaplet, quintet, and singlet, respectively.

The calculated equilibrium interatomic distances of Fo and Fo_{75} (010) surfaces are given in Table 2, and the optimized cell parameters are given in Table 3. The calculated slab models are

Table 3. B3LYP-Optimized Cell Parameters of Forsterite (Fo^{surf}) and Fe-Containing Olivine (010) Surfaces ($\text{Fo}_{75}^{\text{top}}$, $\text{Fo}_{75}^{\text{mid}}$, and $\text{Fo}_{75}^{\text{int}}$) for the Different Spin State per Fe^{2+} Ion (Quintet, qt; Triplet, tp; Singlet, sg)^a

| | <i>a</i> | <i>c</i> | area | E_{surf} |
|--|----------|----------|-------|-------------------|
| Fo^{surf} | 4.831 | 6.141 | 29.67 | 1.160 |
| $\text{Fo}_{75}^{\text{top}}(\text{qt})$ | 4.817 | 6.153 | 29.65 | 0.870 |
| $\text{Fo}_{75}^{\text{top}}(\text{tp})$ | 4.805 | 6.176 | 29.68 | 1.538 |
| $\text{Fo}_{75}^{\text{top}}(\text{sg})$ | 4.809 | 6.016 | 28.94 | 2.201 |
| $\text{Fo}_{75}^{\text{mid}}(\text{qt})$ | 4.875 | 6.163 | 30.05 | 1.111 |
| $\text{Fo}_{75}^{\text{mid}}(\text{tp})$ | 4.830 | 6.102 | 29.48 | 1.644 |
| $\text{Fo}_{75}^{\text{mid}}(\text{sg})$ | 4.813 | 6.128 | 29.50 | 1.709 |
| $\text{Fo}_{75}^{\text{int}}(\text{qt})$ | 4.839 | 6.203 | 30.02 | 1.097 |
| $\text{Fo}_{75}^{\text{int}}(\text{tp})$ | 4.836 | 6.197 | 29.97 | 1.768 |
| $\text{Fo}_{75}^{\text{int}}(\text{sg})$ | 4.807 | 6.107 | 29.36 | 2.039 |

^aSurface areas (in \AA^2) and calculated surface energies (J m^{-2}) are included.

almost bulk-terminated surfaces with slight undulating surface topologies. This is in agreement with the experimental study of Hochella,⁷² in which the forsteritic {010} crystal form was found to be 1×1 surface unit cells with small relaxations using low energy electron diffraction. The internal Si–O and metal–oxygen distances are very similar to those present in the respective bulk structures, demonstrating the low reconstruction suffered by these surfaces. However, the outermost Mg–O and Fe–O (for $\text{Fo}_{75}^{\text{top}}$) distances are significantly shorter (about 0.2 Å) because these metal ions are coordinatively unsaturated. Moreover, the outermost Si–O distances are also shorter (about 0.025 Å) than the internal ones. Consequently,

the lattice parameters of the surfaces are somewhat shorter compared to the corresponding bulk values (i.e., about 1% for *a* and 2.3% for *c*). On the other hand, for Fo_{75} surfaces, it is observed that the Fe–O distances are larger for Fe^{2+} in the quintet state than in the triplet and the singlet states, and accordingly surface areas decrease with the spin multiplicity. This is due to the larger electronic repulsion between the Fe^{2+} 3d electrons and O^{2-} in the quintet state than in the triplet and singlet ones.

The relative stability of Fo_{75} (010) surfaces has been calculated considering the electronic state and the position of the Fe^{2+} cations (Figure 3). The most stable surface concerns the Fe^{2+} ions placed at the outermost positions in a quintet spin state (i.e., hereafter referred as $\text{Fo}_{75}^{\text{top}}(\text{qt})$). Moreover, for the three surfaces, the relative stability of the three spin states considered follows the order qt > tp > sg, i.e., the most stable Fe^{2+} spin configuration is the quintet high spin state, in

