

Crystal lattice parameters from direct-space images at two tilts

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Abstract

Lattices in 3D are oft studied by diffraction and hence a “reciprocal-space” perspective. Today, however, location as well as diffraction data can be incorporated into direct space images. From such images a superset (often the full) lattice of a crystal can be inferred from spacing/orientation data on three sets of non-parallel lattice planes. Such data may be obtained from electron-phase or Z contrast images taken at two tilts, provided that one image shows two non-parallel lattice periodicities, and the other shows a periodicity not coplanar with the first two. We show here how to find, and implement, protocols for measuring the 3D parameters of any lattice type in this way. In the case of crystals with cell side greater than twice the continuous transfer limit, we show that orthogonal $\pm 15^\circ$ and $\pm 10^\circ$ tilt ranges may allow one to measure 3D parameters of all cubic nanocrystal varieties in a specimen from only two well-chosen images. The strategy is illustrated by measuring the lattice parameters of a 10 nm WC_{1-x} crystal in a plasma-enhanced chemical-vapor deposited thin film.

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I. INTRODUCTION

Since the discoveries of X-ray ray and electron diffraction in the early part of this century, the study of lattices in three dimensions has focussed on 3D relationships between reciprocal lattice vectors, as determined by diffraction. Even though most three-dimensional lattice determinations are done with X-rays, various techniques in electron microscopy have been developed to infer the 3D relationships between reciprocal lattice vectors from 2D diffraction patterns taken at different specimen orientations (in part because these relationships have on-line uses which go beyond simple lattice determination). Such electron techniques include determination of crystal orientation,^{1,2} , grain boundary parameters,³ crystallographic basis triplet,⁴ specimen orientation adjustment,⁵ indexing diffraction patterns,⁶ and phase identification.⁷ These techniques are relevant here because, in the past several decades, it has become possible to incorporate lattice information directly into images of a lattice as projected through a specimen onto a two dimensional screen. In effect, diffraction (periodicity amplitude) and location (periodicity phase) can be recorded simultaneously. As resolutions for doing this below 0.2 nm in electron microscopes become more widespread, along with the capability of microscopes to examine the same crystal from more than one direction, prospects for three-dimensional lattice determination from direct space images, even of the most compact elemental solids with arbitrarily small crystallite size, could become routine.

The basic approach of electron diffraction techniques for converting information from 2D patterns into 3D models consists of 3 parts: locating evidence for specimen periodicities lying in more than one plane, inferring the relative positions of those periodicities in the three-dimensional reciprocal space of the specimen, and lastly inferring from those observations models of specimen crystallography.⁸ When the crystal is only nano-meters in size, the broad probes of conventional SAED may not be able to extract lattice information specific to individual crystals. Recent developments in field emission gun (FEG) transmission electron microscopy (TEM) make it possible to achieve nano-diffraction^{9,10}. Characteristic of most diffraction methods, of course, this does not record information on periodicity and probe

position (i.e. source volume position or Fourier phase) at the same time. This problem is exacerbated by the high current dose accompanying high-intensity spatially-confined electron probes.

Applications thus exist for analytical microscopy techniques able to acquire vector lattice periodicity and lattice location information at once, if possible with less radiation damage and wider accessibility than the diffraction techniques mentioned above. Inferring the 3D lattice of a crystal from HREM or Z-contrast images is a possibility, since one may in favorable cases record 3D data on hundreds of crystals at the microscope resolution limit, with only a few one-second exposures at 240,000x.

Due to the transmitted nature of the electron beam, a TEM image presents 3D information averaged throughout the thickness of the specimen on each micrograph. Much pioneering work has been done to acquire 3D information on non-periodic structures, like crystal defects and biomolecules, from TEM images. It includes stereomicroscopy (e.g. to characterize irregular dislocation networks),¹¹⁻¹³ 3D reconstruction of non-periodic macromolecular assemblies in biology,¹⁴ among which are the reconstruction of tobacco mosaic virus,¹⁵ purple membrane,¹⁶ hemoglobin molecule,^{17,18}, protein,¹⁹ nucleosomes,^{20,21} and various other viruses.²² Prospects for 3D HREM of non-periodic structures have been discussed.²⁴ Three-dimensional reconstruction of periodic structures has also been described.^{25,26}, as have finding the 3D lattice parameters of nano-crystals from HREM images taken at different specimen orientations.²⁷

Here we discuss the geometry of crystals from the perspective of lattice imaging in direct space, with limited tilt and spatial resolution. The required instrumentation consists of a TEM able to deliver phase or Z contrast lattice images of desired periodicities (e.g. spacings down to half the unit cell side for cubic crystals), and a specimen stage with adequate tilt (e.g. two-axes with a combined tilt range of $\pm 18^\circ$). For crystals with lattice spacings of 0.25nm and larger, many analytical TEM's will work, while a HREM with continuous contrast transfer to spatial frequencies beyond $1/(0.2\text{nm})$ can do this for most crystals. We exemplify with lattice parameter measurement of a small-cell nano-crystal using a Philips

EM430ST TEM. Appropriately orienting the crystal, so as to reveal its three-dimensional structure in images, is a key part of the experimental design and will be discussed in detail. In the process, strategies for supporting on-line electron-crystallography, for three-dimensional lattice-correlation darkfield studies of nanocrystalline and paracrystalline materials, and for stereo-diffraction analyses, are suggested as well.

II. CALCULATIONS

A. Overview of “tilt protocols”

In the stereo lattice imaging strategy discussed here, low Miller index (hence large) spacings are both easier to see, and more diagnostic of the lattice. Targeted orientation changes can speed up the search for such spacings. Tilt protocols optimized for getting 3D data from one abundant class of lattice types (namely cubic crystals) are surveyed in this section. A list of possible lattices, for example based on diffraction or compositional information, may thus be of help in getting 3D information, especially when only the largest spacings in the crystal are visible. When many crystals are visible in each image, as we show near the paper’s end, studies of cross-fringe abundance, and 3D darkfield studies, may further limit the range of possible lattices present.

In general 3 non-coplanar reciprocal lattice vectors seen along 2 different zone axes are sufficient for inferring a subset of the 3D reciprocal lattice of a single crystal. Often these are adequate to infer the whole lattice. The goal of the experimental design is thus to look for 3 lattice spatial frequencies, within the first transfer-function pass-band, orthogonal to 2 beam directions whose angular separation is within the tilt limit of a TEM. Images with “aberration limits” r_a smaller than the analyzed spacings are specified, to lessen chances of missing other comparable (or larger) spacings in the exit-surface wavefield. In tilting from one zone to another, the crystal must be oriented so that the plane which includes both zones is perpendicular to the tilt axis (or effective tilt axis in the double tilt case used here).

To illustrate, we exploit the fact (considered more fully below) that *all* cubic crystals will provide data on their three dimensional lattice parameters if imaged down [001] and then again near to a [112] zone, provided that spacings at least as large as half the cell side a are reported in the images. Our rule of thumb for meeting this requirement is that the (damping and) aberration limit r_a of the microscope *in the images of interest* obey $a > 2r_a$. With the images discussed here we thus expect to “cast a net” for 3D data on any cubic crystals whose cell side a is larger than $2 \times 0.19nm = 0.38nm$. More than 85% of the cubic close packed crystals and nearly 40% of the elemental b.c.c. crystals tabulated in Wyckoff,²⁸ for example, meet this requirement, as of course would most cubic crystals with asymmetric units comprised of more than one atom.

