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Dedicated to the memory of B.K. Vainshtein

Crystal Structure of Lepidocrocite FeO(OH) from the Electron-Diffractometry Data

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Abstract—The crystal structure of lepidocrocite γ-FeO(OH) with the lattice parameters $a = 3.072(2)$, $b = 12.516(3)$, $c = 3.873(2)$ Å, sp. gr. *Cmcm* has been refined by the electron-diffractometry data for 135 crystallographically nonequivalent reflections up to $R = 0.048$. Using the difference syntheses of the Fourier potential, we established, for the first time, the anisotropy in the distribution of the electrostatic potential of hydrogen and the statistical occupancy (with the probability of 1/2) by hydrogen atoms of two positions in the *m* plane normal to the *a*-axis at a distance of 0.27 Å from the twofold axis. The O–H distance equals 0.97(3) Å, the O–H···O angle, 135°. The average Fe–O distance in octahedra is 2.022 Å. © *2001 MAIK "Nauka/Interperiodica".*

The crystal structure of lepidocrocite γ-FeO(OH) (sp. gr. *Cmcm*) was first determined by the X-ray diffraction method by Ewing in 1935 [1]. The structure is built by double layers of Fe-octahedra, with the hydroxyl groups being located on their external surfaces and providing hydrogen bonding between the layers. It was assumed that hydrogen atoms occupy the centers of inversion and are located at the same distances from two oxygen atoms of the adjacent layers, thus forming continuous O–H–O–H–O chains with symmetric hydrogen bonds.

In the following years, the atomic positions of hydrogen atoms in lepidocrocite [2, 3], its aluminum analogue boehmite (γ-AlO(OH) [4], and their deuterium varieties [5, 6] were refined mainly by the method of powder neutron diffraction (the Rietveld profile analysis). It was established that hydrogen atoms in these structures form asymmetric hydrogen bonds. The refinement was performed within two models—with hydrogen atoms statistically occupying (with the probability 1/2) two positions in the plane *m* normal to the *a*-axis (sp. gr. *Cmcm*) and orderly occupying one of these positions (sp. gr. $Cmc2_1$). The most probable model for lepidocrocite [5] and boehmite [4, 6] seems to be the model with the statistically disordered distribution of hydrogen atoms in sp. gr. *Cmcm*.

At the same time, the positions of hydrogen atoms in lepidocrocite determined by the powder neutron-diffraction method differ considerably. Thus, hydrogen atoms are located at the centers of symmetry with the O–H distance being 1.35 Å [2]. At the same time, the orderly distributed H-atoms are displaced from these positions toward one of the oxygen atoms participating in hydrogen bonding and are located in the vicinity of the line connecting these oxygen atoms, O–H = 0.93 and H···O = 1.75 Å and the angle O–H···O = 178° [3]. In the deuterium variety of lepidocrocite [5], the D(H) atoms are statistically disordered and are displaced from the line connecting the O atoms of the adjacent layers with the interatomic distances O–D(H) = 0.86, D(H)···O = 1.95 Å, and the angle O-D(H)···O = 157.9°. The angle θ formed by the vector O–H with the direction [010] is 48 [3] and 31.8° [5], respectively. Moreover, it was established that in the lepidocrocite structure, both average interatomic Fe^{3+}–O distances in octahedra vary within 2.00–2.04 Å, and the individual Fe^{3+}–O distances show considerable scatter [1–3, 5]. All these facts make the structure refinement of lepidocrocite by data provided by the oblique-texture electron diffraction patterns (where all the reflections superimposed on powder neutron diffraction patterns are resolved) quite timely. It is also possible to use the advantages offered by electron diffractometry. The efficiency of the latter method was demonstrated in the studies of hydrogen-containing brucite $Mg(OH)_2$ [7] and serpentine mineral—lizardite 1*T* [8].

The crystal structure of natural lepidocrocite FeO(OH) was refined by oblique-texture electron diffraction pattern from the specimen from the Chukhrov collection (no. 2184). The parameters of the orthorhombic unit cell of lepidocrocite determined from the electron diffraction patterns with the internal standard (NaCl) are $a = 3.072(2)$, $b = 12.516(3)$, and $c = 3.873(2)$ Å.

