A Model of the OH Positions in Olivine, Derived from Infrared-Spectroscopic Investigations

A. Beran[1] and A. Putnis[2]

[1] Institut für Mineralogie und Kristallographie der Universität Wien, Dr. Karl Lueger-Ring 1, 1010 Vienna, Austria
[2] Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, England

Abstract. Polarized *infrared* (IR) spectroscopy of olivine crystals from Zabargad, Red Sea shows the existence of four pleochroic absorption bands at 3,590, 3,570, 3,520 and 3,230 cm^{-1}, and of one non pleochroic band at 3,400 cm^{-1}. The bands are assigned to OH stretching frequencies. *Transmission electron microscopy* (TEM) shows no oriented intergrowths in this olivine; it is concluded that OH is structural. On the basis of the pleochroic scheme of the absorption spectra it is proposed that $[\square O(OH)_3]$ and $[\square O_2(OH)_2]$ tetrahedra occur as structural elements, assuming that the vacancies are on Si sites. If $M2$ site vacancies were assumed $[SiO_3(OH)]$ and $[SiO_2(OH)_2]$ tetrahedra occur as structural elements.

Introduction

The presence of small amounts of water in nominally anhydrous silicate minerals has considerable effects on their physical properties, and on the rate of diffusion controlled processes. The fact that the equilibrium solid solubility of OH ions in minerals such as quartz and olivine is exceedingly small, coupled with the possibility of the presence of liquid inclusions or of hydrous alteration products, has made the study of this problem a difficult one. However, it is known that quartz containing as little as 0.002 weight percent H_2O can be deformed under stresses 10 to 20 times lower than a 'dry' crystal (Griggs 1967). This effect, known as hydrolytic weakening has also been recognized in olivine (Blacic 1972; Blacic and Christie 1973) and although the effect is less marked than in quartz, indicates a structural role of OH^- ions in the control of the activation energy for dislocation glide. Clearly, data on the role of OH^- ions in olivine has considerable implications to our understanding of the rheology of olivine-rich rocks specifically with reference to mantle properties.

The recognition of an OH content in olivine was initially based on the observation of a weak absorption band at 3,500 cm^{-1} in the *infrared* (IR) spectrum of a hydrothermally formed crystal from Norway (Beran 1969; Beran 1976). Probable OH absorption bands in olivine from Fort Defiance, Arizona between 3,300 and 3,700 cm^{-1} were reported by Wilkins and Sabine (1973). According to Freund (1981) olivine contains dissolved "water" in the form of OH^- and H_2 which implies the presence of O^-.

In this paper we report a polarized IR study of the OH absorption spectrum in olivine and propose a model for the OH^- positions in the structure.

Experimental

The olivine crystals used for this work come from Zabargad, Red Sea. The locality of the sample was described by Wilson (1976) and Kurat et al. (1982). Oriented polished plane-parallel crystal plates of light-green coloured crystals of gem quality were produced. IR spectroscopic measurements have been performed on these plates with a computer controlled IR spectrophotometer (Perkin-Elmer 580B, Interdata 6/16). The diameter of the circular measuring area was 2 mm, the thickness of the crystal plates was 0.5 mm.

Only microscopically inclusion-free, optically clear, and homogeneous parts of the crystal plates were chosen as measuring areas. However, in view of the hydrothermal recrystallization of the Zabargad peridotites and the known presence of fluid inclusions and possibly submicroscopic intergrowths of hydrous phases (Clocchiatti et al. 1981), a thin section of the olivine crystals was also prepared for *transmission electron microscopy* (TEM). Repeated ion-beam thinning and observation ensured that a relatively large volume of the olivine section could be examined.

The crystals were analysed by electron microprobe and checked for chemical homogeneity (Table 1). A semiquantitative OH determination performed with convergent unpolarized IR radiation (Beran et al. 1981) yielded an analytical H_2O^+ content of 0.04 ± 0.01 equivalent weight percent.

