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LETTER

A transmission electron microscopy study on the real structure of synthetic hematite

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The magnetic properties of hematite (α-Fe_2O_3), the most important iron ore, have been extensively studied. It shows a Morin transition—a magnetic phase transition from an antiferromagnetic state to a weakly ferromagnetic one. The spins of the low-temperature phase order antiferromagnetically along the rhombohedral [111] direction. Those of the high-temperature phase order antiferromagnetically in the (111) plane, with a slight tilt out of plane, which leads to the ferromagnetic component. The Morin transition in pure hematite is known to be strongly dependent on the real structure of the investigated sample: Grain size, substitution for Fe by other metals, incorporation of water or OH^- groups due to various synthesis routes influence the spin ordering of the hematite. Dang et al. [1] reviewed published work and successfully established a correlation between the lattice parameters and the Morin transition. They correlated the varying lattice parameters to different defect structures, which have been called protohematite and hydrohematite with reference to Wolska and Schwertmann [2]. This correlation between magnetic properties and lattice imperfections makes it important to carefully study the real structure of hematite.

Matijevic and Schreiner [3] were the first to introduce the method of forced hydrolysis to produce synthetic hematite from an aqueous metal salt solution at elevated temperatures. By controlling the temperature, pH-value and concentration of different anions, particles of metal(hydrous)oxides with narrow size distribution were obtained. But investigations of the structure of hematite particles prepared by this method have brought up the possible existence of small, not perfectly ordered subunits within single particles. Thus, Matijevic et al. [4], Rath et al. [5] and Sahu et al. [6] concluded from the linewidth of x-ray powder diffraction patterns that the investigated particles could not be single crystalline, but were composed of smaller subunits.

The present TEM-study is focused on the question, whether synthetic hematite is composed of the suggested subunits. A commercial hematite sample as well as a sample of own production obtained by forced hydrolysis were compared. Different TEM methods were used to identify the internal structure of the particles, including high resolution (HR) TEM as well as convergent-beam electron diffraction (CBED) and large-angle (LA) CBED. The latter ones are very sensitive to lattice defects [7–9]. They still provide information about the real structure of a sample even in cases if conventional TEM and HRTEM methods fail. It will be demonstrated that the synthetic hematite particles of our study, both bought and from own production, show a 'pseudo single crystallinity', whereas an analogue study on a naturally grown hematite indicated a perfect crystallinity.

Samples were prepared by dissolving ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in water at room temperature. The result was a clear 0.02 M solution of yellow color. The solution was filled in a pyrex bottle, heated to 100 ± 5 °C and aged at that temperature for 3 days. It was observed that the liquid turned cloudy during heating. A part of the as-prepared dispersion was further diluted and dropped onto a carbon coated grid for the TEM investigation. A commercial hematite (Wako Pure Chemical Industries,

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Ltd., purity: 99.99%) and a natural hematite of Brazilian source were mortared and dispersed in ethanol to use them as reference material. The dispersions were dropped onto carbon coated grids as well. TEM investigations were carried out using a JEOL 2010FEF with in-column Ω-type energy filter at an acceleration voltage of 100 kV.

Figure 1, left, shows a conventional TEM image of hematite particles of own production with a rather uniform size of 180 ± 20 nm. High resolution images (Fig. 1, right) were taken in the center (image a) and at the edge (image b) of the circled particle. The incident beam was parallel to the threefold axis of hematite, the zone-axis is therefore [111] (rhombohedral setting). Image a is taken in the center of the particle. The ideal hematite lattice can only be seen at the lower right corner of the image, the rest of the image shows a deviating periodicity. The inset in the lower left is the fourier transform of the image, showing the hematite peaks (compare b) and additional maxima. The high resolution image taken at the edge (image b) demonstrates the periodicity and lattice spacings which are expected for hematite, no lattice defects are observed. The inset shows the fourier transform of the displayed area.

All convergent-beam electron diffraction patterns (Figs. 2–4) were taken with a spot size of 0.5 nm and later modified to represent the gradient of the intensity, which is necessary for showing the whole observed pattern in one image. Like the high resolution images, they were taken at different positions of the observed particles: in the central part and near the edge.

The CBED pattern taken in the central part (Fig. 2a) of the particle shows major deviations from the ideal threefold symmetry, even though the correct alignment of the crystal can be seen by the symmetric higher order Laue zone (HOLZ) line triangle in the central disc. The ring of the first order Laue zone (FOLZ) reflection intensities appears doubled in the lower left. Figure 2b shows the pattern taken at the edge of the circled particle shown in Fig. 1. The sixfold symmetry of the intensity distribution of zeroth order Laue zone (ZOLZ) reflection and the threefold whole pattern symmetry of the intensities of the HOLZ reflections is almost perfect. Due to the thin sample edge, no HOLZ lines are observed within the ZOLZ diffraction discs.