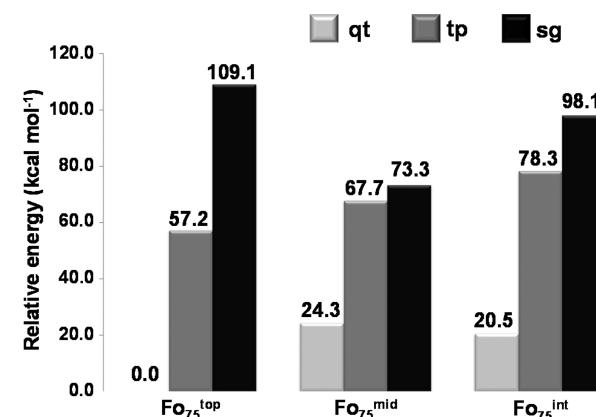


Figure 3. Relative stability of the nonpolar (010) Fe-containing surfaces as a function of the spin configuration per Fe^{2+} ion (quintet, qt; triplet, tp; singlet, sg) and the position of the Fe^{2+} ions in the slab models.

consistency with what is known for bulk solid solutions. Noteworthy, for the Fe^{2+} in the quintet and triplet spin states, $\text{Fo}_{75}^{\text{top}}$ surfaces are more stable than $\text{Fo}_{75}^{\text{mid}}$ and $\text{Fo}_{75}^{\text{int}}$, whereas for the singlet state, $\text{Fo}_{75}^{\text{mid}}$ becomes the most stable surface, in agreement with the fact that saturated coordination environments stabilize low spin versus high spin states. Note that saturated environments induce a larger splitting of 3d orbitals.

The surface energy of Fo^{surf} has been calculated to be 1.16 J m^{-2} , implying that the cleavage of the bulk crystal to create this surface is not a highly energetic process. Its stability may be due to the formation of O–Mg–O bridges on the surface, similar to O–Si–O and O–Na–O bridges, which were found to stabilize α -quartz-based surfaces.⁷³ The presence of alternating O–Si–O and O–Mg–O surface bridge groups gives rise to a surface energy similar to that for the (010) MgO surface (1.20 J m^{-2}). The calculated surface energy of $\text{Fo}_{75}^{\text{top}}(\text{qt})$ is 0.87 J m^{-2} , 0.29 J m^{-2} lower than Fo^{surf} , meaning that less energy is needed to cut the corresponding bulk system and that the $\text{Fo}_{75}^{\text{top}}(\text{qt})$ is expected to be less reactive than Fo^{surf} . This lower surface energy of $\text{Fo}_{75}^{\text{top}}(\text{qt})$ is associated with the high spin of Fe^{2+} (note that triplet and singlet states exhibit higher surface energies) since the loss of Fe–O electrostatic interactions in $\text{Fo}_{75}^{\text{top}}(\text{qt})$ is partly compensated by a larger decrease of electron repulsion between Fe^{2+} 3d electrons and O^{2-} in this spin state quintet state upon generating the surface.

Electrostatic Potentials and Spin Densities. Electrostatic potential maps (EPMs) show regions of negative and positive potentials and provide clues about the most favorable adsorption sites and of the driving forces involved. Figures 4a and 4b show the B3LYP-EPMs for Fo^{surf} and $\text{Fo}_{75}^{\text{top}}(\text{qt})$ on a surface enclosing 90% of the electron density. Both EPDs show prominent positive and negative valued regions, which are associated with the outermost Mg/Fe and O surface atoms, respectively. This suggests that Mg/Fe atoms are the best candidates to interact with electron donor atoms and surface O atoms for H-bonding interactions and electrophilic molecules. It is worth pointing out that these two well-defined potential regions are less pronounced in the $\text{Fo}_{75}^{\text{top}}(\text{qt})$ surface, suggesting that favorable electrostatic interactions are expected to be larger in Fo^{surf} rather than in $\text{Fo}_{75}^{\text{top}}(\text{qt})$. Net charges obtained by a Mulliken population analysis confirms this trend as they are found to be +1.60el and -1.22el for Mg and O, respectively, in Fo^{surf} and +1.40el and -1.19el for Fe and O, respectively, in $\text{Fo}_{75}^{\text{top}}(\text{qt})$.

