

The Lattice Parameters of Natural Single Crystal and Synthetically Produced Goethite (α -FeOOH)

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Forsyth, Hedley & Johnson (*J. Phys. C. (Proc. Phys. Soc.)*, (1968) **1**, 179) have determined the magnetic structure of goethite (α -FeOOH) using natural and synthetic material. They observed a significant narrowing in the Mössbauer spectrum line width after annealing a synthetic specimen at 160°C for several hours. The present X-ray diffraction investigation has been carried out on the same material and shows that there are no significant differences between the cell dimensions of the natural and synthetic crystals. Weighted means of the observed lattice parameters for the natural and synthetic materials are $a = 4.602 \pm 0.003$, $b = 9.952 \pm 0.004$ and $c = 3.021 \pm 0.002$ Å. No changes were detected in the cell dimensions or microdensitometer traces of the diffraction profiles after a heat treatment similar to that used in the Mössbauer study. It is therefore concluded that the mechanism which produces this line narrowing does not have sizeable long-range effects on the atomic arrangements.

Introduction and review of previous work

Peacock (1942) reported natural goethite to be orthorhombic with a space group $Pbnm$ and cell dimensions $a = 4.587$, $b = 9.937$, and $c = 3.015$ Å with axial ratios $a:b:c = 0.4616:1:0.3034$. No errors were quoted for these cell dimensions. (*Structure Reports*, 1942–44, shows Peacock's cell dimensions for goethite increased by a factor of 1.0020, *i.e.* it was assumed that Peacock's values were in kX units. The original paper, however, quite clearly states that the results are quoted in Å units).

A neutron-diffraction investigation has recently been undertaken by Forsyth, Hedley & Johnson (1968). They have determined the magnetic structure of the material and observed a narrowing in the line width of the Mössbauer absorption spectra at room temperature after having heated the synthetic material to 135°C.

Further X-ray diffraction measurements of the cell dimensions of a natural single crystal and synthetic powdered goethite have been made to complete the neutron-diffraction investigation and to investigate the mechanism which produces the narrowing in the Mössbauer spectrum.

Material

In the present investigation three samples of materials were examined. The first was naturally occurring goethite from the Restormel mines, Lostwithiel, Cornwall. A single crystal was chosen from the same mineral sample which was used by Forsyth *et al.* in their determination of the magnetic structure of α -FeOOH. The second was a synthetic powder obtained from the same batch used in the neutron diffraction experiment. A third sample was prepared by heating the synthetic material to 160°C for 48 hours. A room temperature study was made to observe changes in line profiles or lattice parameters.

Results

Natural material

A crystal which approximated to a parallelepiped with edges of 0.1, 0.1 and 0.25 mm was selected from the mineral sample. A 3 cm radius rotation camera, modified as described by Farquhar & Lipson (1946) and capable of measuring angles up to $2\theta = 177.0^\circ$, was used for the X-ray single-crystal photographs which were taken with a Straumanis method of film mounting. All the X-ray photographs were measured using a travelling microscope and making a visual estimation of the peak position for each diffraction profile. Oscillation photographs were taken about the [001] and [010] zone axes. Iron, copper, chromium and cobalt $K\alpha$ radiations were used for the [001] axis photographs, whereas only cobalt $K\alpha$ radiation was found to be suitable for the [001] axis photographs.

Data obtained from these photographs are set out in Table 1. The reflexions were indexed using values for a , b and c given by Peacock (1942), and a least-squares computer program (Mueller & Heaton, 1961) used to obtain accurate values of the lattice parameters. The computer program has alternative extrapolation functions and a means of weighting the observations. For the single-crystal photographs reflexions were weighted according to a scheme $w = \tan \theta$ and extrapolation against $\sin^2\theta$ for values of θ near 90° . The lattice constants from the [001] zone photographs were $a = 4.601 \pm 0.003$, $b = 9.958 \pm 0.007$ Å and from the [010] zone photographs $a = 4.6013 \pm 0.0003$, $c = 3.0209 \pm 0.0002$ Å. In addition, single crystals from the mineral sample were powdered and an X-ray powder photograph taken with an 11.483 cm diameter Philips powder camera with chromium $K\alpha$ radiation. Five pairs of high-angle lines on the photographs were well defined and resolved. A least-squares fit using an extrapolation function $\frac{1}{2}(\cos^2\theta/\sin \theta + \cos^2\theta/\theta)$ and a weighting scheme $w =$

$\tan \theta$ for 39 lines gave $a=4.598 \pm 0.005$, $b=9.951 \pm 0.004$ and $c=3.021 \pm 0.002$ Å.

