The impact of STEM aberration correction on materials science

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ABSTRACT

Over the last three decades the scanning transmission electron microscope (STEM) has gone from a spe-
cialized instrument for nanoscale analysis to the microscope of choice for atomic resolution imaging of
materials, allowing incoherent high-angle annular dark field (Z-contrast) imaging, coherent phase con-
trast modes (conventional and annular bright field), electron energy loss and energy dispersive X-ray
spectroscopy. All signals are achieving atomic resolution and several are available simultaneously.
This would not have been possible without the development of an aberration corrector for the STEM, spear-
headed by Ondrej Krivanek in the late 1990s, which finally allowed the benefits of the STEM to translate
from “in-principle” to actual daily practice. Here I will recall my own experiences with the aberration-
corrected STEM in partnership with Ondrej, a truly exciting and rewarding journey.

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1. Introduction

This account is largely my personal view on how aberration correction on the STEM has transformed the field of electron mi-
croscope. Let’s start with a brief history of the STEM (for a more detailed account of the development see [1]). The potential ben-
fits have long been appreciated; Manfred von Ardenne invented the STEM in 1938 [2,3], following Ernst Ruska’s invention of the
TEM in 1932 [4], because he realized that the STEM did not need to refocus transmitted electrons back into an image, and therefore
would not be hampered by chromatic aberration in the same way as the TEM. However, his first images immediately revealed the
Achilles heel of STEM, noise. It was not possible to get enough cur-
rent into the probe to form a good quality image and von Ardenne
gave up the STEM in favor of the TEM [5].

It is Albert Crewe who is commonly regarded as the father of the modern STEM. Not only did he invent the cold field emission
gun which enabled orders of magnitude more current in the probe [6], he also understood the benefits in placing the critical optics
before the sample, and advocated the use of a spectrometer to col-
clect the inelastic scattering [7]. A few years later the annular dark
field (ADF) detector appeared and the first direct images of indi-
vidual single heavy atoms were reported [8]. The term Z-contrast
made its appearance, referring to a ratio image between the elas-
tic (ADF) and inelastic signals, which, for single atoms, is propor-
tional to atomic number Z [9]. The technique became widely used in
the biological sciences for mass measurement [10–12], but was
not useful in most materials applications because of strong diffraction
contrast effects which masked any Z-contrast [13].

To overcome the strong diffraction contrast required higher
scattering angles be collected, when coherent Bragg scattering
would be replaced with incoherently generated thermal diffuse
scattering [14–17]. This was my introduction to Z-contrast imag-
ing. At that time, as a student in the Cavendish Laboratory I was
working on cathodoluminescence, which is also an incoherently
generated signal [18–20]. Michael Treacy wanted to try his ideas
on imaging with high angle Rutherford scattering and we modified
my cathodoluminescence detector accordingly, obtaining the first
HAADF images of catalysts which showed the anticipated improved
visibility and reduced Bragg contrast, as shown in Fig. 1 [21–24].

In 1982 I joined Oak Ridge National Laboratory as a staff mem-
ber in the group of Jagdish Narayan and started to apply the Z-
contrast technique to ion-implanted semiconductors. Again, the changeover from diffraction contrast imaging of structure to Z-
contrast imaging of the implanted dopants was striking [25], see
Fig. 2. I began to wonder what the image would look like with an
atomic sized probe; surely in thin enough crystals we would have
to see a direct Z-contrast structure image [26]? The Department of
Energy granted me the chance to investigate further with a VG
Microscopes HB501UX equipped with a high resolution pole piece and a set of masks to exclude low angle scattering from the an-
nu lar detector. In the summer of 1988 I obtained what I thought were
the first incoherent, Z-contrast images at atomic resolution [27], see
Fig. 3. It was only later I discovered that John Cowley at Ari-
 zona State University had published a STEM bright field and ADF
image of Ti2Nb19O39, using a VG Microscopes HB5 [28]. He com-
mented on the enhanced resolution of the dark field image but did

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not mention if the image showed other incoherent characteristics, such as no contrast reversals. These characteristics had been predicted previously by Engel based on simulations of single atoms [29]. The most surprising feature of the HAADF images was perhaps the thickness dependence, which also showed predominantly incoherent characteristics. Instead of thickness fringes or contrast reversals as in bright field imaging, the HAADF images showed no obvious change in form, just a slowly decreasing contrast with increasing thickness, see Fig. 4.

