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The structure of hydrohematite

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Abstract. Hydrohematite beside 'weakly bound' water removable at 160–200° C, contains about 3–4.5 % of tightly held H_2O, the complete withdrawal of which requires a very high temperature, of about 1000° C. IR investigations have shown that this kind of water exists in the form of hydroxyl groups. For this reason it has been assumed that OH^- ions occupy anion positions in the close-packed anionic sublattice of hematite together with oxygen anions and that the electrostatic neutrality is preserved by Fe^{3+} deficiency in the cationic positions.

Accurate measurements of X-ray reflection intensities of hydrohematites revealed a decrease in intensity of all reflections due to Fe^{3+}, and an unchanged intensity of (113)-reflection. The intensity of this reflection is exclusively dependent on anions.

The results obtained agree well with the calculated values for the model assumed and fully confirm the defect character of hydrohematite structure. Thus the formula of hydrohematite should be written $Fe_{2-\frac{x}{3}}(OH)_xO_{3-x}$.

Discussion

The definition of hydrohematite stems from Hüttig who introduced it in order to distinguish the alpha iron sesquioxide (α-Fe_2O_3) from the one having the same structure but containing certain amounts of water (Hüttig and Strotzer, 1936). According to some authors this substance (α-$Fe_2O_3 \cdot aq$) may contain up to 8% H_2O, only part of which dehydrates at 160–200°C (Kurnakow and Rode, 1928). The removal of other parts requires a very much higher temperature; by IR investigations it was found that small quantities of water in this species resist heating even at 1000°C (Wolska, 1977). In general terms, hydrohematite, in accordance with our current knowledge, may be considered as an alpha iron sesquioxide containing, beside loosely bound water, 3 – 4.5 % of tightly held H_2O, abnormally resisting thermal treatment. The transition hydrohematite → hematite takes place steadily with increasing temperature, as a gradual dehydroxylation process, without characteristic transition temperature.

The only suggestion which might be offered to explain the strong resistance of hydrohematite to change completely into α-Fe_2O_3 is the assumption, that water molecules are present in the form of hydroxyl groups replacing oxygen anions in their positions of the hematite lattice. Thus the occurrence of a certain kind of water in 'hydrous ferric oxide' which vaporizes only at about 300° C, has already been explained, with the support of experimental evidence, as being in the form of OH groups (Okamoto et al., 1967). In this connection the authors put forward a suggestion that in order to counterbalance the fall in negative charge, some divalent, instead of trivalent iron ions should occur.

The first unambiguous experimental indication that hydroxyl groups do exist, has been found by studying the IR spectra of the products of thermal decomposition of amorphous iron(III)hydroxide and hydrothermally prepared aluminium substituted hydrated alpha iron(III) oxide. Figure 1 presents the striking evidence of quite different absorption curves for hematite and hydrohematite. In the hydrohematite IR spectra, beside characteristic lattice modes for hematite, two supplement bands at 950 cm^{-1} and 630 cm^{-1} related to hydroxyl groups are present (Wolska, 1977).

We may then presume that hydroxyl groups occupy positions of some oxygen anions, and that electrostatic neutrality is preserved by some unoccupied cation sites. Such an iron(III) ions deficiency should be detectable by X-ray reflection intensity measurements. In Fig. 2 two frag-

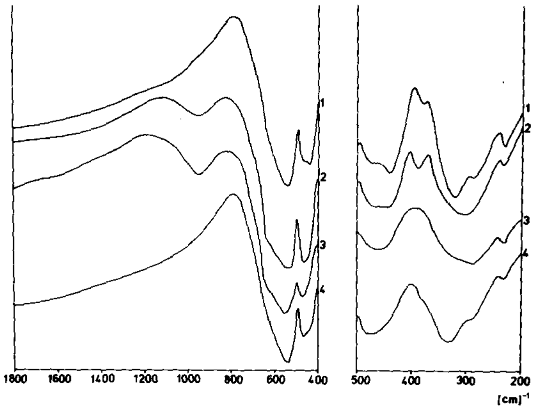

Fig. 1. Infrared spectra of samples with hematite structure: 1. Fe_2O_3; 2. $Fe_{1.83}(OH)_{0.5}O_{2.5}$; 3. $Al_{0.05}Fe_{1.73}(OH)_{0.66}O_{2.34}$; 4. $Al_{0.06}Fe_{1.94}O_3$. (Perkin-Elmer IR-180; 400–1800^{-1} KBr pellets, 200 – 500 cm^{-1} polyethylene pellets)