Synthetic material

Powder photographs were taken before and after heat treatment. A least-squares fit of the observed and calculated 'd' spacings for the untreated sample using the same extrapolation and weighting scheme as for the powdered natural material gave $a=4.605 \pm 0.001$, $b=9.952 \pm 0.003$, $c=3.021 \pm 0.001$ Å.

After the specimen had been heat treated in the way described by Forsyth, Hedley & Johnson, its cell di-

mensions were determined as $a=4.605 \pm 0.002$, $b=9.952 \pm 0.005$ and $c=3.020 \pm 0.001$ Å. Microdensitometer traces were made of the films of the treated and untreated specimens. No differences could be detected in the full width at half height of corresponding high angle peaks on these films, nor could any improved resolution of the α_1, α_2 doublet be detected.

Discussion

The lattice constants are in all cases larger than those reported by Peacock but the differences may not be sig-

Table 1. Calculated and observed 'd' spacings for (α -FeOOH) from single-crystal photographs

Radiation $K\alpha, K\alpha_1, K\alpha_2$	<i>h</i>	<i>k</i>	<i>l</i>	'd' spacing, observed	'd' spacing, calculated	$d=(d_{obs}-d_{calc})$		
Cr	$K\alpha_1$	4	0	0	1.15037Å	1.15064Å	-0.00027Å	
	$K\alpha_2$	4	0	0	1.15023	1.15059	-0.00037	
Cu	$K\alpha_1$	3	5	0	1.21397	1.21351	0.00046	
	$K\alpha_2$	3	5	0	1.21418	1.21345	0.00073	
Co	$K\alpha_1$	4	9	0	0.79708	0.79726	-0.00019	
	$K\alpha_2$	4	9	0	0.79712	0.79724	-0.00012	
	$K\alpha_1$	5	6	0	0.80549	0.80461	0.00088	
	$K\alpha_2$	5	6	0	0.80435	0.80460	-0.00026	
	$K\alpha_1$	5	4	0	0.86185	0.86220	-0.00035	
	$K\alpha_2$	5	4	0	0.86205	0.86218	-0.00013	
	$K\alpha_1$	1	11	0	0.88640	0.88665	-0.00025	
	$K\alpha_2$	1	11	0	0.88622	0.88663	-0.00040	
	$K\alpha_1$	3	9	0	0.89783	0.89565	0.00217	
	$K\alpha_2$	3	9	0	0.89800	0.89563	0.00237	
	$K\alpha_1$	2	10	0	0.90774	0.91194	-0.00421	
	$K\alpha_2$	2	10	0	0.90778	0.91192	-0.00413	
	Fe	$K\alpha_1$	5	2	0	0.90485	0.90511	-0.00026
		$K\alpha_2$	5	2	0	0.90481	0.90508	-0.00027
		$K\alpha_1$	2	10	0	0.91356	0.91365	-0.00009
		$K\alpha_2$	2	10	0	0.91359	0.91361	-0.00002
$K\alpha_1$		5	1	0	0.91726	0.91633	0.00093	
$K\alpha_2$		5	1	0	0.91615	0.91632	-0.00016	
$K\alpha_1$		4	6	0	0.94467	0.94482	-0.00015	
$K\alpha_2$		4	6	0	0.94498	0.94478	0.00020	
$K\alpha_1$		3	8	0	0.96493	0.96542	-0.00049	
$K\alpha_2$		3	8	0	0.96532	0.96538	-0.00006	
$K\alpha_1$		0	10	0	0.99418	0.99400	0.00018	
$K\alpha_2$		0	10	0	0.99492	0.99396	0.00096	
$K\alpha_1$		3	7	0	1.04053	1.04040	0.00013	
$K\alpha_2$		3	7	0	1.04109	1.04036	0.00072	
Co	$K\alpha_1$	0	10	0	0.99571	0.99531	0.00040	
	$K\alpha_2$	0	10	0	0.99591	0.99526	0.00065	
	$K\alpha_1$	4	4	0	1.04166	1.04303	-0.00137	
	$K\alpha_2$	4	4	0	1.04196	1.04299	-0.00103	
	$K\alpha_1$	1	9	0	1.07389	1.07356	0.00033	
	$K\alpha_2$	1	9	0	1.07419	1.07352	0.00067	
	$K\alpha_1$	4	3	0	1.08520	1.08473	0.00047	
	$K\alpha_2$	4	3	0	1.08560	1.08469	0.00091	
	$K\alpha_1$	2	8	0	1.09254	1.09218	0.00036	
	$K\alpha_2$	2	8	0	1.09324	1.09213	0.00110	
	$K\alpha_1$	3	6	0	1.12408	1.12316	0.00092	
	$K\alpha_2$	3	6	0	1.12444	1.12312	0.00131	
	Co	$K\alpha$	3	0	1	1.36584	1.36555	0.00029
		$K\alpha$	2	0	2	1.26061	1.26108	-0.00046
$K\alpha$		4	0	0	1.14949	1.14937	0.00012	
$K\alpha_1$		1	0	3	0.98329	0.98331	-0.00002	
$K\alpha_2$		1	0	3	0.98340	0.98331	0.00008	
$K\alpha_1$		4	0	2	0.91505	0.91507	-0.00002	
$K\alpha_2$	4	0	2	0.91506	0.91506	0.00000		

