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The location of the hydrogen in YOOH. By R. F. GIESE JR, *Department of Geological Sciences, State University of New York at Buffalo, P.O. Box U Station B, Buffalo, New York 14207, U.S.A., and Wave Propagation Branch, Terrestrial Sciences Laboratory, Air Force Cambridge Research Laboratories, Hanscom Air Force Base, MA 01731, U.S.A.*

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The electrostatic energy of YOOH has been calculated as a function of the hydroxyl orientation. Two minima are found and the one with greater energy corresponds to the correct hydroxyl orientation. The three Y–O–H angles are 144.1, 93.2 and 93.2°.

Introduction

The positions of the hydroxyl hydrogen atoms in a series of MOOH compounds (where M=Al, Fe³⁺ and Mn) have been determined by minimizing the electrostatic potential energy of the structure as a function of hydroxyl orientation (Giese, Weller & Datta, 1971). The cations in these structures are small and occupy octahedral sites such that the hydroxyl oxygen is coordinated by two filled octahedra and one vacant octahedron. In such an environment, the OH is able to form a long hydrogen bond to an oxygen 2.650 Å distant (for AlOOH). A much different situation is found for larger M ions such as in the compound YOOH where the cation is coordinated by seven oxygens and the hydroxyl oxygen is bonded to three cations (Christensen, 1965). Such an arrangement makes it more difficult, if not impossible, to form long hydrogen bonds and may also result in unusual hydroxyl orientations.

Baur (1972) in a summary of empirical rules governing the hydrogen atom positions in crystals included the

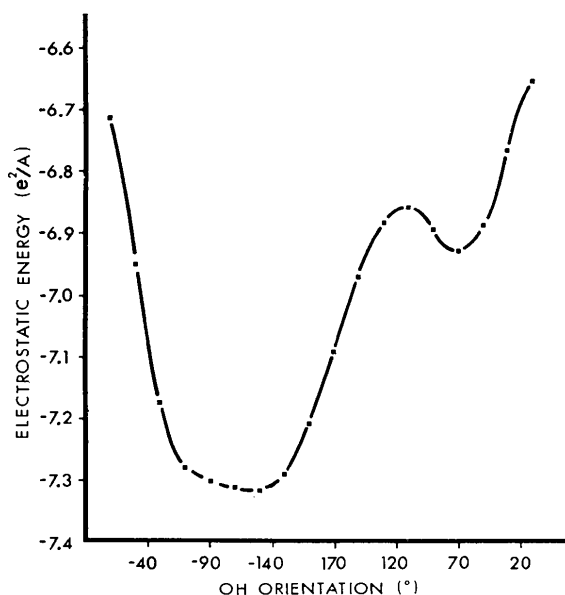


Fig. 1. A plot of the electrostatic energy versus the hydroxyl orientation. The hydrogen atom lies on a circle of radius 0.97 Å centered on the hydroxyl oxygen. The angles referred to are the Y–O–H angles with both the yttrium and oxygen being in the same mirror plane. Negative angles correspond to a clockwise rotation of the hydroxyl group with the structure oriented as in Fig. 2.

criterion that the M–O–H angles should be at least 90° and usually greater than 100°. The structure determination of YOOH did not include hydrogen positions but subsequently Christensen (1966) studied YOOD using neutron diffraction powder data in an attempt to locate the deuterium atoms. He proposed two possible sites, one of which [D(b), Table 1] gave better agreement between calculated and observed diffraction intensities. Both proposed sites corresponded to small Y–O–D angles near or less than 90°. The data available from the neutron powder diffraction experiment were not adequate for an accurate refinement of the deuterium positional parameters. In an effort to determine the hydroxyl orientation more accurately and thus to provide more reliable Y–O–H angles, the structure of the hydroxyl in YOOH has been re-examined using electrostatic potential energy calculations.

