

# Experimental charge density of hematite in its magnetic low temperature and high temperature phases

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Hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, is extensively studied by different communities of solid-state physicists. As a transition metal oxide, it is representative for the physics of correlated 3d-electron systems in which the role of multi-electron correlation effects dominate over the properties expected from bandstructure calculations. Furthermore, the magnetic properties of hematite attract interest of physicists. It orders magnetically below 950 K. At 250 K, a magnetic phase transition, called Morin transition, occurs. It is characterized by a transformation from a weak ferromagnetic high-temperature state to a collinear antiferromagnetic low-temperature one [1].

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is isotypic with corundum,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and crystallizes in the rhombohedral space group R-3c [2, 3]. Within the corundum crystal structure, the oxygen atoms arrange almost hexagonally closed packed. The iron atoms occupy two thirds of the octahedral interstices and have six oxygen neighbours in a slightly distorted octahedral environment. Three of them are located at the corners of a triangle above the iron atom, three of them at a corresponding position below the central iron atom, which is located on the threefold axis. The two triangles are not equidistant from the centre, defining two different Fe-O as well as two different O-O distances (**Figure 2**). Each oxygen atom is surrounded by four iron atoms, each two of them with the same Fe-O bond distance.

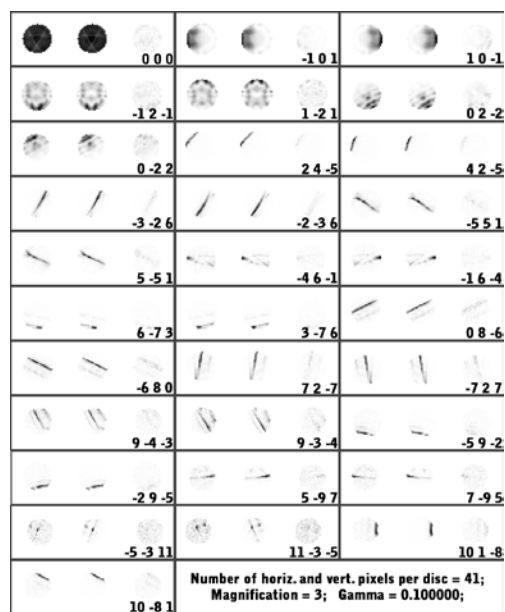
The structural parameters of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) including the valence electron distribution have been investigated using convergent beam electron diffraction (CBED) at room temperature in the canted antiferromagnetic phase and at 90 K in the collinear antiferromagnetic phase. The CBED experiments were conducted using a JEM-2010FEF transmission electron microscope equipped with a Schottky-type field-emission gun and an in-column  $\Omega$ -type energy filter which is used to remove inelastically scattered electrons [4]. Energy-filtered CBED patterns were taken with a high acceptance angle of about 10°, which corresponds to a lattice spacing of 0.21 Å, at a nominal accelerating voltage of 100 kV and an acceptance energy width of  $\pm 10$  eV. The CBED patterns were recorded from specimen areas of a few nanometers in diameter. They were recorded at the [111]<sub>rh</sub>, [110]<sub>rh</sub> and [11-2]<sub>rh</sub> zone-axis incidences, the subscript indicates that the rhombohedral setting is used, and for each incidence at 90 K and 293 K.

For the fitting of the structural parameters and the low-order structure factors, the reconstruction of the electrostatic potential and the electron density, the software-package mffit [4], which is based on dynamic diffraction theory, was used. Visualization of the deformation charge densities was done with the software VESTA, developed by Momma and Izumi [5]. In a first step, thickness, scale-factor and isotropic Debye-Waller factors were refined. In a second step, the three patterns of each temperature were combined, so that the refinement of the 90K data was based on 273 2-dimensional rocking curves and the refinement of the 273K data was based on 237 2-dimensional rocking curves. The anisotropic Debye-Waller factors were refined based on the data of the three incident directions. In a last step, the real and imaginary part of eleven low order structure factors and the real part of the 000-reflection were refined together with all other structural parameters. The main part of the evaluation of the CBED patterns was done on the Cray super computer of the University of Duisburg-Essen, Germany. Exemplarily, a set of 31 (out of 91) reflection discs obtained for the incident direction [111] at 90 K is given in **Figure 1**.

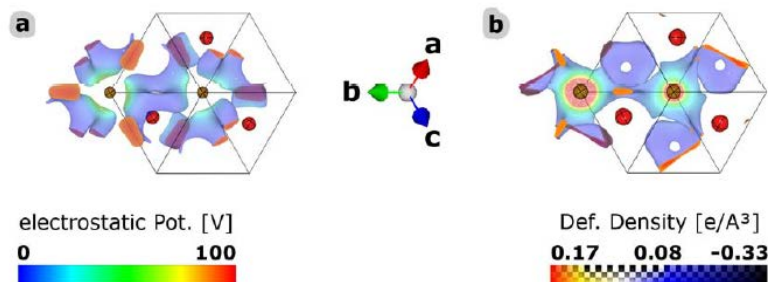
The refined charge density maps are interpreted as a direct result of electron-electron interaction in a correlated system. A negative deformation density is observed as a consequence of closed shell interaction, positive deformation densities are interpreted as a shift of electron density to antibinding molecular orbitals. Following this interpretation, the collinear antiferromagnetic phase shows the characteristic of a Mott-Hubbard type insulator whereas the high temperature canted antiferromagnetic phase shows the characteristic of a charge transfer insulator. The break of the threefold symmetry in the canted antiferromagnetic phase is shown to be correlated to the presence of oxygen-oxygen bonding, which is caused by a shift of spin polarized charge density from iron 3d-orbitals to the oxygen ions. We propose a triangular magnetic coupling in the oxygen planes causing a frustrated triangular spin arrangement with all spins lying in the oxygen planes. This frustrated arrangement polarizes the super-exchange between iron ions and causes the spins located at the iron ions to orient in the same plane, perpendicular to the threefold axis.

### References

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**Figure 1.** Set of 31 selected reflections discs, each labeled with its Miller indices, for the incident direction 111, measured at 90 K. The disc from left to right: measured intensity, calculated intensity, difference



**Figure 2.** Experimental deformation charge density maps along [111] direction observed at 90 K (a) and 293 K (b); the isosurfaces are colored with the values of the absolute electrostatic potential