The angle between [001] and [112] is 35.3° .³⁴ Although this is too far for the eucentric tilt axis in our microscope, combining two tilts gives us a range of 35.6° . Two images can therefore be taken at orientations 35.3° apart, namely at $(\vartheta_1 = 15.0^\circ, \vartheta_2 = 9.7^\circ)$ and $(\vartheta_1 = -15.0^\circ, \vartheta_2 = -9.7^\circ)$, respectively, where ϑ_1 and ϑ_2 are goniometer readings on our double tilt holder. This yields an “effective” tilt axis, which runs perpendicular to the electron beam and hence parallel to the micrographs in this case. Its azimuth is 123.5° in the xy plane of our images. The coordinate system used will be discussed in more detail later. Since the $(2\bar{2}0)$ lattice planes are parallel to both desired zones, the tilt must be along these planes. That is, the $(2\bar{2}0)$ spot must be roughly parallel to that of the effective tilt axis. In an image field of a hundred crystals, this is not unlikely to occur. The results were unambiguous. We found many four-fold symmetric images with spacings consistent with WC_{1-x} . This has an f.c.c. lattice with $a = 0.4248nm$.^{29–31} When such a zone was found with fringes 45° to the effective tilt in the first image, a new spacing was seen in the second image, making a 3D lattice parameter measurement possible. The experimental result is illustrated in Figure 1.

B. Experimental designs

Recall that we seek three non-coplanar periodicities, from two images. Given Miller indices $(h_1k_1l_1)$ and $(h_2k_2l_2)$ for any two periodicities (i.e. vectors \mathbf{g}_1 and \mathbf{g}_2 , respectively, in the reciprocal lattice) of any crystal, first find zone indices $[u_Av_Aw_A]$ of the beam direction $\mathbf{r}_A \equiv \mathbf{g}_1 \times \mathbf{g}_2$ needed to view both spacings in one image. The axis for the smallest tilt that will make the beam orthogonal to a third periodicity with indices $(h_3k_3l_3)$, and reciprocal lattice vector \mathbf{g}_3 , may then be defined by the vector $\mathbf{v}_t \equiv \mathbf{g}_3 \times \mathbf{r}_A$. Lastly, zone indices $[u_Bv_Bw_B]$ for the beam after the specimen has been tilted around this axis so as to image the third periodicity, may be obtained from the expression $\mathbf{r}_B \equiv \mathbf{v}_t \times \mathbf{g}_3$. Note here that we treat the Bragg angle for electrons as small (i.e. less than one degree). Thus the actual tilt required will be a fraction of a degree less.

Although these cross product calculations can be done by first converting for example to “c-axis” cartesian coordinates⁴, perhaps the simplest determination of needed parameters may be done using the metric matrix G of a prospective lattice:³²

$$G \equiv \begin{bmatrix} \mathbf{a} \bullet \mathbf{a} & \mathbf{a} \bullet \mathbf{b} & \mathbf{a} \bullet \mathbf{c} \\ \mathbf{b} \bullet \mathbf{a} & \mathbf{b} \bullet \mathbf{b} & \mathbf{b} \bullet \mathbf{c} \\ \mathbf{c} \bullet \mathbf{a} & \mathbf{c} \bullet \mathbf{b} & \mathbf{c} \bullet \mathbf{c} \end{bmatrix} = \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix}. \quad (1)$$

If we denote row vectors formed from Miller (or lattice) indices as $\langle ijk \rangle$, and column vectors as $|ijk \rangle$, then the zone A indices obey $\mathbf{g}_1 \bullet \mathbf{r}_A = \langle h_1k_1l_1 | u_Av_Aw_A \rangle = 0$ and $\mathbf{g}_2 \bullet \mathbf{r}_A = \langle h_2k_2l_2 | u_Av_Aw_A \rangle = 0$. From these two equations, $[u_Av_Aw_A]$ follows simply except for a multiplicative constant which is not important. Similarly, the (possibly irrational) Miller indices of the tilt axis (h_t, k_t, l_t) may be determined from $\mathbf{g}_t \bullet \mathbf{r}_A = \langle h_tk_tl_t | u_Av_Aw_A \rangle = 0$ and $\mathbf{v}_t \bullet \mathbf{g}_3 = 0 = \langle h_tk_tl_t | G^{-1} | h_3k_3l_3 \rangle$.³³ Only in this fourth equality does G affect the calculation, and for cubic crystals it then simply offers a multiplying constant. Finally, the zone B indices follow (to within a factor) simply from $\mathbf{g}_t \bullet \mathbf{r}_B = \langle h_tk_tl_t | u_Bv_Bw_B \rangle = 0$ and $\mathbf{g}_3 \bullet \mathbf{r}_B = \langle h_3k_3l_3 | u_Bv_Bw_B \rangle = 0$.

Two parameters which determine the attractiveness and feasibility of a given experiment

are the spatial resolution, and range of specimen tilts, that the microscope must be able to provide. For a candidate lattice type, it is thus useful to go through the list of all pairs of periodicities, to calculate the tilt between the zone associated with that pair and any third spacing of possible interest, and then to rank the findings according to the minimum-spacing that must be resolved, and range-of-tilt that the specimen undergoes. This has been done for face-centered, body-centered, and simple-cubic lattices, and the results illustrated in Figure 2, with examples for fcc and bcc spacings no less than half of the cell side illustrated in Figure 3. Note that this calculation needs to be done only once for each unit cell shape. Factors like the multiplicity of a given zone type might also figure into the design of experiments with randomly-oriented crystals, although we have not considered them here.

High tilts can be used to lower measured spacing uncertainties, in directions perpendicular to the electron microscope specimen plane.²⁷ Hence the protocols of interest for a given experiment may be those which approach goniometer tilt limits, or at least the limits of specimen tiltability.

Concerning the resolution limit to use, we suggest the spacing associated with the end of the first transfer function passband *in the micrograph of interest*, sometimes inferrable from regions in the image showing disordered material. Even in this case, possible thickness and misorientation effects warrant caution.^{39,42}

One may of course explore spatial frequencies in the specimen up to the microscope information limit. However, this introduces the possibility of missing spatial frequencies present in the subspecimen electron wavefield. In this case HREM images taken at different focus settings might work, if the foci are chosen so that the spatial frequencies lost at one defocus are likely to be recorded at another. This would allow measurement of three non-coplanar reciprocal lattice vectors, without missing any whose (reciprocal) length is shorter than the longest among those three.

Lastly, of course, the protocol chosen may depend also on the specimen. For an image field containing hundreds of non-overlapping but randomly-oriented nano-crystals, only two micrographs could allow one to measure the three-dimensional lattice parameters of all cubic

crystal types present with cell sides a greater than $2r_a$. On the other hand, for a single crystal specimen of unknown structure, both a great deal of tilt range, and considerable trial and error tilting (or guess work based on lattice models), might be required before a single set of three indexable non-coplanar spacings is found.