The oblique-texture electron diffraction patterns were obtained on an electron diffractometer based on an EMR-102 industrial electron diffraction camera

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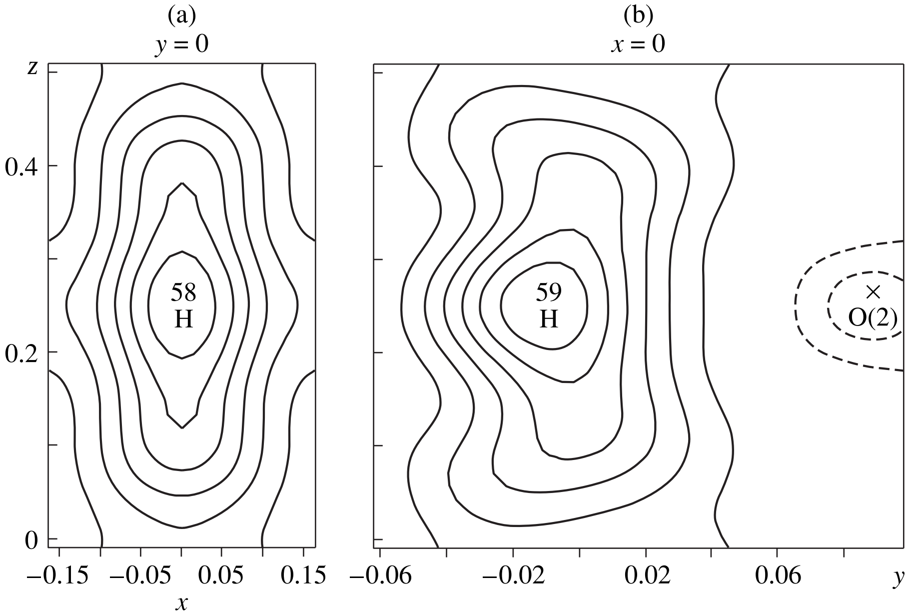

Fig. 1. Sections of the electrostatic potential passing through the hydrogen atoms for lepidocrocite (with subtracted oxygen atoms): (a) the *x*0*z* section; the elongation of the isolines in the *c*-direction favors the two-positional model for H atoms; (b) the 0*yz* section; the cross indicates the positions of the O(2) located, as well as the H atom, on the twofold axis parallel to the *b*-axis. The isolines are spaced by 10 V. The figures indicate the values of the potential at the maxima.

modified for recording two-dimensional intensity distributions in the digital form [9]. The reflection intensities and intensity-distribution profiles across individual archlike reflections were measured by scanning the diffraction pattern along the radial directions and the immobile detector (scinitillator, photoelectron multiplier). All the reflection intensities were normalized to the intensity of the reference reflection. The reflection intensities were determined as the sums of the intensities recorded at each point of the transverse profile with the subtraction of the background. The transition from the intensities, I_{hkl}, to the structure factors, F_{hkl}, was made by the formula for local intensities: $|F_{hkl}(\exp)| = \sqrt{I_{hkl}(\exp)/d_{hkl}d_{h0l}p}$, where the *h*0*l* and *hkl* indices are attributed to the reflections of the same *hl* ellipse and *p* is the repetition factor [10]. The structural computations were performed by the AREN-90 complex of programs [11] with the use of the atomic scattering factors for neutral atoms. We used the intensities of 135 crystallographically independent reflections up to $\sin\theta/\lambda = 1.01$ located on 37 ellipses. The analysis of the reflection intensities showed that for most reflections, scattering occurs by the kinematic law. The intensities of 021, 002, 022, and 152 reflections were corrected for primary extinction in the Blackman two-beam approximation by the technique described elsewhere [12] with the calculated average effective crystallite thicknesses being t_{av} = 324 Å.

The lepidocrocite structure was refined within the sp. gr. *Cmcm* with the use the coordinates of nonhydrogen atoms of the ideal model as the starting coordinates. The LSM refinement of the coordinates and the thermal parameters of Fe and O atoms on the difference *x*0*z* and 0*yz* sections of the Fourier potential revealed the maximum elongated in the direction of the *c*-axis with its center being on twofold symmetry axis parallel to the *b*-axis. The maximum was attributed to a hydrogen atom (Fig. 1). The observed anisotropy in the distribution of the electrostatic potential indicates the possible superposition of two maxima located in the plane *m* normal to the *a*-axis and related by the twofold axis, which correspond to the statistic (with the probability 1/2) occupancy by hydrogen atoms of the positions displaced from the twofold axes. The refinement of the lepidocrocite structure with the split hydrogen position by the least-squares method in the anisotropic approximation up to *R* = 0.048 yielded the atomic coordinates and the anisotropic thermal parameters listed in Table 1 and the interatomic distances listed in Table 2. The structure refinement with hydrogen atom on the twofold axis up to *R* = 0.049 indicated much more pronounced thermal vibrations along the *c*-axes, which, in turn, indicated that hydrogen atoms are statistically distributed over the structure.