nificant since no errors were quoted with Peacock's results. It would appear that the results in this communication are typical of the pure material since there is good agreement between the cell dimensions of the natural single crystal and those of the synthetic material. Weighted means for the lattice constants of the single crystal, powdered single crystal and untreated synthetic material are $a = 4.602 \pm 0.003$, $b = 9.952 \pm 0.004$ and $c = 3.021 \pm 0.002 \text{ \AA}$. All the observations lie within two standard deviations of these mean values and there are no significant changes in the room temperature cell dimensions of the synthetic material after heat treatment. Microdensitometer traces showed no improved resolution on the films after heat treatment; this observation, together with the evidence of the unchanged unit-cell dimensions, suggests that the mechanism which produces the narrowing of the Mössbauer spec-

trum is sufficiently short-ranged to prevent its being detected in the present study.

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Structure Protonique et Deutonique de l'Acide Ferrocyanhydrique

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The positions of the hydrogen atoms in $\text{H}_4\text{Fe}(\text{CN})_6$ crystals already found by the authors, with X-rays, are confirmed by neutron diffraction. There are two, non-equivalent, dissymmetric and forked hydrogen bonds. $\text{D}_4\text{Fe}(\text{CN})_6$ crystals which have the same unit cell within 0.01 \AA show a strong isotopic effect: the D atoms are in positions distant by 0.15 and 0.40 \AA from the proton positions. A calculation of the electrostatic energy gives approximately the same positions. Therefore the hydrogen positions are imposed by the crystalline field. The energy of the proton in the structure is $\approx 2.3 \text{ kcal.mole}^{-1}$. Zero point energy is probably responsible for the difference in the H and D positions.

Introduction

L'étude de l'acide ferrocyanhydrique $\text{H}_4\text{Fe}(\text{CN})_6$ ($P2_1/a$) par diffraction des rayons X (Pierrot, Kern & Weiss, 1966) a permis de mettre en évidence dans cette structure deux ponts hydrogène non équivalents, dissymétriques et fourchus. Les protons participant à ces liaisons ont été localisés par le calcul des sections de densité électronique. Afin de confirmer ces résultats, et de préciser le caractère de ces liaisons hydrogène, nous avons entrepris une étude par diffraction des neutrons.

Mesures

Des monocristaux suffisamment gros ne pouvant être obtenus, nous avons préparé une poudre de $\text{H}_4\text{Fe}(\text{CN})_6$ et de son homologue deutérié $\text{D}_4\text{Fe}(\text{CN})_6$. La deutériation de $\text{H}_4\text{Fe}(\text{CN})_6$ s'effectue par échange isotopique dans l'eau lourde (99,8%). Le taux de deutériation a été mesuré par absorption infrarouge (Ceccaldi, 1964). Dès la troisième recristallisation, un seuil de saturation

de 95% D est atteint, valeur plus élevée que celle obtenue avec une autre méthode par les spectroscopistes ayant étudié $\text{D}_4\text{Fe}(\text{CN})_6$ (Ginsberg & Koubek, 1965).

Aux rayons X, $\text{H}_4\text{Fe}(\text{CN})_6$ et $\text{D}_4\text{Fe}(\text{CN})_6$ sont isomorphes, les équidistances des plans réticulaires diffèrent de moins de $1 \cdot 10^{-2} \text{ \AA}$, les intensités diffractées sont identiques, ce qui atteste que les positions de tous les atomes sont les mêmes, à la sensibilité des rayons X près.

Les intensités diffractées par les neutrons ont été enregistrées à l'aide d'un spectromètre à haute résolution, par comptage point par point, toutes les trois minutes (en 2θ) à nombre de coups constant au moniteur ($1,1 \cdot 10^5$). Le porte échantillon est un tube en aluminium de 15 mm de diamètre et de $0,2 \text{ mm}$ d'épaisseur de paroi. Les amplitudes observées $|F_o|$ sur les deux acides sont mises à l'échelle absolue à l'aide d'un échantillon de référence de nickel (Bacon, 1962). Ces valeurs pour les raies tout à fait isolées sont rassemblées dans le Tableau 1 ainsi que l'erreur expérimentale ΔF_o . Cette erreur est due essentiellement à la correction du fond de diffusion.