Table 1. Data on the OH-bearing olivine used for the IR spectroscopic investigations

Locality of sample: Zabargad (St. John's Island), Red Sea, Egypt

Chemical composition (average values of 5 microprobe point analyses in wt.%):
CaO—0.01, MgO—48.4, Al_2O_3—0.01, SiO_2—41.5, Cr_2O_3—0.01, MnO—0.12, FeO—9.5, NiO—0.37

IR spectroscopically determined equiv. H_2O^+ content: 0.04 ± 0.01 wt.%

Lattice constants (ref. Nover and Will 1981, unit cell according to Bragg and Brown 1926):
$a = 4,767(1)$, $b = 10,239(1)$, $c = 6,003(1)$ Å

Space group: $Pbnm$, $Z = 4$ $(Mg,Fe)_2SiO_4$
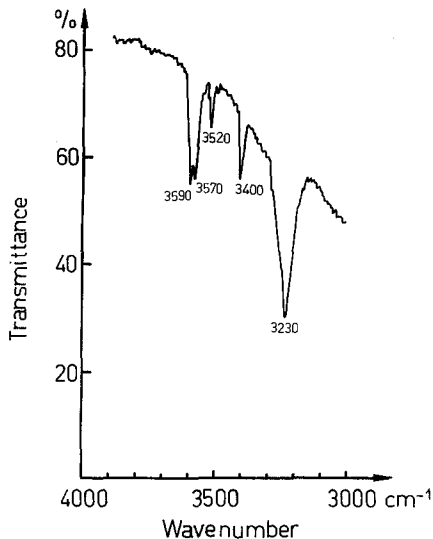
Fig. 1. Infra-red spectrum of the Zabargad olivine showing five absorption bands at 3,590, 3,570, 3,520, 3,400 and 3,230 cm^{-1}. Only the band at 3,400 cm^{-1} is non pleochroic. The spectrum is a computer replot from 15 accumulated scans of a crystal plate of thickness 0.5 mm

Results

Infrared Spectroscopy

The IR spectrum of the Zabargad olivine shows five absorption bands at 3,590, 3,570, 3,520, 3,400 and 3,230 cm^{-1}, which have been assigned to OH stretching frequencies (Fig. 1). Using polarized IR radiation, made by a gold-plated silver bromide polarizer, strong pleochroism of all but the 3,400 cm^{-1} band has been observed. This non-pleochroic band will be referred to in a later section.

The results of the orientation dependent absorption in the four bands showing pleochroism are summarized in Fig. 2a and b in crystal plates parallel to (100) and (001) respectively. The orientation of the crystal plates was checked by the X-ray diffraction precession method. The indices refer to the unit cell described in Table 1.

At a constant thickness of crystal plates the individual absorption bands of OH containing olivines from other localities, e.g. hydrothermally formed olivine from Norway and from the Stubachtal (Salzburg, Austria), and olivine in "bombs" from Tobaj (Burgenland), and from Kapfenstein (Steiermark, Austria), show the same IR pleochroism but an originally different distribution of their intensities. Hence, we may assume that the individual OH positions of olivines from different localities are occupied to a different extent. The olivines of Zabargad are characterized by a relatively high intensity of the absorption band at 3,230 cm^{-1} whereas the olivines of Tobaj are characterized by a relatively high intensity of the absorption band at 3,570 cm^{-1}. In olivine samples of meteorites no OH groups have been detected.

Figure 2 shows that the absorption band at 3,590 cm^{-1} has maximum absorption when the dielectric vector E of the polarized radiation vibrates parallel to [010] in both (100) and (001) sections. The band at 3,570 cm^{-1} similarly has maximum absorption in (100) when E vibrates parallel to [010], whereas in (001) maximum absorption occurs when E is parallel to [100]. The absorption band at 3,520 cm^{-1} shows no pleochroism in (100), but a strong
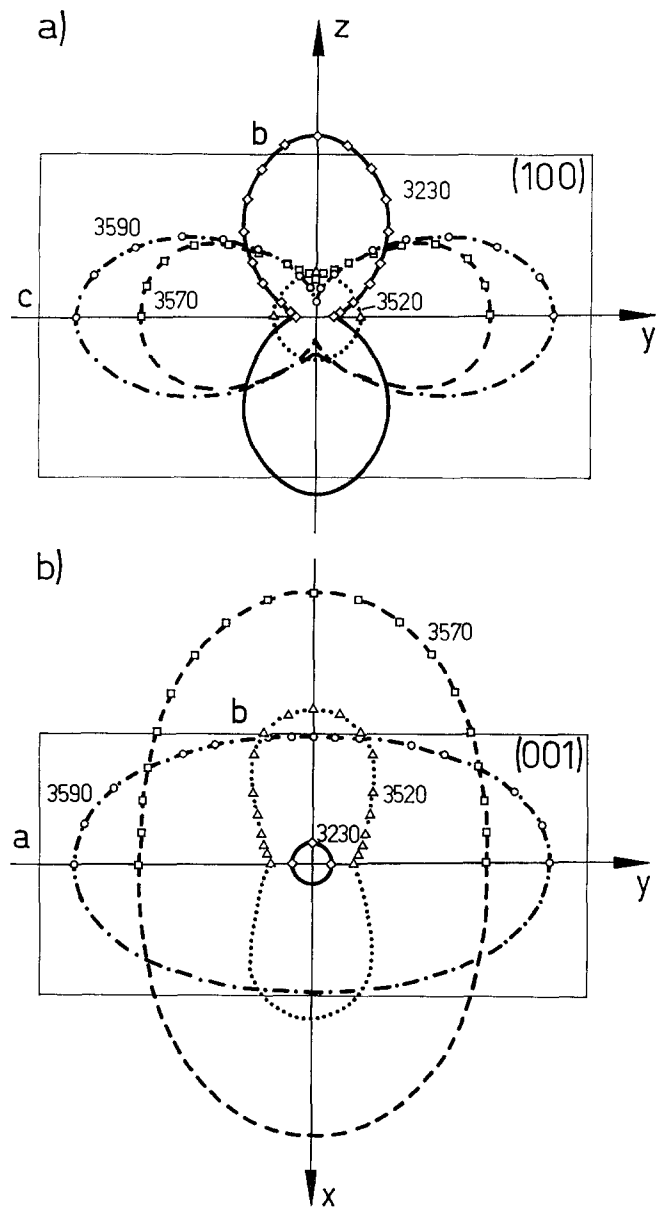