Taking into account the possible ordered distribution of H atoms over one of two statistically occupied positions, the lepidocrocite structure was also refined in the noncentrosymmetric sp. gr. $Cmc2_1$ (to *R* = 0.054). Lepidocrocite structures refined within the sp. gr. *Cmcm* and $Cmc2_1$ showed the most pronounced differences in the *z*-coordinates of the O(1) and O(2) atoms. However, the *z*-coordinates refined in the sp. gr. $Cmc2_1$ yield the standard deviations exceeding the differences

Table 1. Atomic coordinates and anisotropic thermal parameters (Å$^2 \times 10^{-4}$) for the lepidocrocite structure

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{11}	B_{22}	B_{33}	B_{23}
Fe	1/2	0.1778(1)	1/4	62(12)	15(1)	127(10)	
O(1)	0	0.2889(4)	1/4	108(36)	22(3)	112(29)	
O(2)	0	0.0738(4)	1/4	105(42)	24(3)	212(31)	
H	0	−0.001(3)	0.179(10)	360(240)	30(27)	300(212)	−5(154)

Table 2. Interatomic distances (Å) in the lepidocrocite structure

Octahedron				Interlayer space	
Fe–O(1) × 2	2.072(3)	O(1)–O(1) × 4	2.657(3)	O(2)–H	0.97(3)
–O(1) × 2	1.981(1)	O(1)–O(2) × 2	2.692(7)	H–O(2)	1.89(3)
–O(2) × 2	2.013(3)	O(1)–O(1) × 4	3.010(4)	O(2)–O(2)	2.676(4)
Average	2.022	O(1)–O(1)	3.072(2)		
		O(2)–O(2)	3.072(2)		
		Average	2.850		

in the *z*-coordinates of oxygen atoms in these structures. Moreover, the H atoms in the sp. gr. *Cmc*2_1 are characterized by a considerable increase of atomic thermal vibrations along the *c*-axis. Thus, the electron-diffraction refinement of the lepidocrocite structure justified the choice of the sp. gr. *Cmcm* and disordered distribution of H atoms over two positions.

The interatomic distances in the lepidocrocite structure are O(2)–H = 0.97(3), H···O(2)' = 1.89(3), and O(2)···O(2)' = 2.676(5) Å; the angle O(2)–H···O(2)' equals 135°. The angle θ formed by the O–H vector with the [010] direction equals 17°. Figure 2 shows the positions statistically occupied by H atoms in the interlayer spaces of lepidocrocite structure. In fact, the H atoms in the structure occupy one of two positions (H or H') and form two different types of chains of hydrogen bonds (solid and dashed lines). Disordering can be caused by the variations either inside the chains of one type or in the chains of both types. As is seen from Fig. 2, each oxygen atom of hydroxyl groups participates in the formation of two hydrogen bonds—either as a donor or as an acceptor.

The average interatomic Fe^{3+}–O distance equals 2.022 Å (in goethite α-FeOOH [13] and hematite F_2O_3 [14]); the interatomic distances (Fe^{3+}–O)$_{av}$ are equal to 2.021 and 2.025 Å, respectively. The Fe–Fe distance for Fe atoms located within one octahedral lepidocrocite sheet equals 3.072(2) Å; in the adjacent octahedral sheets, 2.062(2) Å; whereas the shared octahedron edges are equal to 2.692(7) and 2.657(3) Å, with the average O–O distance in the octahedron being 2.850 Å. The octahedron distortions are caused by the necessity of screening the mutual repulsion of Fe^{3+} cations. Thus, an increase in the Fe–Fe distance within one octahedral sheet is caused by a considerable elongation of the octahedron edge in the direction of the *a*-axis (3.072 Å) in comparison with edge elongation in the direction of the *b*-axis (2.692 Å), so that the octahedron section by the *ab* plane is an elongated rectangle and not a square. An additional increase in the Fe–Fe distance in the adjacent octahedral sheets of the double layer is attained due to stagger of octahedron vertices [the O(1) atoms] along the *b*-axis. In the projection onto the *ab* plane, the octahedron vertices are displaced by 0.37 Å from the center