For the case of $\text{Fo}_{75}^{\text{top}}(\text{qt})$, the spin density features have also been analyzed through its spin density map (Figure 4c), which shows the spin localization at the surface atoms. The map clearly shows that the spin of $\text{Fo}_{75}^{\text{top}}(\text{qt})$ lies mainly at the Fe^{2+} cations, in line with the calculated Mulliken atomic integrated spin density for the Fe atom of +3.7el (out of 4el), and about +0.15el of the neighboring O atoms. This means that, in addition to establish electrostatic interactions with electron donor atoms, Fe^{2+} sites will be active with respect to adsorbed radical species.

Infrared and Reflectance Properties. Olivines have an orthorhombic structure and present 28 atoms in the unit cell (four formula units per cell), giving rise to 84 vibrational modes (35 IR active modes, 36 Raman active modes, 10 inactive modes, and 3 modes to rigid translations). Vibrational modes in silicates are usually classified in two main categories: i) the internal modes (I), which include the stretching and bending

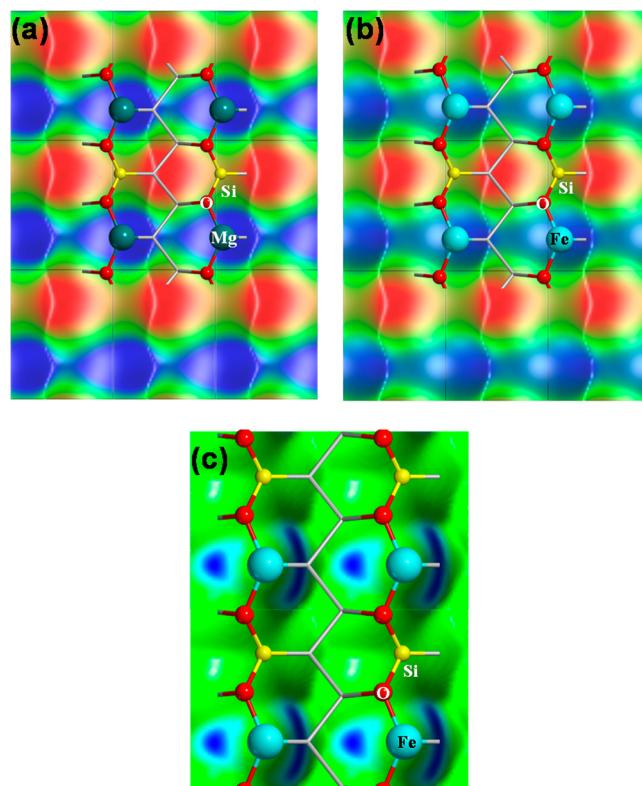


Figure 4. Top views of the electrostatic potential maps of the Fo^{surf} (a) and $\text{Fo}_{75}^{\text{top}}(\text{qt})$ (b) slab models and of the spin density map of the $\text{Fo}_{75}^{\text{top}}(\text{qt})$ surface (c) mapped on surfaces enclosing 90% of the total electron density. Negative values (-0.02 au) coded as red colors; positive values ($+0.02 \text{ au}$) coded as blue colors; green color indicates $\approx 0.0 \text{ au}$ electrostatic potential values or spin density values.

vibrations of the SiO_4 tetrahedra; and ii) the external modes (E), which include rotations and translations of the SiO_4 tetrahedra and translations of the metal cations. In previous works,^{74–80} mode classification and band assignments of olivinic crystals have exhaustively been discussed by means of infrared, Raman, and reflectance spectroscopic measurements. In this part, we focus our attention on the most important IR active modes for Fo, $\text{Fo}_{75}^{\text{M2}}$, Fo^{surf} , and $\text{Fo}_{75}^{\text{top}}(\text{qt})$ in order to evaluate the different spectral signatures between the bulk and the surfaces and due to the presence of Fe^{2+} .

