

Structural fingerprinting of nanocrystals in the transmission electron microscope: the challenges of determining projected crystal symmetries

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ABSTRACT

Structural fingerprinting of sufficiently thin nanocrystals in the transmission electron microscope (TEM) utilizes information on the projected reciprocal lattice geometry, two-dimensional (2D) symmetry, and structure factors. A high resolution (phase contrast) transmission electron microscope image (HRTEM-I) and a precession electron diffraction spot pattern (PED-SP) from the same crystal in the same orientation do, however, possess different 2D symmetry groups although the underlying projected electrostatic potential is the same. In order to facilitate the correct usage of 2D symmetry group information for structural fingerprinting in the TEM, we will illustrate this effect, explain its causes, and determine 2D space groups (plane groups) by means of crystallographic image processing.

Keywords: transmission electron microscopy, structural fingerprinting

INTRODUCTION

Since nanocrystals cannot be fingerprinted structurally from laboratory-based powder X-ray diffraction patterns [1], novel TEM based structural fingerprinting strategies have recently been proposed [2]. These strategies utilize information on the projected reciprocal lattice geometry, 2D symmetry group, and structure factors. While HRTEM-Is allow for the extraction of both structure factor amplitudes and phase angles of nanocrystals that are less than 5 to 10 nm thin, PED-SPs allow for the extraction of structure factor amplitudes only. The nanocrystal thicknesses can then, however, be up to five times thicker. The point resolution of mid-voltage TEMs (without aberration correctors) limits the direct space resolution of the structure factors to about 0.24 to 0.17 nm, while one can extract structure factor amplitudes with a resolution of 0.1 to 0.05 nm from PED-SPs for many inorganic crystals.

As far as the projected reciprocal lattice geometry is concerned, its extraction from both sources of structural fingerprinting data is analogous and the respective initial structural fingerprinting step is facilitated by lattice fringe fingerprint plots in the kinematic and two-beam dynamic limits [2,3]. A HRTEM-I and PED-SP from the same crystal in the same orientation do, however, possess different 2D symmetry groups. This somewhat confusing fact is briefly explained in this paper in order to facilitate

the correct usage of 2D symmetry information for structural fingerprinting in the TEM.

HRTEM-Is from nanocrystals from a mixture of magnetite ($Fd\bar{3}m$) and cubic maghemite ($P4_132$) will be used to demonstrate the utility of 2D symmetry groups for structural fingerprinting. Note that the projected reciprocal lattice geometry is for magnetite and maghemite too similar to distinguish between these crystal structures [4], but we can securely make this distinction for a [001] projection on the basis of the plane groups as long as a sufficiently powerful TEM has been used for the recording of the experimental data. A PED-SP from a silicon crystal ($Fd\bar{3}m$) in the [110] orientation is used to illustrate the fact that its 2D symmetry group (i.e. $2mm$) differs from that of a HRTEM-I from a crystal with the same space group and orientation (i.e. $c2mm$).

GENERAL BACKGROUND

When a crystal is transmitted by a plane wave of fast electrons, the periodic (3D) electrostatic potential scatters electrons in directions that are defined by the intersection of the Ewald sphere with the reciprocal crystal lattice. Fast refers here to some 50 to 80 % of the speed of light, corresponding to acceleration potentials of some 100 to 300 kV, as available in mid-voltage TEMs. The Ewald sphere is rather flat for such electrons so that an ordinary parallel-illumination diffraction spot pattern and a digital diffractogram of an HRTEM-I can typically be considered as plane sections through the reciprocal lattice where all reflections obey Weiss' zone law for the zero order Laue zone.

Electron scattering in a crystal in the TEM can, thus, be considered as resulting in an orthogonal 2D projection of the electrostatic potential in the direction of the primary electron beam. The symmetry elements of the electrostatic potential form one of the 230 space groups. Their projections follow the rules outlined in refs. [5,6]. Reference [5] list for each of the space groups the projected plane groups for three major zone axes. For all projections, the plane groups can be calculated by a procedure outlined in ref. [7].

2D SYMMETRY OF DIFFRACTION SPOT PATTERNS

In the case of an electron diffraction spot pattern, a two-fold axis will be added to the plane group of the projected electrostatic potential [8] and the 2D symmetry of the diffraction spot pattern will be that of the

corresponding 2D point group. If the two-fold axis is already contained in the plane group of the projected electrostatic potential, the 2D symmetry of the diffraction spot pattern will be that of the point group that corresponds to the plane group of this potential.

The additional two-fold axis will be located at the origin of the reciprocal lattice. Electron diffraction spot patterns that show only reflections of the zero order Laue zone can, therefore, have only one of the 2D point groups: 2, 2mm, 4, 4mm, 6, or 6mm*. This effect of the added two-fold axis is known as Friedel's law as applied to a plane section in reciprocal space*.