C. Inferring 3D reciprocal lattice vectors from micrographs

Consider a specimen stage with two orthogonal tilt axes, ϑ_1 and ϑ_2 , both perpendicular to the electron beam (the second only so when the first axis is set at zero tilt). When the specimen is untilted ($\vartheta_1 = 0^\circ$, $\vartheta_2 = 0^\circ$), vectors in the reciprocal lattice of the specimen may be described, in coordinates referenced to the microscope, as a column vector $|\mathbf{g}\rangle$. When this reciprocal lattice vector is tilted to intersect the Ewald sphere by some double tilt in the sequence $T_2(\vartheta_2)$ then $T_1(\vartheta_1)$, it's presence may be inferred from diffraction patterns or micrograph power spectra. In our fixed coordinate system, $|g\rangle$ has become $|g_m\rangle$, where the m means that $|g_m\rangle$ is associated with the lattice periodicity $d_m = 1/g_m$ recorded on a micrograph. Using matrix notation, we might then write:

$$|\mathbf{g}_m\rangle = T_1(\vartheta_1)T_2(\vartheta_2)|\mathbf{g}\rangle \quad (2)$$

Of course components of g_m may be determined from the polar coordinates (g, φ) of a spot in the power spectrum of a recorded image, following:

$$|\mathbf{g}_m\rangle \equiv \begin{pmatrix} g_{mx} \\ g_{my} \\ g_{mz} \end{pmatrix} = \begin{pmatrix} g \cos(\varphi) \\ g \sin(\varphi) \\ 0 \end{pmatrix} \quad (3)$$

where g is the length of the diffraction vector (e.g. in reciprocal nm) and φ is its azimuth corrected for lens rotation.

Hence we can calculate the ‘‘untilted-coordinates’’ $|g\rangle$, of reciprocal lattice objects at $|g_m\rangle$ inferred experimentally from micrographs, using

$$|g\rangle = T_2^{-1}(\vartheta_2)T_1^{-1}(\vartheta_1)|\mathbf{g}_m\rangle = A(\vartheta_1, \vartheta_2)|\mathbf{g}_m\rangle, \quad (4)$$

where we've defined:

$$A(\vartheta_1, \vartheta_2) \equiv T_2^{-1}(\vartheta_2)T_1^{-1}(\vartheta_1) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(\vartheta_2) & \sin(\vartheta_2) \\ 0 & -\sin(\vartheta_2) & \cos(\vartheta_2) \end{bmatrix} \begin{bmatrix} \cos(\vartheta_1) & 0 & \sin(\vartheta_1) \\ 0 & 1 & 0 \\ -\sin(\vartheta_1) & 0 & \cos(\vartheta_1) \end{bmatrix}. \quad (5)$$

The resulting xyz coordinates of reciprocal lattice features g , associated with the crystal at an untilted specimen orientation but referenceable from micrographs taken at any orientation, provide the language we use for speaking of our measurements in three dimensions.

D. Calculating lattice parameters

Given 3D cartesian coordinates of “points” in the reciprocal lattice of a crystal, we are in much the same situation as if we had diffraction patterns of the crystal from two directions containing three (or more) non-coplanar spots. Hence methods for stereo-analysis of diffraction data^{4,7} can be used at this point. We recap briefly here. Given measured reciprocal lattice vector coordinates, the next step is to infer a basis triplet for the crystal’s reciprocal lattice. Three alternate paths to this basis triplet might be referred to as “matching”, “building”,⁷ and “presumed”.⁴

a. Lattice matching: To “match”, one simply tests observed spacings and interspot angles against those possible for a list of known candidate structures. This process in three dimensions is much more discriminating than when working with two dimensional data (e.g. from a single diffraction pattern), even if the angle and spacing uncertainties are a bit larger. The test can be done with adjustable tolerances on one’s spacing and angle measurements, it is able to rule out candidates unambiguously, and it automatically indexes spots with respect to the conventional basis triplet for the candidate structure of interest. Once the spots are indexed with respect to the conventional structure, a purely experimental basis triplet then follows by simply using coordinates of the indexed spots to calculate coordinates for a^* , b^* and c^* .

b. Lattice building: To “build”, one assumes that integral linear combinations of the observed reciprocal lattice points “span” the full reciprocal lattice of the crystal. Although this assumption is strengthened if more than three “observed spots” have been measured, it works quite frequently when only three are in hand as well. For example, in the case of an fcc lattice, three observed spots with “all even” or “all odd” Miller indices span only a subset of the full lattice, but this is less likely than finding a triplet which spans the full lattice. For our imaging work, this question can be addressed explicitly when choosing a tilt protocol up front, since we know in advance what tilts the protocols will provide access to.

Assuming that the spots span the reciprocal lattice, a primitive reciprocal basis triplet or set of three vectors defined as a^* , b^* and c^* , may be selected from a list of integral linear combinations of the reciprocal vectors. This basis triplet should be chosen so as to define a unit cell of minimum volume. In this work, we have only selected primitive cells via the “build method”. Delauney reduction can also be used to infer the “conventional” unit cell.³⁸ Of course, in this latter case there will remain some ambiguity in the choice, when measurement errors are large and evidence concerning symmetries is weak.

c. Lattice presumed: If you already have ideas how to index the observed spacings, an approximate oriented basis triplet can be calculated from only two indexed directions (e.g. from two diffraction spots or a spot and a recognized zone axis).⁴ This strategy may be especially useful when only one crystal is available in the field of view. One then tilts until the zone of a possible candidate lattice can be tentatively recognized, and then measures the angles needed to estimate an oriented triplet. From this (as discussed below) goniometer settings for a 2nd imaging orientation may be inferred. Once three or more non-coplanar spacings are in hand, of course, then either “match” or “build” may be used for a full three-dimensional measurement.

Regardless of the path to a basis, if more than three spots have been measured, a least-squares optimized triplet may then be calculated analytically from the proposed spot indices, in place of the 3-spot basis used here.⁷ This will provide better accuracy, and also a measure of spot coordinate reproducibility in the form of standard deviations in x , y and z .

d. Applying an oriented triplet Given an experimental basis triplet from any of these sources, lattice parameters $(a, b, c, \alpha, \beta, \gamma)$, goniometer settings for other zones, and many other things follow simply from the oriented triplet matrix defined below:

$$\mathbf{W} \equiv \begin{bmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{bmatrix} = \begin{bmatrix} a_x^* & b_x^* & c_x^* \\ a_y^* & b_y^* & c_y^* \\ a_z^* & b_z^* & c_z^* \end{bmatrix}^{-1} \quad (6)$$

Given W , for example, Cartesian coordinates *in the microscope* for any direct lattice vector with indices $[uvw]$ follow from $|r\rangle = W|uvw\rangle$, while cartesian coordinates for the reciprocal lattice vector with indices (hkl) may be predicted from $\langle g| = \langle hkl|W^{-1}$. These rules of course include instructions for calculating basis vectors of the lattice, such as $\mathbf{a} \equiv [100]$, and reciprocal lattice, such as $\mathbf{b}^* \equiv (010)$, and the angles between. Moreover, the oriented cartesian triplet W is simply related to the metric matrix for the lattice in equation 1 by $G = WW^T$. From G , of course, all the familiar orientation-independent properties of the lattice follow, including cell volume $V_{cell} = \sqrt{|G|}$, Miller/lattice vector dot products $\langle g_{hkl}|r_{uvw}\rangle = \langle hkl|uvw\rangle$, reciprocal lattice vector and interplanar spacing magnitudes $g_{hkl}^2 = 1/d_{hkl}^2 = \langle hkl|G^{-1}|hkl\rangle$, lattice vector magnitudes $r_{uvw}^2 = \langle uvw|G|uvw\rangle$, reciprocal lattice dot products $\langle g_1|g_2\rangle = \langle h_1k_1l_1|G^{-1}|h_2k_2l_2\rangle$, interspot angles $\theta_{12} = \cos^{-1}[\langle g_1|g_2\rangle/(g_1g_2)]$, etc.³³

E. Indexing new directions and structures

Before a basis triplet is selected, indexing of observed reciprocal lattice vectors g can be attempted by matching spacings and interspot angles to candidate lattices. Because of the uniqueness of non-coplanar triplets in three dimensions, as a significant subset (at least) of the whole reciprocal lattice, the matches are very discriminating even for low-symmetry lattices. After a basis triplet is selected, the indices (hkl) of any observed spot $\langle g|$ in a diffraction pattern follows from $\langle hkl| = \langle g|W$. Similarly, indices $[uvw]$ of any observed lattice displacement $|r\rangle$ in an image follow from $|uvw\rangle = W^{-1}|r\rangle$, once a basis triplet is in

hand. One can similarly calculate the goniometer settings required to align the beam with any other crystallographic zone of interest as well!