Method

The procedure used in determining the hydroxyl orientation by calculating the electrostatic energy has been described elsewhere (Giese, 1971; Giese *et al.*, 1971). For this study the O–H distance was fixed at 0.97 Å, which has given good results in other inorganic structures and does not differ significantly from the O–D distance of 0.96 Å found by Christensen (1966). All atoms were assumed to be fully ionized (Giese *et al.*, 1971). The space group for YOOH is *P*2₁/*m* with all atoms lying on the mirror planes at *y* = ½ and ¾. Thus the hydrogen atom must lie on a circle with a radius of 0.97 Å in the mirror plane centred on the hydroxyl oxygen. The electrostatic energy was calculated for hydroxyl orientations every 20° around the circle and these values are

Table 1. Atomic positional parameters for YOOH and YOOD

	<i>x</i>	<i>y</i>	<i>z</i>	Electrostatic energy
From Christensen (1965)				
Y	0.1898	¾	0.3314	
O	0.065	¾	0.770	
O(H)	0.566	¾	0.755	
From Christensen (1966)				
D(a)	0.42	¾	0.82*	
D(b)	0.643	¾	0.989†	
Electrostatic energy calculations				
H(1)	0.595	¾	0.991‡	–2426 kcal mol ⁻¹
H(2)	0.585	¾	0.539§	–2297

* Unrefined parameters.

† Partially refined. These parameters give better agreement between observed and calculated intensities.

‡ These correspond to the minimum at –50° (Fig. 1).

§ These correspond to the minimum at 110° (Fig. 1).

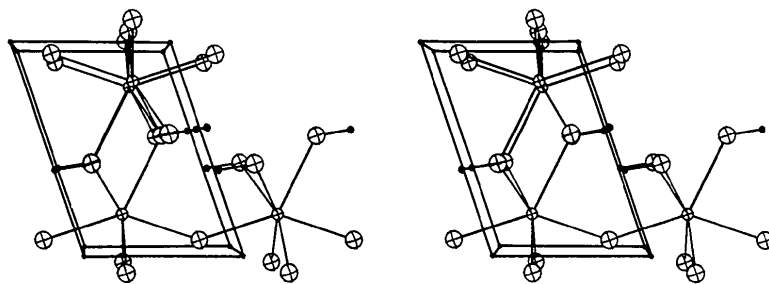


Fig. 2. A stereoscopic view of the YOOH structure down the b axis. The hydrogen position corresponds to the minimum in the electrostatic energy curve (at -130°) shown in Fig. 1.

plotted in Fig. 1, where the angles are the Y–O–H angles with positive values referring to a counterclockwise rotation as viewed in Fig. 2. There are two minima in Fig. 1; one at 70° and a deeper one at -130° . These positions (Table 1) are close to the two sites proposed by Christensen (1966) with the deeper minimum being the position favored by the neutron diffraction data.

Discussion

The hydroxyl oxygen and the three coordinating yttrium ions form a tetrahedron with the three cations at corners and the oxygen in the center of the polyhedron (Fig. 2). The maximum distance between the cations and hydroxyl hydrogen (and minimum electrostatic repulsion) occurs when the hydroxyl is oriented toward the fourth (empty) vertex of the tetrahedron and this corresponds to the minimum at -130° in Fig. 1. The smaller minimum refers to the opposite orientation of the hydroxyl when directed toward the center of the triangle of yttrium ions and away from the empty vertex of the tetrahedron. The latter orientation is less stable because of the shorter Y–H distances and corresponds to the minimum in Fig. 1 at 70° . The OH is not oriented exactly normal to the triangle of cations because of the repulsion from hydrogen ions in adjacent mirror planes (Fig. 2).

The hydrogen position reported here is 0.29 \AA from that reported for deuterium by Christensen (1966) and this difference is significant since the Y–O–H angles change from 144.1° (one angle) and 93.2° (two angles) for Y–O–D to 127.0° (one angle) and 104.3° (two angles) for the hydrogen position reported here. Thus there is considerably less strain in the Y–O–H angles and Baur's proposal that these angles will generally be greater than 100° if geometrically possible is true for YOOH.

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