PED-SPs that were recorded with large precession angles (i.e. of a few degrees) frequently show reflections from higher order Laue zones. Such reflections are not subject to the restriction of Friedel's law so that the 2D point groups 1, m, 3, 3m1, 31m are also possible for the 2D point symmetries of these reflections. In addition, large precession angles lead to a more effective integration of the reflection intensities so that small misorientations effects of the zone axis can be tolerated [7]. This enormously reduces the experimental effort to record data for structural fingerprinting of nanocrystals and makes structural fingerprinting from PED-SPs the method of choice for inorganic crystals that are up to a few tens of nanometer thick [9]. Fig. 1 shows a PED-SP (left) from a silicon crystal and compares it to an ordinary (parallel-illumination) selected area electron diffraction spot pattern (SAED-SP) from the same area and with the same crystal orientation.

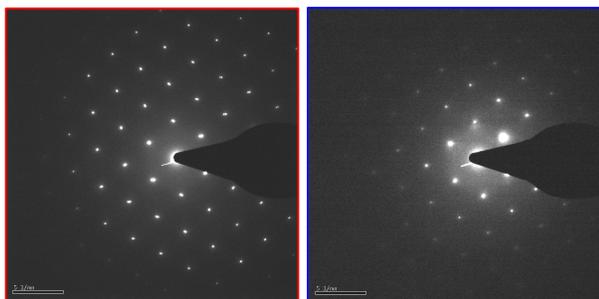


Fig. 1: PED-SP with 1.1° precession angle (left) and SAED-SP (right) from the same area of an approximately 60 nm thick silicon crystals, 200 kV, orientation close to [110]. While the 2D symmetry in the left spot pattern is 2mm, the right spot pattern has only the symmetry 2.

2D SYMMETRY OF HRTEM IMAGES

A HRTEM-I results from the interference of the transmitted beam with the diffracted beams. For sufficiently thin crystals, the symmetry of the projected electrostatic potential is then directly transferred to the HRTEM-I. All 17 plane groups (i.e. including p1) are therefore possible for the plane symmetry of a HRTEM-I from a crystal that is not centrosymmetric. For centrosymmetric crystals, all HRTEM-I will possess at least the symmetry of plane group p2, i.e. there are 16

possible plane groups left that will match the plane groups of the projected electrostatic potential directly. (This is again a consequence of Friedel's law as applied to a plane section in reciprocal space.)

Crystallographic image processing (CIP) with the programs CRISP (for IBM compatible Personal Computers) [10,11] or ALLSPACE (for Unix and Linux machines) [12,13] facilitate the determination of the plane group from HRTEM-Is. When the image features an area from an amorphous carbon support film, CIP can remove of the contrast transfer function (CTF) of the TEM and correct for two-fold astigmatism in the HRTEM-I. This removal is, however, not strictly necessary to determine the correct plane symmetry group of the HRTEM-I when the two-fold astigmatism is negligible and when the image was recorded close to the Scherzer (de)focus (in an non-aberration corrected TEM). Figures 2 and 3 show HRTEM-Is from iron-oxide nanocrystals from the above mentioned mixture of magnetite and maghemite.

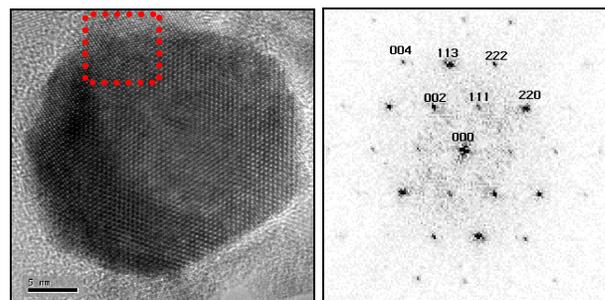


Fig. 2: HRTEM-I (left) and the amplitude part of its (contrast inverted) Fourier transform (right), also known as digital diffractogram, of an iron-oxide nanocrystal, 200 kV, [110] orientation. The digital diffractogram was calculated for some of the thinnest area of this nanocrystal (that is marked in the image). While the plane group of the image area (left) is c2mm, the 2D point group of its optical diffractogram (right) is 2mm. The 2D point group of the “full” Fourier transform of the image area (i.e. with the inclusion of the phase angle part) is also 2mm, while its plane group is c2mm.