III. THE EXPERIMENTAL SETUP

A. Instruments

The Philips EM430ST TEM used is housed in a building designed for low vibration, and provides continuous contrast transfer to $1/(0.19nm)$ at Scherzer defocus. It is equipped with a $\pm 15^\circ$ side-entry goniometer specimen stage. A Gatan double tilt holder enables $\pm 10^\circ$ tilt around an orthogonal tilt axis. The largest orientation difference which can be achieved using this double tilt holder in the microscope is therefore 35.6° .³⁴

B. Determining the angle of effective tilt projected onto an image

In order to establish the spatial relationship between reciprocal lattice vectors inferred from images taken at different specimen tilts, the direction of the tilt axis relative to those images must be known. The tilt axis direction is defined via the right hand rule, as orthogonal to the relative motion of parts of the specimen as the goniometer reading is increased. In a single tilt, the axis is perpendicular to the electron beam and parallel to the micrographs. This is true also of the effective tilt axis in a double tilt, provided the two specimen orientations are symmetric about the zero tilt position. We limit our discussion of double tilts to this case.

We determined the projection of both tilt axes of a Gatan double tilt holder onto 700K HREM images using Kikuchi line shifts during tilt in the 1200mm diffraction pattern of single crystal silicon, and then correcting for the rotation between that diffraction pattern and the image.⁴³ To be specific, with a micrograph placed in front of the operator with emulsion side up as in the microscope, with zero azimuth defined as a vector from left to right, and with counterclockwise defined as the direction of increasing azimuth, the projection of

T_1 on 1200mm camera-length diffraction patterns in our microscope is along 114.0° . The rotation angle between electron diffraction patterns at the camera length of 1200mm and 700K HREM images is 42.9° . Therefore the direction of the projection of T_1 on 700K HREM images is along -156.9° . The direction of the projection of the second tilt axis, T_2 , on 700K HREM images is along 113.1° .

C. A reference coordinate system

We then consider a coordinate system fixed to the microscope, for measuring reciprocal lattice vectors from the power spectra of 700K HREM images. The y and z directions are defined to be along $-T_1$ and the electron beam direction, respectively, as shown in Figure 4. The projection of these tilts on the power spectrum of a 700K HREM image is shown in the 2nd inset of Figure 1. Azimuths in the remainder of this paper are all measured in the xy plane of this coordinate system, with the x or T_2 direction set to zero. Because the T_1 direction is defined in our coordinate system as the negative y -direction, azimuthal angles are measured on micrographs from a direction 90° clockwise from the T_1 direction, when the emulsion side is up.

D. Double tilting

The specimen was first tilted about T_2 to $\vartheta_2 = 9.7^\circ$ while ϑ_1 remained at 0° , made eucentric, then tilted about T_1 to $\vartheta_1 = 15.0^\circ$. The first HREM image was taken at this specimen orientation of $(\vartheta_1 = 15^\circ, \vartheta_2 = 9.7^\circ)$. A similar sequence was applied to take a second HREM image at the second specimen orientation of $(\vartheta_1 = 15^\circ, \vartheta_2 = -9.7^\circ)$. The process can be modeled with a simple matrix calculation.^{5,6}

Because of the importance of repeatable quantitative tilts, effects of “mechanical hysteresis” were minimized by inferring all relative changes in tilt from goniometer readings taken with a common direction of goniometer rotation. The rotation sequences were “initialized” by first tilting past the starting line, and then returning to it in the direction of subsequent

motion. Nonetheless both the precision of angle measurement, and our inability to observe lattice fringes *during* rotation, were shortcomings that microscopes designed to apply these strategies routinely must address.

E. Specimen preparation

The tungsten carbide thin film was deposited by PECVD on glass substrates by introducing a gaseous mixture of tungsten hexacarbonyl and hydrogen into a RF-induced plasma reactor at a substrate temperature of 330°C.³¹ The specimen was disk-cut, abraded from the glass substrate side and dimpled by a Gatan Model 601 Disk Cutter, a South Bay Technology Model 900 Grinder and a Gatan Model 656 Precision Dimpler, respectively. The specimen was then argon ion-milled by a Gatan DuoMill for about 5 hours to perforation prior to the TEM study, at an incidence angle of 3°.

IV. EXPERIMENTAL RESULTS

A. Checking the method with a known

Calibration of this technique has been done using a Si crystal. Diffraction patterns of a Si (110) specimen along the $[1\bar{1}\bar{6}]$ and $[1\bar{1}6]$ zone axes were obtained by tilting about T_1 and T_2 . The lattice parameters determined are ($a = 0.383\text{nm}$, $b = 0.387\text{nm}$, $c = 0.386\text{nm}$, $\alpha = 60.0^\circ$, $\beta = 119.6^\circ$, $\gamma = 119.1^\circ$). This set of chosen basis defines the rhombohedral primitive cell of the Si f.c.c lattice. Compared with the literature values of Si, ($a = 0.384\text{nm}$, $b = 0.384\text{nm}$, $c = 0.384\text{nm}$, $\alpha = 60^\circ$, $\beta = 120^\circ$, $\gamma = 120^\circ$), the angular disagreements are less than 1° and spatial disagreements are less than 1%. The accuracy is competitive compared with other techniques of submicron crystal analysis^{1,3,5-7}.

B. Crystallographic Analysis

1. *Inference of the Lattice parameters of WC_{1-x}*

Figures 5 and 6 show a tungsten carbide nano-crystal at the orientations of ($\vartheta_1 = 15^\circ$, $\vartheta_2 = 9.7^\circ$) and ($\vartheta_1 = -15^\circ$, $\vartheta_2 = -9.7^\circ$), respectively. The “a” insets show the region of selected crystal *A*, at these two orientations. The “b” insets show their respective power spectra. The coordinates of these points in the micrographs, as well as in the common reference coordinate system, are listed in Table I, in much the same format as is diffraction data for stereo analysis.⁷

a. Matching the lattice: The lattice spacings and inter-spot angles of periodicities in image power spectra were used to look for consistent indexing alternatives from a set of 36 tungsten carbide and oxide candidate lattices including WC_{1-x}. When an angular tolerance of 2° and a spatial tolerance of 2 percent are imposed, only WC_{1-x} provides a consistent indexing alternative. As summarized in Table II, the Miller indices of the three observed spots then become (200), (020) and (11 $\bar{1}$). The (a) insets in Figures 5 and 6 then become HREM images of WC_{1-x} [001] and [112] zones, respectively. The azimuth of the reciprocal lattice vector ($2\bar{2}0$)

$$\varphi_{(2\bar{2}0)} = \frac{(\varphi_{(200)} + [180^\circ + \varphi_{(020)}])}{2} = \frac{(79.2^\circ + [180^\circ - 11.6^\circ])}{2} = 123.8^\circ, \quad (7)$$

which deviates from the projection of the effective tilt axis by only 0.3°. Therefore the ($2\bar{2}0$) lattice planes are perpendicular to the effective tilt axis as per Figure 3, and the data acquired are consistent with the expectation for fcc crystals outlined in Figure 1. These two zone images and the actual tilting path in the Kikuchi map of crystal *A* are shown in Figure 7.