Table 4 reports the computed and experimental vibrational frequencies for Fo. As already described,⁴³ B3LYP frequencies reproduce very well the experimental values, with a mean average of 4.8 cm^{-1} and a largest deviation of 9 cm^{-1} . Remarkably, the largest deviations are associated with the SiO_4 bending modes. Figure 5 shows the comparison between the calculated IR spectra of bulk Fo and $\text{Fo}_{75}^{\text{M2}}$. Both systems present 8 common vibrational frequencies in the $200\text{--}1000 \text{ cm}^{-1}$ range. They are due to the translation of the metal cations, the rotation of $[\text{SiO}_4]$, and the bending and stretching motions of the SiO_4 tetrahedra. Results show that the overall spectra of $\text{Fo}_{75}^{\text{M2}}$ are shifted to lower values due to the higher mass of the substituting Fe^{2+} . A comparison of the IR spectrum of $\text{Fo}_{75}^{\text{M2}}$ with that for Fo in which the Mg^{2+} ions that are substituted by Fe^{2+} in $\text{Fo}_{75}^{\text{M2}}$ have the mass of iron (hence reproducing a mass-analog of $\text{Fo}_{75}^{\text{M2}}$) points out that the shifts are mainly due to the higher mass of Fe^{2+} (see Figure S1 of the SI). This bathochromic shift is significantly important in those bands where Fe^{2+} is involved; that is, those associated with the

Table 4. Comparison of the B3LYP Vibrations (cm^{-1}) with the Experimental Ones for the Bulk Forsterite^a

| IR band | vibrations | | | |
|---------|------------|-------------|--------------|----------|
| | B3LYP | [intensity] | experimental | symmetry |
| 293 | 291 | [673.52] | 291 | B_{3u} |
| | 294 | [806.38] | 293 | B_{1u} |
| | 295 | [223.87] | 296 | B_{2u} |
| 350 | 350 | [1035.69] | 352 | B_{3u} |
| 389 | 389 | [1059.96] | 383 | B_{2u} |
| | 404 | [269.18] | 397 | B_{3u} |
| 416 | 412 | [1288.46] | 412 | B_{1u} |
| | 420 | [985.05] | 419 | B_{1u} |
| | 421 | [31.42] | 420 | B_{3u} |
| 514 | 513 | [527.73] | 505 | B_{2u} |
| | 514 | [641.76] | 506 | B_{1u} |
| | 517 | [74.45] | 508 | B_{3u} |
| 614 | 614 | [463.53] | 606 | B_{2u} |
| 873 | 870 | [1561.67] | 873 | B_{3u} |
| | 874 | [2659.78] | 874 | B_{1u} |
| 982 | 982 | [1413.29] | 978 | B_{2u} |
| | 989 | [43.58] | 987 | B_{3u} |

^aIR bands (see Figure 5) refers to those bands shown in Figure 5. Calculated intensities (values in brackets) are in km mol^{-1} . Assignment of the vibration symmetry is also included.

| Fo bands (cm^{-1}) | Fo ₇₅ ^{M2} bands (cm^{-1}) | Vibrational Mode |
|-------------------------------|---|-----------------------------|
| 293 | 276 | Transl. Mg (+ Fe) |
| 350 | 280 | Transl. Mg (+ Fe) |
| 389 | 373 | Rot. SiO ₄ |
| 416 | 406 | Rot. SiO ₄ |
| 514 | 513 | Bending SiO ₄ |
| 614 | 603 | Bending SiO ₄ |
| 873 | 855 | Stretching SiO ₄ |
| 982 | 978 | Stretching SiO ₄ |

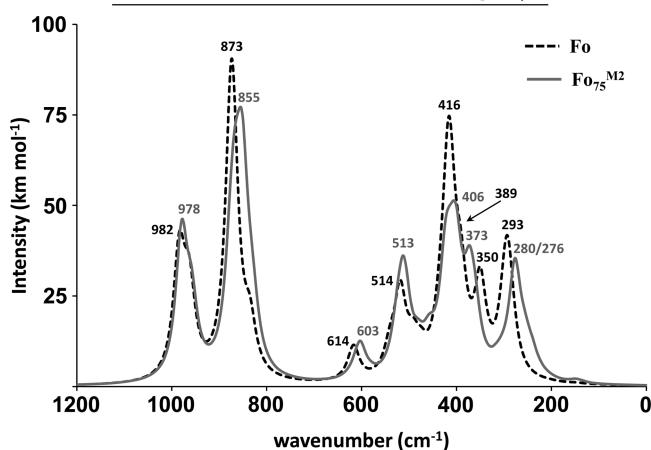


Figure 5. B3LYP-simulated infrared spectra of the Fo (dashed-black) and Fo₇₅^{M2} (solid-gray) bulk structures.

