

The Micro-Morphology of β -FeOOH

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β -FeOOH can be formed in a number of distinct colloidal states. Hydrolysis of FeCl_3 gives somatoid pseudo-crystals aggregated into rafts and sometimes twinned. Tactoids can be formed in concentrated suspensions of small rods. Solid state formation results in lath frameworks. β -FeOOH also occurs as the mineral akaganeite. Selected area diffraction enabled the crystallography of these various forms and their transformations to be elucidated in terms of a "unit particle" structure.

至大无外謂之大一
至小无内謂之小一。
惠施

The greatest has nothing beyond itself and is called the Great Unit; the smallest has nothing beyond itself and is called the Small Unit.

Hui Shih, 4th cent. B.C.

Introduction

The structure and some of the properties of β -FeOOH have already been described (Mackay, 1960) but further studies have disclosed many interesting features and provide an example in which several different microscopic and diffraction techniques can, and indeed must, be combined. The complementarity of the evidence provided by the various methods is particularly striking.

The unit cell of β -FeOOH is tetragonal with $a=10.48$ and $c=3.023\text{\AA}$ and the structure is that of hollandite. Sub-units, each $a/3 \times a/3 \times c$, containing two oxygen atoms in an approximately body-centred cubic arrangement, can be distinguished. The Fe^{+++} ions lie in octahedral interstices.

Occurrence as somatoids

When a dilute solution of FeCl_3 is hydrolysed by heating, β -FeOOH appears in the form of somatoids (Kohlschütter, 1925). These are spindle-shaped particles about $1000\text{--}5000\text{\AA}$ long with a length/diameter ratio of about 5. They are circular in cross-section and are quasi-single crystals built up of a mosaic of unit particles (Takada, 1958). Hydrolysis at $40\text{--}60^\circ$ gives rafts of such somatoids where the spindles are packed in a square lattice with their axes perpendicular to the plane of the single-layer sheet. There is also azimuthal orientation.

Occurrence as sheets

When crystals of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ are slowly

oxidised in air the β -FeOOH is produced in the form of large, textured sheets. The material is very well crystallised. The c -axis may lie in one or two directions in the sheet and further hydrolysis by boiling breaks down the sheets into needle-like splinters which give a shimmering suspension. Here, the immediate precursor of β -FeOOH in this solid state transformation is not necessarily $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

Occurrence as crystalline aggregates

The hydrolysis of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ gives aggregates of small crystals of β -FeOOH and not somatoids.

Occurrence as the mineral akaganeite

β -FeOOH has been found as a mineral, named akaganeite by its discoverer, Dr M. Nambu (private communication, 1961), in material which was apparently limonite. It appears to derive from the weathering of pyrrhotite and to have come through an intermediate sulphate stage. The analysis shows that there is no chloride present but the mineral contains some 3.5% wt. SiO_2 . The particles are extremely small lath-shaped crystals of uniform size.

Occurrence as tactoids

If concentrated FeCl_3 is hydrolysed with ammonia then a paste of β -FeOOH can be formed which contains tactoids (Zocher, 1925, etc.). The paste consists of a suspension of

prismatic crystals about 300Å long with a ratio of length to width of about 5. This is remarkable in that other tactoids (TMV and V_2O_5 sol) this ratio is 10^2 to 10^3 .

The tactoids are describable in terms of the equilibrium of droplets with anisotropic surface tensions σ_1 and σ_2 (parallel and perpendicular to the directions in which the particles cooperatively orient themselves. Their shape is described by the equation $\sigma_1/r_1 + \sigma_2/r_2 = p$ (Bernal and Fankuchen, 1941).

Magnetic properties

Magnetic measurements on β -FeOOH (K.M. Creer, private communication, 1961) indicate

that the material is anti-ferromagnetic but preliminary neutron diffraction tests have been inconclusive.

Solid state transformations

In addition to the inferred transformation from $FeCl_2 \cdot 4H_2O$ an oriented transformation produced by heating β -FeOOH *in vacuo* by electron bombardment has been followed by selected area diffraction. β -FeOOH is dehydrated and eventually reduced to a spinel-type structure. The mechanism is understandable in terms of a unit particle mechanism which would explain how the crystallographic orientation is preserved during the loss of water.