From the indexing suggested by this match, the *x*, *y*, and *z* coordinates of the reciprocal lattice basis vectors a^* , b^* , and c^* may be inferred. This is shown in Table III, along with the resulting lattice parameters, and a comparison to literature values. The resulting errors in *a* and *b* are less than 1.3 percent, while the error in *c* (which is orthogonal to the plane of the first image) is larger (around 2.3 percent). Both because of tilt uncertainties and

reciprocal lattice broadening in the beam direction, uncertainties orthogonal to the plane of the specimen are expected to be larger than in-plane errors.²⁷

b. Building a triplet from scratch: By generating linear integral combinations of the measured periodicities in reciprocal space (i.e. vector triplets of the form $n_1g_1 + n_2g_2 + n_3g_3$ where the n_i are integers) until a minimal volume unit cell is obtained (there will be more than one way to achieve the minimum), a primitive triplet for the measured lattice can be inferred quite independent of any knowledge of candidate lattices. The primitive cell parameters determined are also listed in III. With respect to literature values, these show spatial disagreements less than 1.6%, and angular disagreements less than 1.5°. Although inference of the “conventional cell” from the primitive cell alone is possible, the process has not been attempted here because of complications attendant to measurement error.

2. Phase Identification

Determining a reciprocal lattice triplet, and inferring lattice parameters therefrom, are of course not equivalent to confirming the existence of a particular phase. In order to draw a more robust conclusion about the makeup of crystal A, we extended our analysis of the structure to other lattices capable of indexing the observed spots, albeit with larger errors in spacing and interspot angle. When the spatial and angular tolerances of our candidate match analysis are increased to 3° and 3%, there are many tungsten oxide and carbide candidates in addition to WC_{1-x} which show consistent lattice spacings and inter-planar angles.³¹

In order to eliminate these candidates, it was necessary to confirm, using power spectra of amorphous regions in each image, that the spatial frequencies in Figure 5(a) and 6(a) were continuously transferred within the first passband.^{39,40} By then assuming that projected reciprocal lattice frequencies make their way into the exit surface wavefield (at least at the thin edges of the particle), all the candidates except WC_{1-x} are eliminated. Specifically, it was found that for each of the candidates except WC_{1-x} , along one or more of the suggested

zone axes at least one reciprocal lattice vector shorter than the experimental one(s) is missing in a power spectrum.³¹ An example of this is the match with hexagonal WC_x ($a = 1.058\text{nm}$, $c = 1.335\text{nm}$). In this case the Miller indices suggested for spot 3 ($\bar{4}2\bar{2}$) were inconsistent with the fact that the ($\bar{2}1\bar{1}$) is absent from the power spectrum in Figure 6.

The conclusion that this crystal (and as we see later most of the other crystals in this specimen as well) are WC_{1-x} is also consistent with knowledge of the formation conditions, as well as with X-ray powder and EDS analysis of other parts of this film.

C. The effective tilt direction, and recurring fringes

In addition to serving as a guide for correctly choosing the azimuth of the crystal before tilting between desired zones, knowledge of the tilt axis direction plays another role: that of highlighting lattice fringes present in both specimen orientations, but caused by one and the same set of lattice planes.

In single tilt experiments, the tilt axis is simply T_1 . This is always perpendicular to the electron beam and hence parallel to the micrographs. Any reciprocal lattice vector parallel or antiparallel to T_1 remains in Bragg condition throughout the whole tilting process,³¹ regardless of the amount of tilt ϑ_1 . Thus two spots along a line going through the origin and parallel to the projection of T_1 persist in the diffraction pattern of the crystal taken at any orientation. If the spacing is large enough to be recorded in the images, the same lattice fringes are seen perpendicular to the projection of T_1 in any HREM image as well.

For double tilt experiments, it is convenient to introduce the concept of an *effective tilt axis*. The effective tilt axis is analogous to the tilt axis in a single tilt experiment, in that the double tilt can be characterized by a single tilt around the effective tilt axis of angular size equal to that in the double tilt. This effective axis is perpendicular to the electron beam and hence parallel to the micrographs only if the two specimen orientations are symmetric about the untilted position. Here we only consider double tilts falling into this category. Let $(\vartheta_1, \vartheta_2)$ and $(-\vartheta_1, -\vartheta_2)$ denote the two specimen orientations in a double tilt. Generally

the effective tilt axis direction has an azimuth (with respect to our reference x -direction) of

$$\varphi_{eff} = \tan^{-1} \left[-\frac{\sin(\vartheta_1)}{\tan(\vartheta_2)} \right] \quad (8)$$

A proof of equation 8 is given in Appendix A. There exists a 180° ambiguity in the direction of the effective tilt axis using equation 8. This ambiguity can be resolved through the knowledge of the actual tilting sequence. In our experiment $\vartheta_1 = 15^\circ$, $\vartheta_2 = 9.7^\circ$, $\varphi_{eff} = 123.5^\circ$. This is the effective tilt axis direction mentioned in previous sections.

Lattice planes perpendicular to the effective tilt axis, in the double tilt case, diffract and are visible at initial and final, but not intermediate, specimen orientations. This result inspired further experimental work on, and modeling of, fringe visibility loss during tilt⁴³. One result of this exercise was a prediction that fringes deviating by as much as 4 degrees from the effective tilt direction in these WC specimens will remain visible after a 35.6° tilt. This was confirmed by experiment on these specimens⁴³. The model has is one building block of the probability and error analyses below.

D. Tilt limitations, “SLI” strategy, and chances for success

This section addresses the chances for successful 3D cell determination from images, depending on properties of both microscope and specimen. These matters are considered in more detail elsewhere⁴⁴.

In a microscope with a single-axis tilt of at least $\pm 35.3^\circ$ and a stage capable also of 180° rotation, any cubic crystal with an $[001]$ zone in the beam direction at zero tilt can be re-aligned by azimuthal rotation until its $(2\bar{2}0)$ reciprocal lattice vector is parallel to T_1 . With an untilted tilt-rotate stage, this would allow the nano-crystal’s $[001]$ zone to remain aligned with the beam throughout the rotation. Subsequent tilting by 35.3° will lead to the $[112]$ zone, and the lattice structure in three dimensions confirmed ala Figure 1.