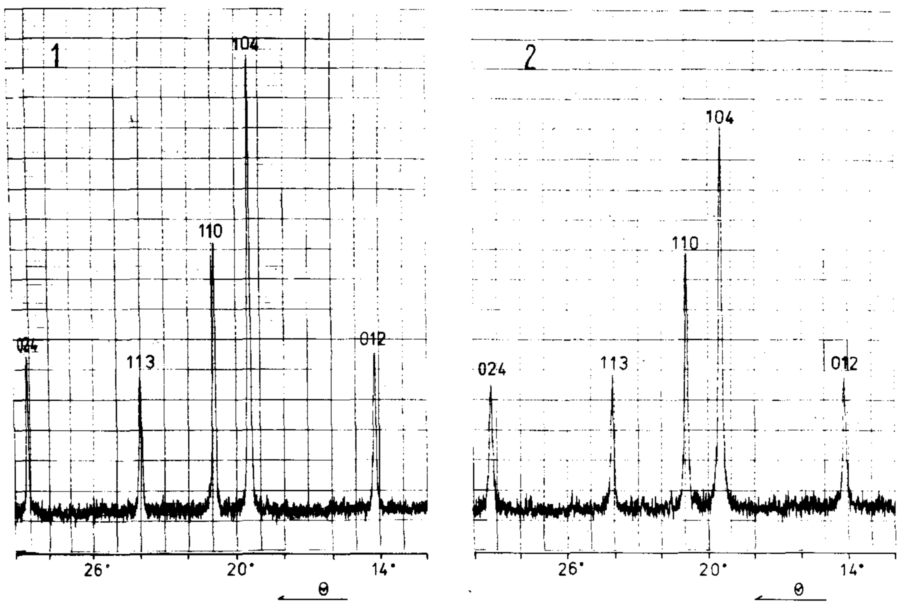

Fig. 2. X-ray powder diffractograms of hematite and hydrohematite: 1. Fe_2O_3; 2. $Fe_{1.83}(OH)_{0.5}O_{2.5}$ ($CoK\alpha$ radiation)

ments of X-ray diffractograms of hematite (1) and hydrohematite (2) are represented, in the most characteristic region for our discussion. Pattern (2) belongs to a hydrohematite, which has been prepared by mild dehydration of amorphous iron(III) hydroxide at 300 °C (24 h). After that treatment it still contained 3 % water.

It should be emphasized that any attempt to obtain pure hydrohematite, never allows more water in the form of hydroxyl groups to be retained than 3 %. In order to increase the presence of that kind of water, in other words, in order to provoke the assumed higher cation deficiency by replacing O^{2-} by OH^- and, hence, to enhance the differences in intensities of corresponding reflections, traces of substances stimulating the process are necessary. However, the condition not to contaminate the structure must be met. The series of appropriate ions is therefore strongly limited; the best ones, simultaneously and succesively eradicating the goethite phase which goes together with the formation of hydrohematite from amorphous iron(III)hydroxide, are Al^{3+}-ions (Wolska, 1976).

Depending on pH, temperature and pressure of preparation, quantities of $1.10^{-2}-3.10^{-2}$ mole Al^{3+} per mole of Fe^{3+} increase the presence of water resisting thermal treatment by about 50 %.

Figure 2 shows that the position of reflections are analogous, but careful examination allows us to find dissimilarities in intensities of all but (113)

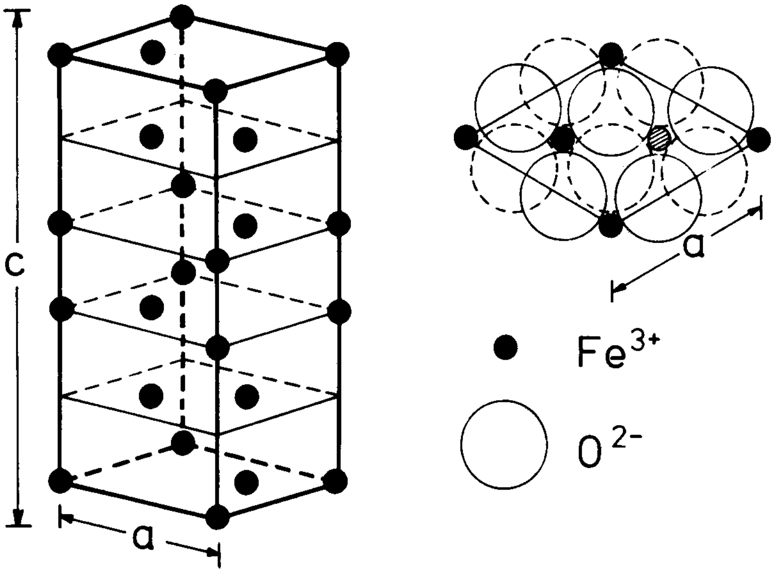

Fig. 3. Cation sublattice and anion positions in the idealized hexagonal elementary cell of hematite

reflections, which depends on oxygen anions only. Remembering that the atomic amplitudes for O^{2-} and OH^- are practically the same, the uneffected intensity of this particular reflection is a matter of course.