Note that the (112) reflection is absent in the digital diffractogram of Fig. 2. This absence indicates that the nanocrystal is magnetite. Note also that this digital diffractogram extends out to at least 0.139 nm direct space resolution, i.e. very close to the information limit of the FEI Tecnai G² F20 ST which with the HRTEM-I in Fig. 2 (left) was recorded. Using CRISP, the amplitude residual of this image in plane group c2mm was determined as 18.2% and the phase residual as 21.4°. Its subgroup cm has the same amplitude residual of 18.2% for both possible orientations of the mirror line, but phase residuals of 10.4° for m_y and 15.4° for m_x.

Maghemite would have for the [110] orientation the plane group p2gm. CRISP gave for the HRTEM-I in Fig. 2 (left) for plane group p2gm reasonably small amplitude

(18.5%) and phase (21.5°) residuals as well. This plane group has, however, only half as many symmetry elements as plane group $c2mm$, i.e. its symmetry elements are much less adhered to in the experimental data. The analysis of the plane groups of this image, thus, also supports also the conclusion that the nanocrystal is magnetite.

Note that the 2D reflection (20) is “effectively invisible” in the amplitude part of the Fourier transform of the HRTEM-I of another iron-oxide nanocrystal in a different orientation, Fig. 3 (right). This reflection has, however, been “picked up” and quantified by CRISP, despite the fact that its amplitude is only about 6.6% of that of the reflection (10), see “HK Edit” table in Fig. 4.

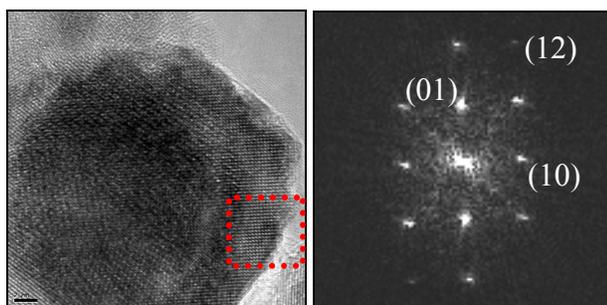


Fig. 3: HRTEM-I (left) and the amplitude part of its Fourier transform (right) of an iron-oxide nanocrystal, 200 kV, [001] orientation. The digital diffractogram was calculated for some of the thinnest area of this nanocrystal (that is marked in the image).

CRISP also picked up and quantified three of the $\{12\}$ reflections, see “HK Edit” table in Fig. 4 (despite the fact that the (21) reflection has less than 1% of the intensity of the (01) reflection.) The presence and quantification of the $\{12\}$ and $\{20\}$ reflections allow for the testing of systematic absences due to projected cell centerings and glide lines. The results of these tests are given as the so called “Ao/Ae” ratios** in the table of the “Origin refinement of ...” window in Fig. 4. From this table, one has to exclude the plane group $p4gm$ is not being born out by the experimental data as the “Ao/Ae” ratio for this group is 3. Since this would be the plane group that a maghemite nanocrystal would possess in the [001] orientation, we can safely conclude that the nanocrystal in Fig. 3 is magnetite.

Although the identification of the nanocrystal is quite unambiguous, it is worthwhile to analyze the data in Fig. 4 in more detail. CRISP determined for the HRTEM-I of Fig. 3 (left) for plane group $p4mm$ the amplitude residual 55.8 % and the phase residual 22.0°. The respective residuals are 55.4% and 22.0° for plane group $p4$. This means that the mirror lines and glide lines which constitute the difference between these two plane groups are well obeyed by the experimental data. The relatively high amplitude residuals for these two plane groups are, thus, largely due to violations of the requirements for the

existence of four-fold rotation axes in the experimental data.

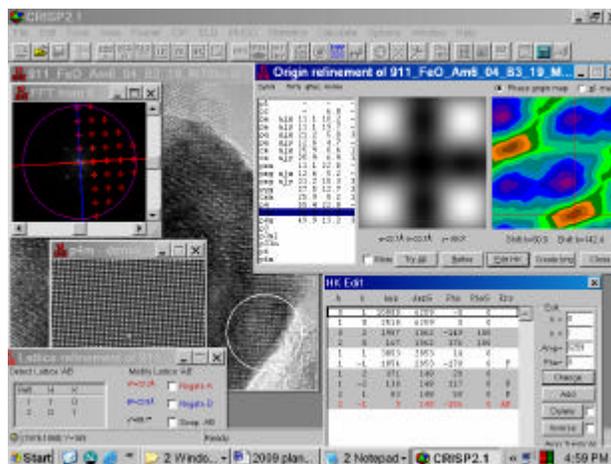


Fig. 4: CRISP on some of the thinnest area of the iron-oxide nanocrystal of Fig. 3 (left), using the default settings of this CIP program.