Under these conditions, any cubic crystal showing $[001]$ zone cross fringes can be tilted so as to reveal a third spacing. Hence the probability of success with any given crystal is that

of finding a randomly-oriented crystal oriented with [001] fringes visible. Fortunately for this method, the spreading of reciprocal lattice points due to finite crystal thickness t allows one to visualize fringes within a half angle Θ_t , surrounding the exact Bragg condition, of order $1/t$. Otherwise, cross-fringes would be rare indeed! The solid angle subtended by this visibility range around intersecting lattice planes then allows us to calculate the probability that a randomly-oriented crystal will show cross-fringes of specified type. For example if we approximate the cross-fringe region with a conical bundle of directions about each zone, then for the special case of spherical particles the fraction of crystals showing the fringes of zone x is:

$$p_x = n(1 - \cos[\Theta_t]), \text{ where } \Theta_t = \arcsin\left[\frac{g_t^2 - g_d^2 + 2g_\lambda g_t}{\sqrt{2}g_d g_\lambda}\right],$$

n is multiplicity of zone x (e.g. equal to 3 for cubic [001]), $g_d = 1/d$, $g_\lambda = 1/\lambda$, and $g_t = f/t$, where t is the thickness of the crystal in the direction of the beam and f is a parameter of order one that empirically adjusts for signal-to-noise in the method used to “visualize” fringes. For example, we expect f to decrease if an amorphous film is superposed on the crystals being imaged. The half-angle Θ_t is related to the foreshortening of fringes in projection, and hence is a pivotal quantity in both the probability and accuracy of fringe measurement.

A plot of the probability for seeing [001] cross-fringes of spacing $d = 0.202\text{nm}$, as a function of specimen thickness t for both spherical and laterally-infinite (rel-rod) particles, is shown in Fig. 8. Here we’ve used fit parameter $f = 0.955$ based on data points (also plotted) that were obtained experimentally from HREM images (two of Au/Pd evaporated onto a carbon film, and a third of Pt catalyst particles in amorphous carbon) for particles of varying size. As you can see, the probability of encountering cross-fringes improves greatly as crystallite size decreases toward a nanometer. Of course, as discussed in the next section, this “reciprocal lattice broadening” is accompanied by a decrease in the precision of measurements for individual lattices.

Due to the tilt limits of the specimen holder in our microscope, the first HREM image

along the [001] zone of a WC_{1-x} nano-crystal had to be taken at a nonzero ϑ_1 orientation. Azimuthal symmetry is thus broken. Our solution was to find a [001] nano-crystal whose $(2\bar{2}0)$ reciprocal lattice vector was by chance parallel to the effective tilt axis, then tilting to the 2nd orientation. Thus nano-crystal *A* was identified to by coincidence have an appropriate azimuth during real time study of the (002) and (020) lattice fringes. Tilting by 35.3° done thereafter.

For the probability of success in our case, we must multiply p_x by the probability of viewing (111) fringes *after* tilting a [001] crystal with random azimuth by 35.26° . This probability of finding a 3rd spacing takes the form $p_3 = m\delta/\pi$, where m is the multiplicity of target spacings (e.g. $m = 4$ for a four-fold symmetric [001] starting zone), and the “azimuthal tolerance half-angle” δ (again in the spherical particle case) obeys the implicit relation:

$$\theta_o = \arctan\left[\frac{\tan \theta_o}{\cos \delta}\right] + \arctan\left[\frac{\cos \gamma}{\sin^2 \gamma - (\cos \theta_o \sin \delta)^2}\right],$$

where θ_o is the required tilt (in our case 35.26°) and

$$\gamma = \arccos\left[\frac{g_d^2 - g_l^2 + 2g_\lambda g_l}{2g_d g_\lambda}\right].$$

The probability p_3 probability is also plotted as a function of specimen thickness in Fig. 8, along with the product $p_x p_3$.

These models predict a probability of success with the strategy adopted in our experiment, for the “large” 10nm WC_{1-x} crystals in our specimen, of $p_x p_3 = 6.5 \times 10^{-4} \times 0.371 = 2.4 \times 10^{-4}$. Hence only one in every 1500 crystals will show [001] cross fringes, and one in every 4000 will be suitably oriented for 3D lattice parameter determination. This is not inconsistent with our experience: The image of crystal *A* was recorded in one negative out of 22, each of which provided an unobstructed view of something on the order of 100 crystals.

As mentioned above, using a microscope capable of side-entry goniometer tilting by $\pm 35.3^\circ$ with a tilt-rotate stage, the 3D parameters of all cubic crystals, when untilted showing [001] zone cross-fringes, could have been determined. According to Fig. 14a, the fraction

of particles, 2 nm in thickness oriented suitably for such analysis approaches 1 in 100. Moreover, with a goniometer capable of tilting by $\pm 45^\circ$ plus computer support for automated tilt/rotation from any starting point, *each unobstructed nano-crystal* in the specimen could have been subjected to this same analysis after a trial-and-error search for accessible [001] zones. Thus a significant fraction of crystals in a specimen become accessible to these techniques, with either a large enough range of computer-supported tilts, or if the crystals are sufficiently thin.

V. PITFALLS AND UNCERTAINTIES

A. Cautions involving specimens and contrast transfer

In this section, we discuss effects to be cautious about. In the next section, models of lattice parameter uncertainty are discussed.

High electron beam intensities can cause lattice rearrangement in sufficiently small nanocrystals, as well as slight changes in the orientation of a thin film (e.g. due to differential expansion). Sequential images of the same region at fixed tilt might allow one to put limits on the magnitude of these effects, for a given specimen.

Loss of periodicities in the recorded image, due to damping and spherical aberration zeros, were discussed in the section above on experimental design. Nonetheless, careful observations of more than one crystal, and image simulation as well, may be useful adjuncts whenever this technique is applied. We illustrate this below, with a “two-dimensional” experiment done to assess the size of errors in our specimen, due to finite crystal size and random orientation. The result is of help in the section on modeling uncertainties that follows.

A recent paper on HREM image simulations⁴² indicated that deviations in orientation of a 2.8nm spherical palladium nano-crystal from the zone axes may result in fringes unrelated to the structure of the particle. Variability in measured lattice spacings was also reported to

be as high as several percent, with the highest reaching 10%. To compare such results with our experimental data, 23 single crystals free of overlap with other crystals, and each showing cross-fringes, were examined. The projected sizes of these crystals range from $3.7\text{nm}\times 3.8\text{nm}$ to $10.8\text{nm}\times 7.8\text{nm}$. The spacings and angles between fringes are plotted in Fig. 9.

Observed cross-fringes in the HREM images fall into two categories, according to their spacings and angles. The first category is characterized by a 90° inter-planar angle between two 2.12\AA lattice spacings. The second one by two inter-planar angles of 55° , 70° and three lattice spacings of 2.12\AA , 2.12\AA , 2.44\AA . Only the spacings of 2.44\AA and 2.12\AA and the corresponding angle of 55° have been shown in Figure 9. Two conclusions can be drawn.

First, since the two categories of cross-fringes match those along the $[001]$ and $[011]$ zone axes of WC_{1-x} , the only two zones which show lattice fringes in our HREM images, the thin film consists mainly of WC_{1-x} . X-ray powder diffraction work on a similar film supports this conclusion.³¹

Secondly, for nano-crystals free of overlap with other crystals, the observed lattice spacings and interplanar angles in HREM images have a standard deviation from the mean of less than 1.5%, and a standard deviation of less than 1.3° , respectively. We have not observed any seriously shortened or bent fringes. Nonetheless we recommend that such fringe abundance analyses go hand in hand with stereo lattice studies of nano-crystal specimens, and that comparative image simulation studies be done where possible as well.

B. Uncertainty forecasts

Earlier estimates²⁷, as well as the typical size of diffraction broadening in the TEM, suggest that lattice parameter spacing errors may in favorable circumstances be on the order of a percent, and angle errors on the order of a degree. Experiment, and a more detailed look at the theory⁴⁴, now support this impression. We will focus the discussion here on equant or spherical nanocrystals. The results should be correct within 10% for other (e.g. thin-foil) geometries of the same thickness.