To demonstrate that the observed loss of symmetry is a more general feature of synthetic hematite, a commercial sample from Wako Pure Chemical Industries, Ltd., was investigated by CBED as well. The patterns taken in the central part and near the edge of a commercial hematite particle show the same characteristic features as the sample of own production: The pattern taken in the central part of the commercial hematite (Fig. 3a) shows similar deviations from the ideal symmetry as observed for the own sample prepared by forced hydrolysis: the ring of the first order Laue zone appears doubled, as circled in the upper left, corresponding to the multiple HOLZ lines in the central disk (see inverted inset). The pattern taken at the edge (Fig. 3b) shows an almost perfect symmetry, for the sixfold intensity distribution of the ZOLZ as well as for the threefold whole pattern symmetry.

A CBED pattern of natural hematite (Fig. 4) shows remarkable differences compared to those of the synthetic ones. The symmetry of the intensity distribution—at a comparable sample thickness to Fig. 2a—shows almost perfect threefold symmetry up to the third order ZOLZ reflections, the HOLZ lines in the central disk are clearly visible and show threefold symmetry.

The LACBED pattern of the natural Brazilian hematite (Fig. 5a) shows sixfold symmetry of the intensity distribution, no indication for lattice defects are observed in the Kikuchi lines. The LACBED patterns of the synthetic particle of own production (Fig. 5b) show clearly observable Kikuchi lines only in the lower right part, which corresponds to the thin sample edge (compare HR-TEM and CBED). The rest of the presented picture shows a blurred intensity distribution, in which vague indications for the existence of a threefold symmetry can be detected.

The natural hematite of Brazilian source showed perfect crystallinity in all applied imaging techniques. For both

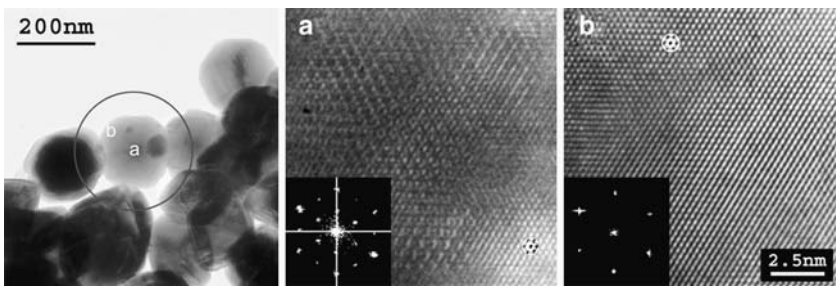

Fig. 1 Conventional TEM (left) and HRTEM (right) of the hematite sample of own production. The high resolution images are taken in the central part –marked with a—and at the edge– marked with b—of the circled particle. Only the high resolution image taken at the edge shows a perfect crystallinity

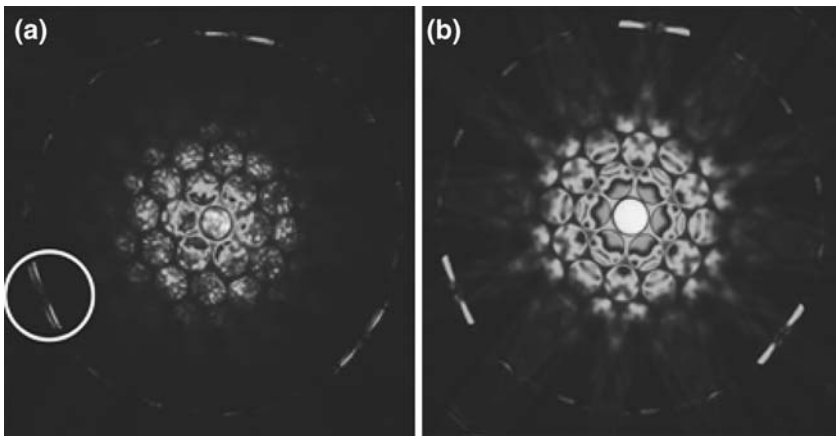

Fig. 2 CBED of the circled particle of Fig.1: (**a**) pattern taken in the central area. (**b**) pattern taken at the thin sample edge

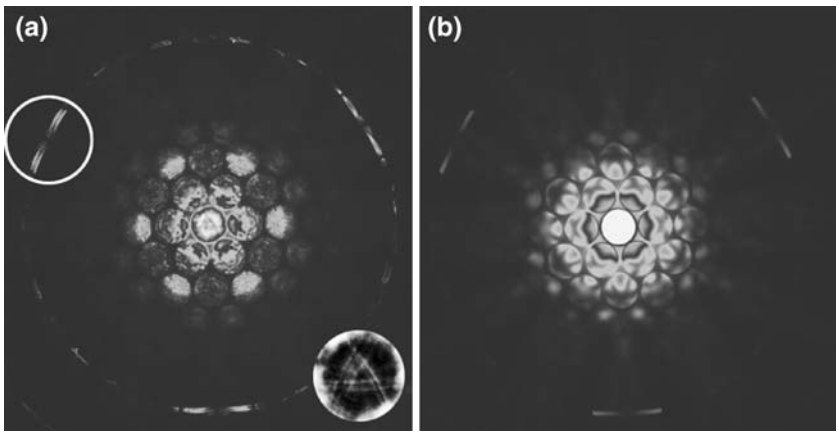

Fig. 3 CBED of the commercial hematite particle from Wako Pure Chemical Industries, Ltd.: (**a**) pattern taken in the central area. (**b**) pattern taken at the thin sample edge