The structure of hematite was determined by Pauling and Hendricks (1925) and refined succesively by Shirane et al. (1959), and recently by Blake et al. (1966). As a result hematite belongs to space group $R\bar{3}c$, with lattice parameters $a = 5.034$ Å and $c = 13.750$ Å. The oxygen anions are located in special positions along the twofold axes at $\pm [u, 0, \frac{1}{4};\ 0, u, \frac{1}{4};\ \bar{u}, \bar{u}, \frac{1}{4}]$ with $u = 0.3059$. The Fe^{3+}-ions lie on threefold axes at $\pm [0, 0, w; 0, 0, w + \frac{1}{2}]$ with $w = 0.3553$. Thus the cation-sublattice and the positions of anions in the elementary cell containing six molecules of Fe_2O_3 might be represented as in Figure 3.

The calculation of structure factors for *hkl* reflections gives the following expressions:

$$\begin{aligned} \mathrm{F}_{hkl} &= 6 f_{\mathrm{Fe}^{3+}} \cdot [\cos 2\pi lw + \cos 2\pi (lw + \tfrac{l}{2})] \\ &\quad + 6 f_{\mathrm{O}^{2-}} \cdot [\cos 2\pi (hu + \tfrac{l}{4}) + \cos 2\pi (ku + \tfrac{l}{4}) + \cos 2\pi (hu + ku - \tfrac{l}{4})], \end{aligned}$$

$$\mathrm{F}_{012} = -\,2.940 f_{\mathrm{Fe}^{3+}} - 1.872 f_{\mathrm{O}^{2-}},$$

$$\mathrm{F}_{104} = -\,10.559 f_{\mathrm{Fe}^{3+}} + 1.872 f_{\mathrm{O}^{2-}},$$

$$\mathrm{F}_{110} = 12.000 f_{\mathrm{Fe}^{3+}} - 8.708 f_{\mathrm{O}^{2-}},$$

$F_{113} = 15.145 f_{O^{2-}}$,

$F_{024} = -10.559 f_{Fe^{3+}} - 3.158 f_{O^{2-}}$.

If hydroxyl groups occupy positions of oxygen anions, we can represent the formula for hydrohematite as

$$\alpha\text{-Fe}_{2-\frac{x}{3}}\,(\text{OH})_x\text{O}_{3-x}, \text{ where } x = \frac{9.07\,y}{51.15+y};\; y = \%\,\text{H}_2\text{O}.$$

For that model, taking $f_{O^{2-}} \cong f_{OH^-}$, the expression for the structure factor could be given by the equation:

$$\begin{aligned} F_{hkl} &= 3\left(2-\tfrac{x}{3}\right) f_{Fe^{3+}} \cdot \left[\cos 2\pi lw + \cos 2\pi \left(lw + \tfrac{l}{2}\right)\right] \\ &\quad + 6 f_{O^{2-}} \cdot \left[\cos 2\pi \left(hu + \tfrac{l}{4}\right) + \cos 2\pi \left(ku + \tfrac{l}{4}\right) + \cos 2\pi \left(hu + ku - \tfrac{l}{4}\right)\right]. \end{aligned}$$

In the case of hydrohematites enriched in OH^- by the introduction of Al^{3+}, the value of the structure factor will be slightly changed since $f_{Al^{3+}} < f_{Fe^{3+}}$. For $\alpha\text{-Al}_z\text{Fe}_{2-z}\text{O}_3$ the corresponding expression for F_{hkl} value will be written

$$\begin{aligned} F_{hkl} &= 3\left[(2-z) f_{Fe^{3+}} + z f_{Al^{3+}}\right] \cdot \left[\cos 2\pi lw + \cos 2\pi \left(lw + \tfrac{l}{2}\right)\right] \\ &\quad + 6 f_{O^{2-}} \cdot \left[\cos 2\pi \left(hu + \tfrac{l}{4}\right) + \cos 2\pi \left(ku + \tfrac{l}{4}\right) + \cos 2\pi \left(hu + ku - \tfrac{l}{4}\right)\right] \end{aligned}$$

and hence for hydrohematites containing Al^{3+}, i.e.,

$$\alpha\text{-Al}_{z(1-\frac{x}{6})}\text{Fe}_{(2-z)(1-\frac{x}{6})}(\text{OH})_x\text{O}_{3-x},$$

$$\begin{aligned} F_{hkl} &= 3\left(2-\tfrac{x}{3}\right)\left[\left(1-\tfrac{z}{2}\right) f_{Fe^{3+}} + \tfrac{z}{2} f_{Al^{3+}}\right]\left[\cos 2\pi lw + \cos 2\pi \left(lw + \tfrac{l}{2}\right)\right] \\ &\quad + 6 f_{O^{2-}} \cdot \left[\cos 2\pi \left(hu + \tfrac{l}{4}\right) + \cos 2\pi \left(ku + \tfrac{l}{4}\right) + \cos 2\pi \left(hu + ku - \tfrac{l}{4}\right)\right]. \end{aligned}$$