The three sources contributing to the lattice spacing measurement uncertainty in images are: expansion of the reciprocal lattice spot in the image plane, uncertainty in the camera constant, and expansion of the reciprocal lattice spot along the electron beam direction, in order of decreasing relative effect.⁴⁴ The uncertainty in our camera constant is measured to be about 0.5%. Uncertainties from the first and third sources above are on the order of 1% and 0.01%, respectively, for a typical lattice spacing of 0.2 nm. The in-plane/out-of-plane error ratio is on the order of 10.

Sources contributing to the measurement uncertainty of lattice parameters along the electron beam direction, when the specimen is un-tilted, include uncertainty in goniometer tilt as well as sources like those above. Observation of reciprocal lattice vectors further out of the specimen plane (i.e. of fringes at high tilt) reduces the measurement uncertainty of “out-of-plane” parameters.

The measurement uncertainty of inter-planar angles in images is due to azimuthal uncertainty in their associated reciprocal lattice spots, due to the finite projected size of the crystals being examined, as well as to tilt uncertainties for those with an out-of-plane component.

Using a mathematical model of these errors⁴⁴, we predict spacing uncertainties in a 10 nm nanocrystal, tilted by $\pm 18^\circ$, of 2.1% for an imaged spacing and of 8.6% for a lattice parameter perpendicular to the plane of the untilted specimen. This large “out-of-plane” uncertainty is a result of the small tilt range available with our high resolution pole piece. The estimated interplanar angle uncertainty is about 2.3° . These predicted uncertainties⁴⁴ are between 2 and 3 times the errors observed here, and hence of the right order of magnitude.

The model suggests that lattice parameter uncertainties will decrease as tilt and camera constant uncertainties decrease, and will also decrease as the tilt range used for the measurement increases. It suggests that the lattice parameter errors will increase as crystal thickness goes down. The ease of locating spacings, however, goes up as crystal thickness decreases. Hence the best candidates for application of the protocols here may be crystals in the 1 to 20 nm range. Improved tilt accuracy (hopefully with computer guidance), and

low-vibration tilting so that fringes may be detected as orientation changes, would make these strategies more accurate and widely applicable as well.

VI. CONCLUSIONS

When considered from the perspective of direct space imaging, crystals offer a discrete set of opportunities for measuring their lattice parameters in three dimensions. Enumerating those opportunities for candidate lattices, or lattice classes, opens doors to the direct experimental determination of nano-crystal lattice parameters in 3D. A method for doing this, and lists of those opportunities for the special case of cubic crystals, are presented here.

We apply this insight to inferring the 3D lattice of a single crystal from electron phase or Z-contrast images taken at two different orientations. For nano-crystals in particular, a double-axis tilt range of $\pm 18^\circ$ degrees allows one to get such data from all correctly-oriented cubic crystals with (002) spacings resolvable in a pair of images taken from directions separated by 35.2° . In the experimental example presented, we find less than 1.5% spatial and 1.6° angular disagreements between the inferred primitive cell lattice parameters of a 10 nm WC_{1-x} nano-crystal, and literature values.

We further present data on the variability of lattice fringe spacings measured from images of such randomly-oriented 10nm WC_{1-x} crystals in electron phase contrast images. The results suggest that measurement accuracies of 2% in spacing and 2° in angle may be attainable routinely from particles in this size range. Smaller size crystals may be easier to obtain data from, but show larger uncertainties, while larger or non-randomly oriented crystals like mica (especially if guesses as to their structure are unavailable) may be more challenging to characterize in three dimensions.

Precise knowledge of the tilt axes, as projected on the plane of a micrograph, is crucial to implementation. This information, if coupled with on-line guidance on how to tilt from an arbitrary two-axis goniometer orientation in any desired direction with respect to the plane of an image or diffraction pattern, could make this strategy and related diffraction

strategies⁷ for lattice parameter measurement more routine.

Lastly, the alternatives for finding three-dimensional lattice information mentioned above do not require lattice imaging for their implementation. They can also be used in this “stereo analysis” mode with crystals large enough to provide diffraction patterns, although the easier accessibility of high spatial frequencies via diffraction often makes the large tilts used here unnecessary. They can further be used in darkfield imaging applications, by forming images of the specimen using “beams” diffracted by the periodicities which serve as diagnostic of a given lattice (for example those associated with each of the protocols of Figure 1).

Images so taken of nano-crystalline specimens, for example at two tilts with three different darkfield conditions, would be expected to show correlations among that subset of the crystals correctly oriented for diffraction with all three reflections. Although this strategy may never allow precise lattice parameter determinations given limits on objective aperture angular size, it may be a very efficient way to search for crystals correctly-oriented and of correct type for one of the imaging protocols described here. Moreover, because such lattice-correlations in three dimensions contain information beyond the pair-correlation function, they may be able to support the new technique of fluctuation microscopy⁴⁵⁻⁴⁷ in the study of paracrystalline specimens (like evaporated silicon and germanium)^{48,49} whose order-range is too small for detection by other techniques.

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APPENDIX A: THE AZIMUTH OF THE EFFECTIVE TILT AXIS

Let $(\vartheta_1, \vartheta_2)$ and $(\vartheta'_1, \vartheta'_2)$ denote orthogonal tilt values for two specimen orientations, and ϕ_{eff} the azimuth of the effective tilt axis between these orientations. Any reciprocal lattice

vector with untilted Cartesian coordinates $|g\rangle$, and with identical micrograph coordinates $|g_m\rangle$ at the two tilted orientations, will following equation 4 obey:

$$A(\vartheta_1, \vartheta_2)|g_m\rangle = |g\rangle = A(\vartheta'_1, \vartheta'_2)|g_m\rangle, \quad (\text{A1})$$

where

$$|g_m\rangle = \begin{pmatrix} g \cos(\varphi_{eff}) \\ g \sin(\varphi_{eff}) \\ 0 \end{pmatrix}. \quad (\text{A2})$$

Expanding, this gives:

$$g_{mx} \cos(\vartheta_1) = g_{mx} \cos(\vartheta'_1) \quad (\text{A3})$$

$$-g_{mx} \sin(\vartheta_2) \sin(\vartheta_1) + g_{my} \cos(\vartheta_2) = -g_{mx} \sin(\vartheta'_2) \sin(\vartheta'_1) + g_{my} \cos(\vartheta'_2) \quad (\text{A4})$$

$$-g_{mx} \cos(\vartheta_2) \sin(\vartheta_1) - g_{my} \sin(\vartheta_2) = -g_{mx} \cos(\vartheta'_2) \sin(\vartheta'_1) - g_{my} \sin(\vartheta'_2). \quad (\text{A5})$$

Since from equation A2 $g_{mx} = g_{my} \tan(\varphi_{eff})$, these three equations can be solved for the three unknowns ϑ'_1 , ϑ'_2 , φ_{eff} , to get:

$$\vartheta'_1 = -\vartheta_1, \vartheta'_2 = -\vartheta_2, \text{ and} \quad (\text{A6})$$

$$\varphi_{eff} = \tan^{-1} \left[-\frac{\sin(\vartheta_1)}{\tan(\vartheta_2)} \right]. \quad (\text{A7})$$

This provides an equation for the azimuth of the effective tilt, and confirms that symmetry about the zero tilt position is a necessary and sufficient condition for the reciprocal lattice vector $|g\rangle$, and it's associated lattice fringe, to show a common direction in micrographs at both tilts.