Fig. 2a, b. Olivine, absorption figures of the OH absorption bands at 3,590 cm^{-1} (dash-dotted line, symbol: circle), 3,570 cm^{-1} (dashed line, symbol: square), 3,520 cm^{-1} (dotted line, symbol: triangle), 3,230 cm^{-1} (continuous line, symbol: rhomb). **a** in (100), **b** in (001)

pleochroism in (001) with maximum absorption when E vibrates parallel to [100]. Finally the absorption band at 3,230 cm^{-1} has a very strong pleochroism in (100) with maximum absorption when E vibrates parallel to [001] whereas in (001) this band has a weak intensity and no pleochroism.

Attempts at deuterium substitution were made to further confirm the presence of OH bands. However, deuteration experiments at different temperatures (200°–300°) for times up to several days invariably led to loss of clarity in the olivine crystals, due to incipient alteration.

Transmission Electron Microscopy

Transmission electron microscope observations were made on the Zabargad olivine to investigate the presence of any submicroscopic defects or intergrowths of OH-bearing
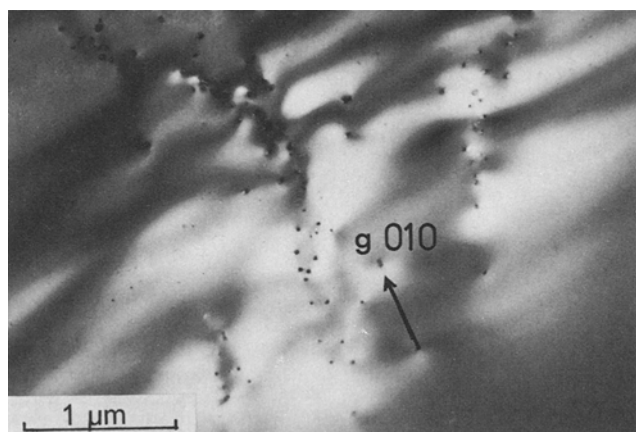
Fig. 3. Transmission electron micrographs of the Zabargad olivine showing characteristic low angle boundaries defined by a single array of dislocations. In this image the dislocations lie normal to the thin crystal surface and parallel to the electron beam

phases. The results of observations on a (001) section indicate that no planar intergrowths of other phases are present.

The section has virtually no free dislocations. The only defects observed were relatively straight arrays of small circular regions (≈ 200 Å diameter) of high contrast (Fig. 3). These defects define boundaries which are a characteristic feature of the olivine. The boundaries are oriented approximately along [010] and have an average spacing of around 5 μm, although locally they may be denser. The strain contrast at the defects consists of a pair of bright and dark lobes, the line between them parallel to the operative reciprocal vector **g**. Such contrast is characteristic of screw dislocations viewed "end-on", i.e. the dislocations lie normal to the (001) section and parallel to the electron beam. The bright-dark contrast of the lobes is often reversed, indicating opposite senses of the Burgers vectors in the defects.

If this interpretation of the contrast is correct, then the boundaries defined by these screw dislocations are twist boundaries separating subgrains related to each other by a rotation about a normal to the boundary. Such boundaries could be formed during annealing by recovery processes involving dislocation glide.