metal translation (i.e., from 293 to 276 cm^{-1} and from 350 to 280 cm^{-1}) and those associated with modes of SiO₄ bonded to the metal cations (e.g., from 873 to 855 cm^{-1}). This is in agreement with the experimental measurements⁸¹ and theoretical results³⁰ that compare the IR features of forsterite with fayalite. The very same difference is given when comparing the IR spectra of the Fo^{surf} surface with the Fo₇₅^{top}(qt) one (see

Figure S2 of the SI); that is, the latter spectrum is globally bathochromic shifted.

A comparison of the IR spectra between the bulk structures and the corresponding (010) surfaces (Fo vs Fo^{surf} and Fo₇₅^{M2} vs Fo₇₅^{top}(qt) presented in Figures 6 and 7, respectively) shows

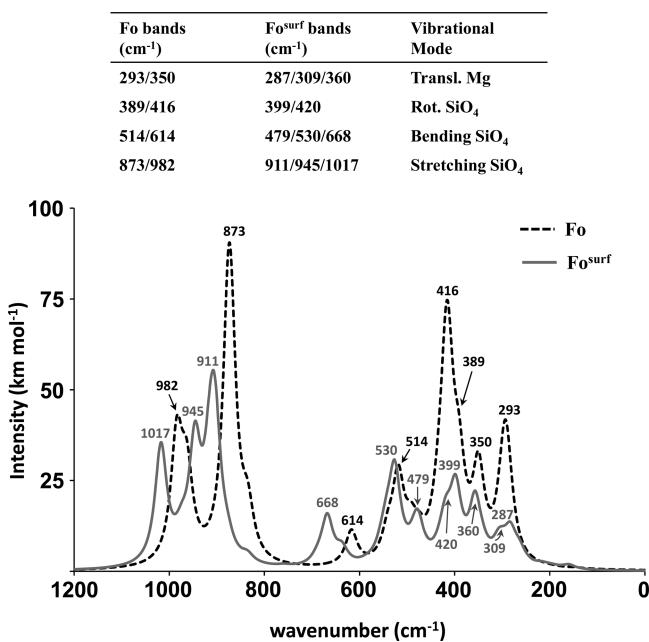


Figure 6. B3LYP-simulated infrared spectra of the Fo bulk structure (dashed-black) and Fo^{surf} nonpolar (010) surface (solid-gray).

that spectra of the surface slabs have two significant differences compared to the bulk ones: i) they have been shifted to upper values and ii) they present more bands. The hypsochromic shift related to point i) is probably due to the shorter distances of the outermost Si—O, Mg—O, and Fe—O bonds because the

