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Goethite, α-FeO(OH), from single-crystal data

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(e–O) = 0.001 Å
R factor = 0.019
wR factor = 0.052
Data-to-parameter ratio = 21.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

This is the first reported structure refinement of goethite, α-FeO(OH), on the basis of a single-crystal X-ray diffraction study. The structure of goethite, isostructural with diaspore, AlO(OH), and groutite, MnO(OH), can be described in terms of a slightly distorted hexagonal close-packed O-atom arrangement with Fe atoms occupying one-half of the octahedral interstices, and with all atoms located on mirror planes. There are two distinct O sites, O1 and O2, each bonded to three Fe atoms, with O2 additionally bonded to an H atom. The O2—H$\cdots$O1 donor–acceptor distance in goethite is significantly longer than that in diaspore or groutite, indicating that the hydrogen bonding in goethite is the weakest of the three minerals. Analysis of refinement data for the three isostructural compounds reveals rigid-body thermal motion behavior of the octahedral groups.

Comment

Goethite, α-FeO(OH), is one of the most widespread forms of iron oxides in terrestrial soils, sediments and ore deposits (Cornell & Schwertmann, 2003; Strucki *et al.* 1988), as well as a common weathering product in rocks of all types (Ozdemir & Dunlop, 2000). It transforms to hematite (α-Fe$_2$O$_3$) between 453 and 543 K through dehydrogenation and has been used extensively in the preparation of maghemite (γ-Fe$_2$O$_3$) in magnetic storage media. The crystal structure of goethite was first determined by Goldsztaub (1935) and Hoppe (1940) using X-ray diffraction photographic techniques. Forsyth *et al.* (1968) and Szytula *et al.* (1968) examined the magnetic structure of goethite with neutron powder diffraction on both natural and synthetic samples and found that it is anti-ferromagnetic below about 373 K (the Néel point). The structural behavior of goethite as a function of temperature and pressure was investigated by Gualtieri & Venturelli (1999) and Nagai *et al.* (2003), respectively, by means of synchrotron X-ray powder diffraction. However, despite both its mineralogical and technological interest, no detailed structural information, such as anisotropic atomic displacement parameters, are available for goethite because of the lack of a single-crystal X-ray diffraction structure analysis.

Goethite is isostructural with diaspore, AlO(OH), and groutite, MnO(OH) (Forsyth *et al.*, 1968; Szytula *et al.*, 1968). Its structure can be described in terms of a slightly distorted hexagonal close-packed O-atom arrangement with Fe atoms occupying one-half of the octahedral interstices. The Fe^{3+}O$_6$ octahedra share edges to form double chains running parallel to c, which are further linked to form a three-dimensional structure by sharing vertices (Fig. 1). There are two distinct O sites, O1 and O2, both coordinated to three Fe atoms, with O2 additionally bonded to an H atom. In spite of the same ionic

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radius of 0.645 Å for six-coordinated Fe^{3+} and Mn^{3+} ions (Shannon, 1976), the average M^{3+}—O bond length within the $Fe^{3+}O_6$ octahedron in goethite (2.026 Å) is slightly shorter than that within the $Mn^{3+}O_6$ octahedron in groutite (2.039 Å), due to the obvious Jahn–Teller effect of Mn^{3+}.

A translational–librational–screw (TLS) rigid-body analysis (Schomaker & Trueblood, 1968; Downs, 2000) was conducted on the FeO_6, AlO_6 and MnO_6 octahedral groups in goethite, diaspore (Hill, 1979) and groutite (Kohler *et al.*, 1997), respectively. The atomic displacement parameters reveal rigid-body behavior with differences in the mean-square displacement amplitudes along the M—O bonds of less than 0.001 $Å^2$. The librational angles are small, at 1.7, 1.3 and 1.5° for goethite, diaspore and groutite, respectively. These magnitudes result in a very small thermal effect on the bond lengths. They are consistent with high-quality diffraction data, and with the edge-sharing topology of the double octahedral chains.

Hydrogen bonding is found between atom O2 of one FeO_6 octahedron and an O1 atom in an adjacent one, with an O2—H distance of 0.88 Å and an O2—H···O1^{i} angle of 161 (3)°. This value is comparable with that in diaspore [160.8 (1)°; Hill, 1979] but notably smaller than that in groutite [171 (4)°; Kohler *et al.*, 1997]. The non-linear hydrogen bonding in goethite is known to be of moderate strength and represents the most common type of hydrogen bond (Jeffrey, 1997). Nevertheless, the donor–acceptor O2—H···O1^{i} distance in goethite [2.747 (1) Å] is significantly longer than those in diaspore [2.649 (1) Å; Hill, 1979] or groutite [2.619 (1) Å; Kohler *et al.*, 1997], indicating that the hydrogen bonding in goethite is the weakest of the three minerals. This observation is consistent with the IR spectroscopic measurements; the ν_{OH} stretching bands decrease from 3100 cm^{-1} in goethite to 2950 cm^{-1} in diaspore (Libowitzky & Rossman, 1997) and to 2685 cm^{-1} in groutite (Kohler *et al.*, 1997).

Experimental

The goethite crystal used in this study is a natural sample from Park County, Colorado, USA (RRUFF project collection, R050142; http://rruff.info). Within experimental uncertainty, the chemical composition determined with an electron microprobe is that of ideal FeO(OH).

Crystal data

FeO(OH)
M_r = 88.86
Orthorhombic, *Pbnm*
a = 4.5979 (2) Å
b = 9.9510 (5) Å
c = 3.0178 (1) Å
V = 138.08 (1) $Å^3$
Z = 4
D_x = 4.275 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 10.30 mm^{-1}
T = 273 (2) K
Block, brown
0.09 × 0.09 × 0.08 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2005)
T_{min} = 0.410, T_{max} = 0.441
2197 measured reflections
483 independent reflections
458 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 40.5°

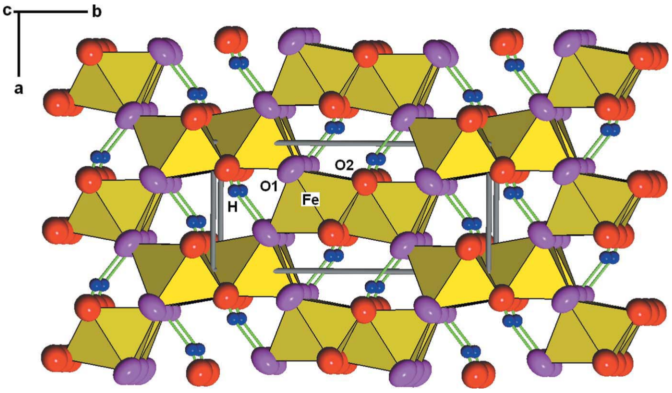

Figure 1
The crystal structure of goethite, α-FeO(OH). O atoms are drawn with anisotropic displacement ellipsoids at the 90% probability level and H atoms with arbitrary radii. Hydrogen bonding is indicated with green lines.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.052
S = 1.15
483 reflections
23 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.034P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.98 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.00 e $Å^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.087 (9)

Table 1
Selected bond lengths (Å).

Fe—O1^{i}	1.9325 (9)	Fe—O2^{iii}	2.0996 (9)
Fe—O1^{ii}	1.9560 (6)	Fe—O2^{iv}	2.1063 (7)

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x, y+1, z$; (iv) $-x, -y+1, -z$.

Consistent with previous studies, the non-standard setting *Pbnm* of space group *Pnma* was used. The H atom was located in a difference Fourier map and its position was refined freely.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: XtalDraw (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

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