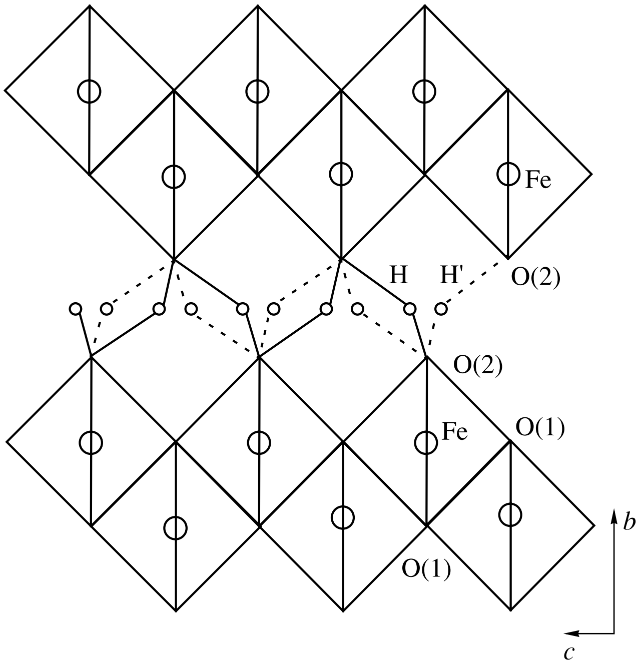

Fig. 2. Hydrogen bonding in the lepidocrocite structure, H and H' are the hydrogen positions statistically (with the probability of 1/2) occupied by hydrogen atoms located in the plane *m* normal to the *a*-axis. Solid and dashed lines indicate two types of chains of hydrogen bonds, O(2)–H···O(2) and O(2)–H'···O(2).

of the rectangle and, thus, give rise to the additional displacement of the octahedral sheets along the *b*-axis with respect to one another in the layer (in an ideal structure, this displacement equals 1/8*b*).

Comparing the electron-diffraction data for lepidocrocite, the most reliable single-crystal X-ray diffraction data for boehmite refinement [4] and the powder neutron-diffraction data (the Rietveld analysis) for the deuterium analogue of boehmite [6] with the unit-cell parameters $a = 2.865$, $b = 12.221$, $c = 3.693$ Å, we see the essential similarity of the structural features of individual layers. The octahedra in these structures are distorted in a similar way, the individual *M*–O distances in the octahedra are also distributed in the same way. Thus, the distances from the octahedral cation to the oxygen atom of the hydroxyl group in lepidocrocite and boehmite are approximately equal to the average *M*–O distance, which is determined by the valence strength *1* for this oxygen atom from the side of the octahedral cations. Despite different unit-cells parameters *b*, the distances between the closest oxygen atoms of hydroxyl groups in the adjacent layers are almost the same (2.676 for lepidocrocite and 2.705 Å for boehmite), which is explained by a certain increase of the interlayer distance in boehmite (1.977 Å) in comparison with this distance in lepidocrocite (1.847 Å).

The most pronounced differences were revealed for hydrogen positions. At the statistical distribution (with the probability 1/2) of hydrogen atoms characteristic of both structures, the hydrogen (deuterium) atom is located in the vicinity of the line connecting the oxygen atoms of the adjacent layers, the O(2)–H···O(2)' angle is 176° [4] and 179° [6] at the interatomic O–H distance 0.75 Å (H was determined from the difference electron-density synthesis without using the LS procedure) and 0.97°, respectively. According to the electron diffraction data, hydrogen atoms in lepidocrocite are located in the vicinity of the twofold axis (the O(2)–H···O(2)' angle equals 135°) at a distance of 0.27 Å from it. It should also be indicated that according to the calculation of the energy by the semiempirical method of molecular orbitals suggested by Hückel for a boehmite cluster consisting of nine hydrogen atoms, the minimum energy was obtained for θ-angle ranging within 22°–32° depending on the orientation of hydroxyl groups OH [4], which corresponded better to the angle θ obtained for lepidocrocite (17° in this study and 31.8° in [5]) than for boehmite (45° [4] and 44° [6]). The angle θ determined for lepidocrocite by the electron diffraction data is on the side of smaller angles, whereas the angle θ determined for lepidocrocite in [3, 5] and boehmite in [4, 6], on the side of large angles with respect to the indicated range of θ angles corresponding to the minimum energy.

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