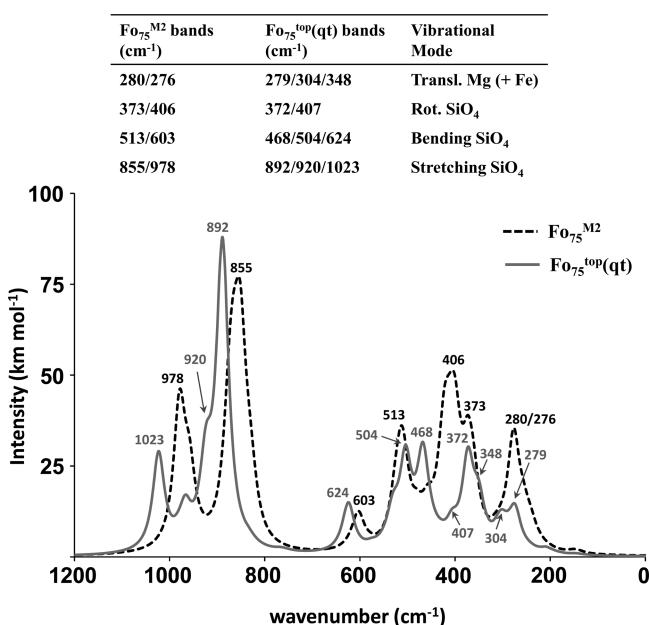


Figure 7. B3LYP-simulated infrared spectra of the Fo₇₅^{M2} bulk structure (dashed-black) and Fo₇₅^{top}(qt) nonpolar (010) surface (solid-gray).

metal ions are coordinatively unsaturated centers (*vida supra*). The presence of more bands in the spectra of the surfaces (point ii)) is due to the splitting of broad bands present in the bulk spectra associated with the vibrations of atoms of the outermost positions of the surfaces. For instance, the peaks at 293 cm^{-1} (Fo) and 276 cm^{-1} ($\text{Fo}_{75}^{\text{M}2}$) belonging to the translations of the metal cation split into the bands at 287 and 309 cm^{-1} (Fo^{surf}) and at 279 and 304 cm^{-1} ($\text{Fo}_{75}^{\text{top}}(\text{qt})$), or the peaks at 873 cm^{-1} (Fo) and 855 cm^{-1} ($\text{Fo}_{75}^{\text{M}2}$) split into the bands at 911 and 945 cm^{-1} (Fo^{surf}) and at 892 and 920 cm^{-1} ($\text{Fo}_{75}^{\text{top}}(\text{qt})$).

As anticipated in the Computational Details section, the reflectance spectrum of a given 3D-periodic system (namely, bulk structures) can be simulated with the CRYSTAL09 code. As mentioned, an important ingredient for the construction of the reflectance curves is the high frequency dielectric constant ϵ_{∞} computed by means of a CPKS scheme. For Fo, the calculated ϵ_{∞} values along the x , y , and z directions are provided in Table 5. Differences with respect to the

Remarkably, such a bathochromic shift was also observed in the comparison of the single-crystal reflectivity of pure Mg_2SiO_4 with the natural $(\text{Mg}_{0.86}\text{Fe}_{0.14})\text{SiO}_4$.⁷⁷ Moreover, the presence of the Fe reduces overall the far-infrared reflectivity of olivine compared to pure forsterite, in agreement with the experimental measurements and caused by the larger refractive index of Fe-containing olivines than the Mg-pure ones.

CONCLUSIONS

The bulk forsterite (Mg_2SiO_4) and the $\text{Mg}_{1.5}\text{Fe}_{0.5}\text{SiO}_4$ Fe-containing analog (25% of Fe substitution) as well as the corresponding nonpolar (010) surfaces have been simulated by means of B3LYP periodic calculations with the CRYSTAL09 code. Their structural features, electronic properties (i.e., electrostatic potentials and spin density distribution) and vibrational features have been analyzed in detail. The following points emerge from the present calculations:

- B3LYP optimized structural parameters reproduce fairly well the crystallographic data for the bulk forsterite, the calculated cell parameters being slightly overestimated and providing a volume variation of about 2%. Fe^{2+} substitution induces an overall enlargement of the bulk structure because of its larger ionic radius. Reconstruction of the surface is minor and mainly corresponds to the shortening of the outermost metal–O bond distances because the metal cations at these positions are coordinatively unsaturated centers.

- Relative energy calculations and the calculated surface energies for different Fe^{2+} -electronic states indicate that the most stable Fe-containing surfaces have the metal cations in the quintet state, followed by the triplet and the singlet states. Moreover, limited to the Fe^{2+} -quintet state, those surfaces with the cations placed at the outermost positions of the slab are more stable than those placed in more internal positions.