An alternative interpretation is that the defects are either dislocation loops or spherical inclusions or cavities. In these cases the line between bright and dark lobes would be perpendicular to **g**. Although this is generally not the case, there are many instances where the lobes are not well defined and ambiguities arise. Moreover, the fact that two-beam conditions are not strictly achieved when tilting the section leads to complications in the diffraction contrast and its interpretation.

Discussion

The existence of the four pleochroic OH absorption bands in the olivine demonstrates that the OH group must have a distinct orientation. Furthermore, the positions of the absorption bands are not consistent with oriented intergrowths of the hydrous phases likely to be intergrown with the olivine, nor were any intergrowths found by TEM. While the non-pleochroic absorption band at 3,400 cm^{-1} is consistent with the presence of hydroxyl ions associated with the observed dislocations on subgrain boundaries, our conclusion regarding the origin of the four pleochroic OH
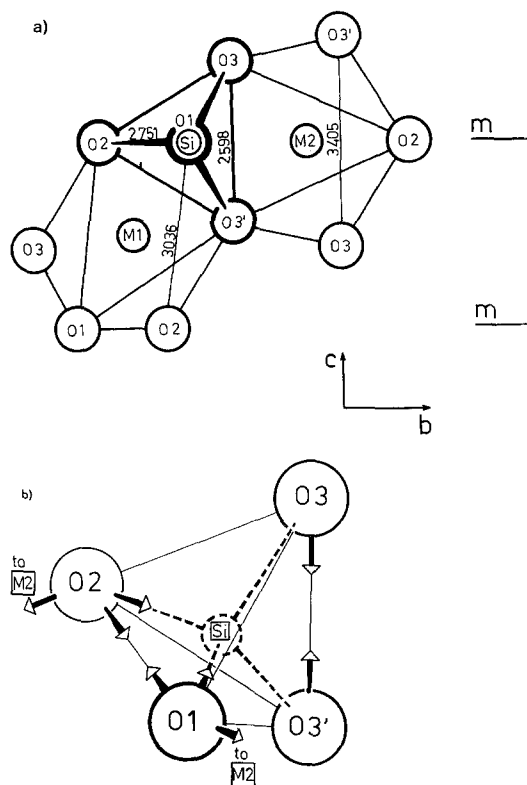
Fig. 4. a Part of the olivine structure showing an $M1$ and an $M2$ octahedron sharing edges with an SiO$_4$ tetrahedron. The bond lengths, referred to in text are in Å. The Si atom lies below the $O1$ oxygen atom in the tetrahedron. **b** Schematic diagram of possible OH dipole directions (represented as arrows) in a single $\square$O$_4$ tetrahedron with Si vacancy. The direction of the dipole along $O1$–$O2$ (alternatively $O2$–$O1$) lying in the symmetry plane results from the pleochroism of the absorption band at 3,570 cm^{-1}; the direction of the dipole $O3$–$O3'$ ($O3'$–$O3$) perpendicular to the symmetry plane results from the pleochroism of the absorption band at 3,230 cm^{-1}; the direction of the dipole $O1$–Si vacancy results from the pleochroism of the absorption band at 3,520 cm^{-1}; three possible dipole directions are derivable from the pleochroism of the OH stretching frequency at 3,590 cm^{-1}: assuming Si vacancies, the direction $O2$–Si vacancy or alternatively assuming $M2$ vacancies, the direction $O1$–$M2$ vacancy and/or the direction $O2$–$M2$ vacancy

absorption bands must be that OH is structural. It is relevant, therefore, by considering the olivine structure and the pleochroic scheme, to propose a model for the OH positions.

The crystal structure of olivine was determined by Bragg and Brown (1926) and first refined by Hanke and Zemann (1963). The structural parameters used in this work refer to the recent structure refinement of an olivine with 10.5 weight percent FeO, by Nover and Will (1981). The structure of olivine is best described as an approximately hexagonal close-packing of oxygens with one half of the distorted octahedral interstices occupied by (Mg, Fe) atoms and one eighth of the tetrahedral interstices occupied by Si. One formula unit (Mg, Fe)$_2$SiO$_4$ contains two crystallographically different (Mg, Fe) sites, $M1$ on a centre of symmetry, $M2$ in a mirror plane. Si is also in a mirror plane. Of the three crystallographically different oxygen positions, two of them, $O1$ and $O2$, are localized in mirror planes while the third ($O3$) occupies a general position. All of the oxygens are coordinated by three (Mg, Fe) and one Si atom in a distorted tetrahedron. Figure 4a shows part of the oliv-

ine structure with $M1$ and $M2$ octahedra, each sharing an edge with an SiO_4 tetrahedron.