Taking – in agreement with the assumed model – the intensity of (113) plane as invariable, the relative intensities for particular reflections have been calculated from the formula $I = |F|^2 \cdot p \cdot PL$, (where p is the multiplicity number, and PL stands for combined polarization-Lorentz factor).

The values (Table 1) clearly indicate that the fall in intensities caused by the deficiency of trivalent iron ions, as a result of occupation of some O^{2-}

Table 1. Calculated intensities of X-ray diffraction patterns of hematite and hydrohematite

hkl	Fe_2O_3		$Al_{0.1}Fe_{1.9}O_3$		$Fe_{1.83}(OH)_{0.5}O_{2.5}$		$Al_{0.05}Fe_{1.73}$-$(OH)_{0.66}O_{2.34}$	
	I %(104)	I %(113)	I %(104)	I %(113)	I %(104)	I %(113)	I %(104)	I %(113)
012	28.6	155	29.0	148	29.8	134	30.5	124
104	100.0	541	100.0	509	100.0	450	100.0	408
110	74.8	404	74.1	377	73.8	332	70.6	288
113	18.5	100	19.6	100	22.2	100	24.5	100
024	39.8	215	40.2	204	40.7	183	41.2	168

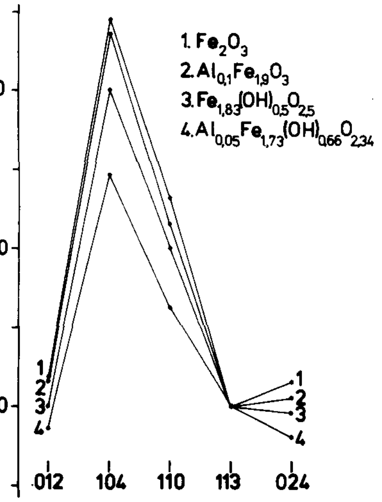

Fig. 4
Experimental values of X-ray reflection intensities of hematities (1.2) and hydrohematites (3.4)

positions by OH^- groups, is much more acute than the drop in intensities influenced by the substitution of cations; in the former case the fall, for example, for $x = 0.5$ exceeds 15 % and for $x = 0.7$ 20 %, respectively, whereas in the latter case for $z = 0.1$ the fall is about 5 % only.

Experimental

The intensity measurements of diffraction lines of hematite and hydrohematite powders were carried out on a TUR-61 diffractometer using Co*Kα* radiation and proportional counter. For hydrohematites obtained by dehydration of amorphous iron(III) hydroxide and those obtained by hydrothermal method with Al^{3+} doping, both previously heated 24 h at 200 °C in order to remove 'weakly bound' water (and still retaining 1—4.5 % H_2O according to methods applied), the integral intensities have been measured for (012), (104), (110), (113), and (024) reflections, and the values compared with the intensities of the same preparations but additionally heated at 1050 °C. This temperature was high enough for the complete removal of hydroxyl groups and fortunately, by far too low to evoke thermal decomposition of hematite. Obviously, in both series of measurements conditions for goniometer and recorder operations have been met. In each case the representative value has been taken as a mean of 10 separate measurements.

The values of intensities as a function of Al^{3+} and H_2O content for respective reflections of hematite and hydrohematite are represented in Figure 4. Changes in intensities caused by Al^{3+} substitution as well as by the presence of hydroxyl groups in hematite lattice fit very well the assumed model of defect structure, characterized by the deficiency of Fe^{3+}-ions in the lattice. The pertinence of the model assumed is also confirmed by the practically invariable value of the intensity of the (113) reflection in all samples examined.

Conclusion

In the light of these results, hydrohematite should be regarded now as a species of hematite with statistically distributed hydroxyl groups in the anion sublattice and displaying iron ions deficiency in cation sublattice.

For example, the hexagonal elementary cell of a hydrohematite (most ussually encountered) with composition $Fe_{1.83}(OH)_{0.5}O_{2.5}$ (corresponding to 3% of tightly held water), should contain 11 Fe^{3+}-ions, 3 OH^- and 15 O^{2-} anions.

Identification of hydrohematite with sufficient accuracy may be carried out on the bases of characteristic absorption bands in the IR spectra and as a result of precise intensity measurements of X-ray reflections.

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