Summary of the application of various techniques to the examination of β -FeOOH in different states of aggregation:

Technique:	Information:
<i>X-ray diffraction</i>	Identification.
Powder photographs	Accurate cell dimensions from indexed photograph. Estimation of tactoid particle size and shape from differential line broadening.
Texture photographs	Orientation of particles in dried smear of tactosol and as liquid in capillaries.
Small angle scattering	Diameter of particles in tactoid.
<i>Electron microscopy</i>	Crystal morphology by direct observation. Estimates of particle size and shape and association of particles.
<i>Selected area electron diffraction</i>	Identification from powder photographs. Identification from single-crystal diffraction. Orientation from single-crystal diffraction. Confirmation of symmetry. Mutual orientation of somatoids in rafts. Following transformation of β -FeOOH to a spinel structure in a preferred orientation. Elucidation of twin law.
<i>Neutron diffraction</i>	Nature of antiferromagnetic ordering (projected study).
<i>Optical microscopy</i>	Powders and somatoids are beyond the optical resolving power. Identification of spontaneous cooperative orientation. Birefringence and dimensions of tactoids. Observations of dislocation in various kinds of tactoids.

References

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DISCUSSION

D.H. DONNAY: You seem to imply that twinning in (112) is common in body-centred tetragonal lattice. In order to get a row quasi-perpendicular to (112) the value of c/a should be critical.

A.L. MACKAY: The appropriate pseudo-cell is really cubic with $a'=3.47$ and $c=3.03\text{\AA}$ and hence closely recalls the situation in Mo and W.

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Structure of Thin Layers of Some F.C.C. Metals Deposited on Oriented Ag, Pd and Ni Films

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Some f.c.c. metals—Ni, Cu, Pd, Al, Au, Ag and Pb—were evaporated *in vacuo* on to oriented Ag, Pd and Ni films and the structure of these films were studied by the transmission method of electron diffraction. Some films were composed of intermetallic compounds of deposit and substrate metals. But some films were composed of two layers of deposit and substrate metals. In the latter case, the deposit metals grew in an oriented overgrowth on a substrate at a temperature higher than an epitaxial temperature. Two kinds of oriented overgrowth were observed and their occurrence depended on the percentage misfit.

1. Introduction

So far cleavage surfaces of some minerals or salts¹⁾ have often been used as the substrates on which oriented overgrowths of some materials from the vapour phase were formed. But there are only a few investigations of the oriented overgrowth of metals deposited on the surface of metallic single crystal²⁾. In order to obtain some informations concerning the mechanism of epitaxy, it seems to be very desirable to make further systematic studies on metal layers deposited on single crystal metal surfaces. In the present paper, an investigations will be described in which some f. c. c. metals—Ni, Cu, Pd, Al, Au, Ag and Pb—were deposited from the vapour *in vacuo* on to oriented Ag, Pd and Ni films and the structure of these films were examined by the transmission method of electron diffraction. Some films were composed of intermetallic compounds of deposit and substrate metals. But some films were composed of two layers of deposit

and substrate metals. In the latter case the deposit metals grew in an oriented overgrowth on a substrate at a temperature higher than an epitaxial temperature. Two kinds of oriented overgrowth were observed. The occurrence of these kinds of oriented overgrowth depended mainly on the percentage misfit.

2. Experimental method

Oriented metal films about $40\text{ m}\mu$ in thickness were deposited *in vacuo* on the cleavage surfaces of NaCl crystal heated to about 200°C (for Ag) or about 400°C (for Pd and Ni). After the dissolution of NaCl crystal in water, the oriented metal film was caught on a hole 0.1 mm in diameter perforated in a thin Ni plate. After it was ascertained by the method of electron diffraction that the metal film was a quasi-single crystal film having the (001) plane parallel to the film surface and the $\{111\}$ twinning was comparatively less marked, it