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TABLES

Spot n	$g_m[nm^{-1}]$	$\varphi_m[^\circ]$	$\vartheta_1[^\circ]$	$\vartheta_2[^\circ]$	$g_x[nm^{-1}]$	$g_y[nm^{-1}]$	$g_z[nm^{-1}]$
1	4.73	79.2	-15.0	-9.7	0.861	4.53	-1.01
2	4.77	-11.6	-15.0	-9.7	4.52	-1.15	-1.03
3	4.14	32.6	+15.0	+9.7	3.37	2.04	1.27

TABLE I. The g-spacings and azimuths of three spots measured from the power spectra of images at two tilts, as well as calculated Cartesian coordinates of those reciprocal lattice spots in a common coordinate system. This constitutes a minimal data set for analyzing the lattice in three-dimensions.

Spot n	$d_n[nm]$	$\varphi_{ij \neq n}[^\circ]$	(hkl)	$d_{hkl}[\widehat{nm}]$	$\frac{\delta d}{d}[\%]$	$\varphi_{ij \neq n}[\widehat{nm}][^\circ]$	$\delta\varphi[^\circ]$
1	0.212	54.2	(200)	0.212	0.5	54.7	0.5
2	0.209	56.2	(020)	0.212	1.4	54.7	1.5
3	0.242	90.8	(11 $\bar{1}$)	0.245	1.2	90.0	0.8

TABLE II. The results of a three-dimensional match of measured spacings and interspot angles, with those predicted from the literature (denoted with a caret) for the face-centered cubic crystal WC_{1-x}. This phase is the only one from a list of 36 tungsten carbides and tungsten oxides whose predicted spacings and interspot angles agreed the measurements within a tolerance of 1.5% and 1.5°, respectively.

primitive cell	a*	b*	c*			
reciprocal triplet	\mathbf{g}_3	$\mathbf{g}_1 + \mathbf{g}_2 - \mathbf{g}_3$	$\mathbf{g}_1 - \mathbf{g}_3$			
<i>measured value</i>	0.298	0.299	0.296	120.0	58.7	119.8
<i>“book” value</i>	0.300	0.300	0.300	120	60	120
<i>lattice parameter</i>	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ
<i>“book” value</i>	0.425	0.425	0.425	90	90	90
<i>measured value</i>	0.424	0.419	0.415	88.5	90.8	89.3
reciprocal triplet	$\frac{\mathbf{g}_1}{2}$	$\frac{\mathbf{g}_2}{2}$	$\frac{\mathbf{g}_1 + \mathbf{g}_2}{2} - \mathbf{g}_3$			
face-centered cell	a*	b*	c*			

TABLE III. Primitive (top) and face-centered (bottom) reciprocal lattice basis triplets inferred from our two HREM images of crystal A, along with a comparison of the lattice parameters for each cell which follow therefrom. The indexing of the observed reciprocal lattice vectors in these two cases was inferred directly for the primitive cell, by minimizing cell volume, and by matching to “textbook” parameters for WC_{1-x} in the case of the face-centered cell. Save for the choice of basis triplet, the two measured cells refer to exactly the same inferred lattice.

FIGURES

FIG. 1. The tilt protocol for inferring the lattice structure of f.c.c. WC_{1-x} by viewing a WC_{1-x} crystal from its $[001]$ zone and $[112]$ zone, along which the two most easily resolved lattice plane sets, the $\{200\}$ and $\{111\}$ lattice planes, will show lattice fringes in HRTEM images. The two zones are 35.3° apart, within the tilting limit of the microscope with a Gatan double tilt holder. The crystal is to be viewed along its $[001]$ zone in the first specimen orientation, then tilted along the $(2\bar{2}0)$ lattice planes to the $[112]$ zone. The $(2\bar{2}0)$ lattice planes must therefore be perpendicular to the effective tilt axis. The projections along the $[001]$ and $[112]$ zones together with the effective tilt axis have been drawn so that their azimuths are consistent with those in the 700K HRTEM images. The experimental HRTEM images of a WC_{1-x} nano-crystal acquired using this protocol and their power spectra are shown in the bottom. The actual tilt sequence is to tilt along $-T_2$ by 19.5° followed by tilting along $-T_1$ by 30.0° , where T_1 and T_2 denote the side-entry goniometer tilt axis and the second tilt axis of a Gatan double tilt holder, respectively.

FIG. 2. Tilt protocols for determining the lattice parameters of face-centered, body-centered, and simple cubic crystals from two high resolution images, plotted according to the required tilt range, and required resolution limit in units of the cubic cell side. Superimposed on this plot are the tilt range, and resolution in units of the unit cell side $a = 0.4248\text{nm}$ of WC_{1-x} , required for the experiment reported here.

FIG. 3. Illustration of all ways (from Figure 2) to verify the three dimensional lattice parameters of fcc and bcc crystals from a pair of lattice images, given an ability to image only lattice spacings down to half the unit cell side, and a tilt range of less than 60 degrees. The image pairs are rotated so as to illustrate the *direction of tilt* between the two zones (crystal orientations) involved. The protocols shown with double arrows provide access to cross-fringes (and hence information on which direction to tilt) at both ends of the tilt sequence. Also note that the first and last entries in each column simply provide low and high resolution views, respectively, of the same experiment.

FIG. 4. A schematic illustration of the coordinate system set-up for measuring reciprocal lattice vectors. The coordinate system is fixed to the microscope. The y and z axes are defined to be along $-T_1$ and the electron beam direction, respectively. The projections of x, y, z and T_1 on an electron micrograph in the camera chamber are shown.

FIG. 5. A high-resolution TEM image showing a WC_{1-x} nano-crystal, "a", along its [001] zone at the specimen orientation of $(\vartheta_1=15.0^\circ, \vartheta_2=9.7^\circ)$. The projections of the two tilt axes of the double tilt holder on a micrograph are marked in the image. Inset (a) is a selected and magnified image of crystal a. Inset (b) is the power spectrum of inset (a), analogous to a SAED of inset (a).

FIG. 6. A high-resolution TEM image showing the WC_{1-x} nano-crystal, "a", along its [112] zone at the specimen orientation of $(\vartheta_1=-15.0^\circ, \vartheta_2=-9.7^\circ)$. Inset (a) is a selected and magnified image of crystal a. Inset (b) is the power spectrum of inset (a), analogous to a SAED of inset (a).

FIG. 7. The [001] and [112] zone images of crystal "a", their power spectra and the actual tilt path shown in the Kikuchi map of the crystal. The actual tilt path was around $-T_2$ by 19.5° , and around $-T_1$ by $30.^\circ$, which is equivalent to tilting around T_{eff} directly from the [001] zone to the [112] zone by 35.3° .

FIG. 8. A plot of the fraction of randomly oriented grains of WC_{1-x} showing [001]-zone cross fringes (p_x), and the fraction of such cross-fringe grains oriented so that a random tilt of 35.3° will allow imaging of a 111 periodicity (p_3), as a function of specimen thickness in the direction of the electron beam.⁴⁴

FIG. 9. The spacings and interplanar angles measured from the cross lattice fringes of 23 nano-crystals free of overlap with other crystals in the HRTEM images. Insets (b) and (c) are magnified plots of the two regions in (a) where all the data are concentrated. The specific combinations of lattice spacings and interplanar angles corresponds to the [001] and [011] zone images of WC_{1-x} and hence indicate WC_{1-x} being the only present phase in the thin film. The measured lattice spacings have a standard deviation from their mean of less than 1.5%, and interplanar angles have a standard deviation of 1.2° .

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