- The simulated IR spectra of the bulk systems and the corresponding surfaces present bands associated with the translation motion of the metal cations, to the rotation of the SiO_4 tetrahedra and to the bending and stretching modes of the SiO_4 bond angles and lengths, respectively. Comparison of the different IR indicate that i) Fe^{2+} substitution induces an overall bathochromic shift of the spectra compared to the Mg-pure ones because of the larger atomic mass of Fe; ii) the IR spectra of the surface slab models are shifted to upper values with respect to the corresponding bulk ones as a consequence of the coordinatively unsaturated metal cations present at the outermost positions of the slab models, which sport shorter metal–O distances; and iii) bands present in the IR spectra of the bulk systems split in the respective surface ones because of the different vibrational signatures of the metal and SiO_4 groups present at the slab edge layers. The calculated reflectance spectra for the bulks of forsterite and the Fe-containing olivine also show the bathochromic shift due to iron substitution.

ASSOCIATED CONTENT

S Supporting Information

Complete author list for refs 2, 41, and 80. Infrared spectra of bulk $\text{Fo}_{75}^{\text{M}2}$ and surface slab models of Fo and $\text{Fo}_{75}^{\text{top}}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 5. B3LYP-Calculated High Frequency Dielectric Constants (ϵ_{∞}) for the Bulk Systems of Fo and $\text{Fo}_{75}^{\text{M}2}$ along the x , y , and z Directions^a

| Mg_2SiO_4 Fo/B3LYP | exptl | dev (%) | $(\text{Mg}_{1.5}\text{Fe}_{0.5})\text{SiO}_4$ $\text{Fo}_{75}^{\text{M}2}/\text{B3LYP}$ | Fe_2SiO_4 exptl |
|---------------------------------------|-------|---------|---|------------------------------------|
| $\epsilon_{\infty,x}$ | 2.571 | 2.789 | -7.8 | 2.715 |
| $\epsilon_{\infty,y}$ | 2.424 | 2.673 | -9.3 | 2.592 |
| $\epsilon_{\infty,z}$ | 2.475 | 2.726 | -9.2 | 2.671 |

^aExperimental (exptl) values for the olivine end-members Mg_2SiO_4 and Fe_2SiO_4 are also included (from ref 82).

experimental values are negative, the deviations spanning the 7.8–9.3% range (see Table 5). The presence of the Fe^{2+} cations in $\text{Fo}_{75}^{\text{M}2}$ induces a tiny but generalized increase of the ϵ_{∞} values, which is in line with the larger experimental ϵ_{∞} values of pure forsterite compared to pure fayalite (Table 5).

The reflectance spectra of Fo and $\text{Fo}_{75}^{\text{M}2}$ along the y direction (the normal direction of the (010) plane) are shown in Figure 8. Expectedly, the reflectance spectrum of $\text{Fo}_{75}^{\text{M}2}$ is shifted to lower wavenumbers compared to the Fo one in consistency to the higher mass of the substituted iron.

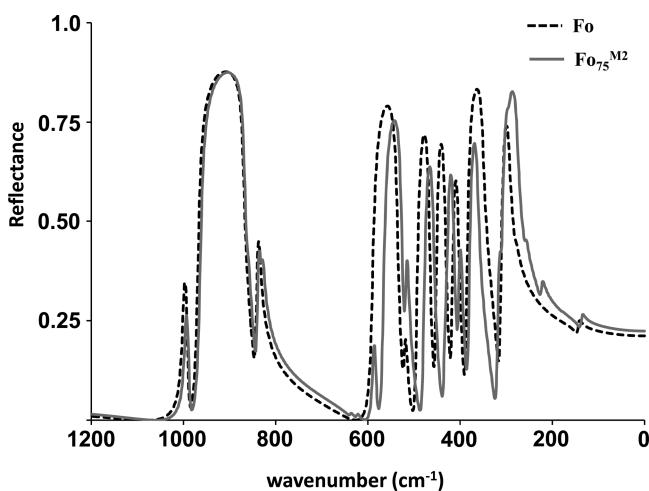


Figure 8. B3LYP-simulated reflectance spectra of the Fo (dashed-black) and $\text{Fo}_{75}^{\text{M}2}$ (solid-gray) bulk structures.

Notes

The authors declare no competing financial interest.

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