A geometrically and crystal chemically plausible model for the OH positions in olivine, based on the IR spectroscopic measurements, is only derivable under the assumption of vacancies in the cation sublattice; no plausible model is derivable assuming a charge imbalance in cation sites.

The pleochroic scheme of the four OH absorption bands allows us to impose certain constraints on the orientation of the OH dipoles. The extremely strong pleochroism of the band at $3,230 \text{ cm}^{-1}$ in (100) requires a strong orientation of the OH dipole parallel to the **c** axis. This is also consistent with a weak absorption band and no pleochroism of this band in (001). The octahedral edges $O3$–$O3'$ in the $M2$ octahedron are both parallel to [001] and perpendicular to the symmetry plane (Fig. 4a). The long $O3$–$O3'$ octahedral edge measures 3,405 Å while the short octahedral (or alternatively tetrahedral) edge $O3$–$O3'$ measures 2,598 Å. The octahedral edge $O1$–$O2$ in the $M1$ octahedron is approximately parallel to [001] and measures 3,036 Å. In accordance with the low wavenumber ($3,230 \text{ cm}^{-1}$) there must be strong H bonding. Assuming an Si vacancy the H position is located on the tetrahedral edge $O3$–$O3'$ where $O3$ as well as $O3'$ are probable donator-acceptor oxygens.

The pleochroism of the absorption band at $3,570 \text{ cm}^{-1}$ suggests that the H position is located on the tetrahedral edge $O1$–$O2$ which lies in the mirror plane. In this case $O1$ as well as $O2$ behave as probable donator-acceptor oxygens.

Compared with the short distance of $O3$–$O3'$ (2.598 Å) the wavenumber of this absorption band is in good agreement with the length of the tetrahedral edge $O1$–$O2$ which measures 2,751 Å.

Similarly, the pleochroism of the absorption bands at 3,590 and $3,520 \text{ cm}^{-1}$ requires positions of the OH directions in the mirror plane, where $O1$ and $O2$ act as donator oxygens. Based on the strong pleochroism of the absorption band at $3,520 \text{ cm}^{-1}$ in (001) the H atom which is correlated to $O1$ is located on the line $O1$-Si vacancy, which is approximately parallel to [100] and which lies practically perpendicular to the plane of the surrounding (Mg,Fe) atoms (Fig. 4a). $O1$ is the top of a steep distorted trigonal pyramid; the sum of the angles $(M1–O1–M1) + 2 (M1–O1–M2)$ amounts to $286.8°$.

By analogy, the pleochroism of the absorption band at $3,590 \text{ cm}^{-1}$ indicates that an H atom correlated to $O2$ is located on the line $O2$-Si vacancy, which is roughly perpendicular to the plane of the surrounding (Mg,Fe) cations. $O2$ is the top of a flat, distorted trigonal pyramid; the sum of the angles $(M1–O2–M1) + 2 (M1–O2–M2)$ amounts to $340.9°$.

If we assumed vacancies in the $M2$ positions instead of Si vacancies the pleochroism of the absorption band at $3,590 \text{ cm}^{-1}$ would be consistent with OH dipole directions along the lines $O1–M2$ vacancy and $O2–M2$ vacancy. However, from a consideration of relative bond strengths Si vacancies are preferred (Donnay and Allmann 1970).

From these IR spectroscopic investigations it is evident that some similarities exist between OH bearing olivines and hydrogarnets, i.e. oxygens of the isolated $\square O_4$ tetrahedra (with Si vacant) are replaced by OH^- groups (Cohen-Addad et al. 1967; Ito and Frondel 1967). The possible OH positions consistent with the IR measurements are shown in Fig. 4b. However, based on geometrical and elec-

trostatic considerations only a maximum of three H atoms can be placed in one single tetrahedron; probably there are $[\square O(OH)_3]$ as well as $[\square O_2(OH)_2]$ tetrahedra as structural elements with a specific combination of H positions. Assuming $M2$ vacancies, probably $[SiO_3(OH)]$ and $[SiO_2(OH)_2]$ tetrahedra occur as structural elements. The fact that there are different combinations of such tetrahedra possible in "hydroolivines" is demonstrated by the different intensity distribution of the OH absorption bands in olivines from different occurrences and paragenesis.

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