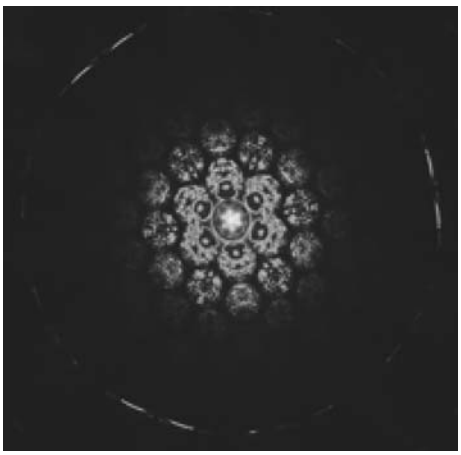

Fig. 4 CBED of the naturally grown hematite of Brazilian source. The pattern is taken at a comparable sample thickness as the central area of the above presented CBED images of synthetic production

synthetic hematite samples, bought and from own production, the presented images show distinct differences between the central part of the particle and the thin edge.

The CBED patterns clearly demonstrated that the projected symmetry through the thicker central part of the two synthetic hematite samples showed severe deviations from the ideal case. The doubling of the first order Laue zone reflections leads to the conclusion that the break of the symmetry is caused by slightly misaligned fractions of the particle relative to each other, either caused by tilted orientations or shifted lattices.

On a larger scale, the break down of the projected symmetry is also observed in the LACBED pattern. The comparison of Fig. 5b with Fig. 5a shows that the projected symmetry of the synthetic particle of own production matches the quality of the natural sample only in the area near the sample edge, which corresponds to the lower right of the image. The thicker areas, especially the central part, show only a blurred image of the expected sixfold symmetry of the intensity distribution. The quality of the pattern continuously decreases from the edge to the center, which gives a strong indication that the quality of the projected symmetry is a function of distance from the particle center.

The combination of these results leads to the conclusion that the synthetic hematite samples were composed out of

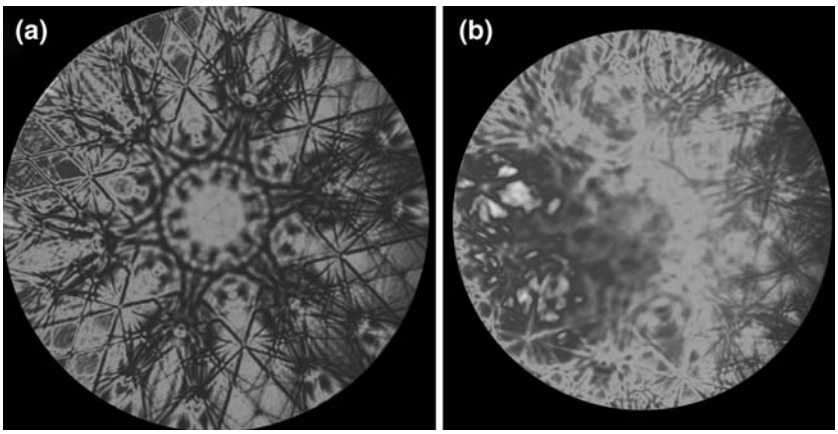

Fig. 5 LACBED patterns (**a**) of the natural Brazilian hematite and (**b**) the investigated particle of Fig. 1

smaller subunits which are slightly misaligned relative to each other. The incorporation of small subunits would lead to the break down of symmetry in the CBED pattern as well as to the blur of the LACBED patterns. The probability of being able to observe effects of the slightly mismatching lattices caused by such subunits within the hematite particles decreases with increasing distance from the particle core, as seen in the experiments. We therefore conclude, that the initial nucleation phase of hematite particles from forced hydrolysis happens very fast—the subunits do not have the time to order themselves perfectly. During the subsequent particle growth, the growth rate slows down and the subunits can order without detectable defects.

We have also varied parameters of the synthesis like aging time and temperature and pH-value. CBED patterns *always* were characterized by the break down of symmetry as seen for the demonstrated sample. This is not only a characteristic feature of hematite samples of own production, but also of commercially available hematite samples. Independent on the details of the synthesis which are also supposed to vary between our lab and Wako Pure Chemicals Industries, Ltd., synthetic hematite is characterized by the almost epitaxial arrangement of slightly misaligned subunits of 'primary' hematite particles. The naturally grown hematite of Brazilian source was the only investigated sample showing perfect crystallinity.

The presence of the subunits suggested by x-ray powder diffraction experiments is clearly demonstrated by our experiments. Also, the locality of the subunits is rather limited around the core of synthetic hematite crystalline particles. Thus, the imaging techniques, representing local symmetry investigations in the case of CBED and imaging of the symmetry on the scale of approximately 100 nm by using LACBED have proven to be appropriate tools for analyzing this kind of defect structure. A significant influence of the observed real structure on the magnetic properties of hematite is likely but not yet investigated.

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