This conclusion agrees well with the approximately 1.3% difference in the length of the projected unit cell vectors and the 0.3° deviation from the orthogonality condition between these two vectors in the experimental data; see the respective numbers in the “Lattice refinement of ...” window in Fig. 4. Residual two-fold astigmatism in the HRTEM-I of Fig. 3 may be the cause of these observed deviations from “tetragonality”.

The peculiar shapes of the amplitudes of the Fourier coefficients in Fig. 3 (right) are possibly due to structural defects in the selected nanocrystal area. Note, however, that these shapes did not impede the plane symmetry determination with CRISP and the identification of the respective nanocrystal as magnetite.

INFLUENCE OF INSUFFICIENT SPATIAL RESOLUTION OF AN HRTEM IMAGE ON THE DETERMINATION OF ITS PLANE GROUP

The effect of limited spatial resolution in the experimental data might be demonstrated simply by setting the Fourier transform amplitude threshold value in CRISP to a value that is 20 times higher than its default setting, Fig. 5, and re-analyzing the marked area of the nanocrystal in Fig. 3 (left). This should “simulate” in a first approximation the effect of using a less powerful TEM for the recording of “similar experimental data”.

If it were not known that this nanocrystal has to be either magnetite or maghemite, the “novice structural fingerprinter” may perhaps conclude from Fig. 5 that the plane group of the nanocrystal is cm as its phase residual is zero with an amplitude residual of 40.1%. At least the mirror line of its subgroup pm would be well adhered to in the experimental data since CRISP calculated a phase residual of 6.3° and an amplitude residual of 13.7% for

that subgroup of *cm*. Since neither of these two groups possesses a two-fold axis, the nanocrystal would need to belong to a non-centrosymmetric space group. The relatively low (i.e. 10.1°) phase residual of group *p2* would, on the other hand, contradict this conclusion.

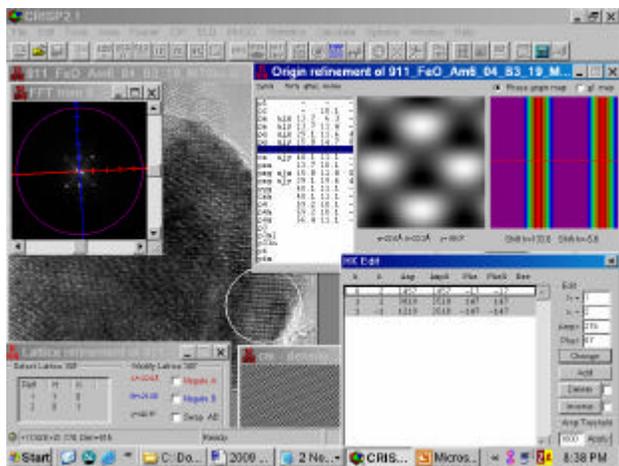


Fig. 5: CRISP on some of the thinnest area of the iron-oxide nanocrystal of Fig. 3 (left), using an unusually high value for the Fourier transform amplitude threshold of this CIP program. This might be considered as roughly equivalent to using a less powerful TEM for the recording of similar experimental data.

The “experienced structural fingerprinter” shall, however, conclude from the odd combination of zero phase residual (which results from just a single pair of reflections that happens to have phase angles that differ by just a minus sign) and high amplitude residual for plane group *cm*, that a more powerful TEM needs to be employed. Note that *cm* is indeed a subgroup of the plane group of the [110] projected electrostatic potential of magnetite, i.e. (*c2mm*). It is not, on the other hand, a subgroup of the [110] projected potential of maghemite, i.e. (*p2gm*), so the CIP procedure did not fail to detect the lower symmetry correctly.

SUMMARY

Two-dimensional symmetries of TEM data have been discussed with respect to structural fingerprinting. Some of intricacies of determining plane groups from high resolution TEM images have been demonstrated.

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* Note that all of these point groups contain the point group 2 as subgroup, which corresponds to an orthogonal projection of a center of 3D symmetry onto a plane. Note also that the point symmetry of electron diffraction spot patterns is higher than that of most X-ray diffraction spot patterns [8], the exception being precession X-ray (Buerger) diffraction patterns. While Friedel’s law is strictly true only for genuine kinematic diffraction conditions, it is reasonably satisfied for sufficiently thin nanocrystals.

** The *Ao/Ae* ratio is defined as the amplitude sum of the reflections that are forbidden by a plane symmetry group but were nevertheless observed (*Ao*) divided by the amplitude sum of the observed reflections (*Ae*) allowed by that plane symmetry. A quantifying number of this ratio means that forbidden Fourier transform amplitudes (that should be zero due to a lattice centering or glide lines) are actually present in the experimental data. When the ratio is high, one has to conclude that the respective plane group does not comply with the experimental data.