The physical explanation lay in the fact that the high angle scattering came predominantly from just the highly localized 1 s type Bloch states [30–37]. In coherent high-resolution TEM (HRTEM) all Bloch states interfere to form the image and the strong thickness dependence results. Only in very thin crystals can the image be interpreted as a structure image, a good example being Ondrej’s famous study of a Ge grain boundary by high voltage TEM [38]. For most materials, especially at lower voltages, image interpretation required construction of candidate model structures, simulations of possible images as a function of defocus and thickness, and finding the best fit. The problem of course is that there is no guarantee that the actual structure would be thought of. The Z-contrast image, being incoherent in nature, immediately suggested the likely structure, and most interfaces were actually found to be more complex than previously imagined. An excellent example is shown in Fig. 5, where Z-contrast imaging of an ultrathin (Si$_4$Ge$_8$)$_{2/4}$ superlattice reveals strong interfacial ordering which indicated an unexpected step-driven atom pump mechanism [39]. Images of superlattices in high-temperature superconductors revealed a much simpler cell-by-cell growth mechanism, see Fig. 6 [40,41].

While these images are noisy with low resolution and poor contrast by today’s standards, the incoherent characteristics were clear. The STEM just needed to wait for advances in engineering, in particular the aberration corrector. And so the field high resolution imaging began the gradual conversion from the TEM to the STEM. Some key milestones along the way include, first, the installation of a 300 kV VG Microscopes HB603U STEM in Oak Ridge with a high resolution pole piece that enabled resolution of the dumbbell in Si [42] and GaAs [43], allowing the sublattice polarity to be seen by inspection, see Fig. 7. Second, the achievement of atomic-resolution EELS [44,45], where the simultaneous, atomic-resolution Z-contrast image unambiguously located the probe position with respect to the atom columns. Third, the development
of an atomic-resolution STEM by a large commercial manufacturer, JEOL, with a 2010F purchased by Nigel Browning at the University of Illinois, Chicago [46]. Ondrej himself mirrors this transition. When I first met him he was about to leave the Metal Physics group at the Cavendish and I was an incoming student. He had already become a legend in the group through his studies of amorphous materials through HRTEM [47] and his method for measuring the coefficient of spherical aberration \( C_\text{s} \) [48]. He went to Japan, and produced the grain boundary structure image with the high voltage microscope [38], then to the University of California, Berkeley, still using conventional HRTEM [49], but after joining Arizona State University he became interested in EELS [50].

Later Ondrej joined the Gatan company where he introduced their parallel detection EEL spectrometer [51]. In a visit to the Orsay group he demonstrates single atom detectability on their HB501 STEM [52]. In this paper he mentions that reducing the \( C_\text{s} \) by a factor of three would “improve the visibility of heavy atoms such as thorium considerably,” referring to an ADF image. As parallel detection spectrometers use multipole lenses, which are one way to correct spherical aberration [53], we can see that Ondrej probably already had his sights on aberration correction. He develops the imaging filter with more complex multipole lenses [54], then in 1995 leaves Gatan to work on aberration correction at the Cavendish Laboratory, using the same VG HB5 microscope I had used for my thesis work almost 20 years earlier.

### 2. Aberration correction for incoherent imaging

Clearly by this time Ondrej had decided that his future would focus on STEM, in contrast to the German aberration correction project that was primarily TEM based [55,56]. The question of who achieved what first has been discussed recently [57–59], but it was during this time my own path crossed Ondrej’s again. The Oak Ridge HB501UX by this time was ageing, not used much for imaging after the installation of the 300 kV HB603, but was still used for EELS since the 300 kV machine had no spectrometer at that time [60]. Together with Niklas Dellby, Ondrej founded the Nion company (initially named Colibrí) to supply Philip Batson, IBM, with an aberration corrector for his HB501. I was rather easily persuaded to apply for funds to do likewise, and also to install a corrector in the HB603U. Ondrej delivered: with Batson he achieved the first sub-Ångstrom STEM probe [61] and with the Oak Ridge group, and Peter Nellist, we achieved the first sub-Ångstrom resolution of a crystal lattice using the 300 kV microscope [62], see Fig. 8. Maria Varela achieved the first spectroscopic identification of a single atom within a bulk crystal with the rejuvenated 100 kV microscope [63]. This microscope now had the resolution of the uncorrected 300 kV machine [64].

![Fig. 3. HAADF images in a planar channeling condition from (a) \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) and (b) \( \text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta} \), with calculated intensity profiles across each unit cell. The expected strong Z-contrast closely matches the experimental result, reproduced from [27].](image)

![Fig. 4. Simultaneously recorded (a) bright field and (b) HAADF images of Si in the (110) zone axis using an objective aperture too small to allow bright field lattice images. In this case the bright field image shows thickness fringes allowing the Z-contrast image to be measured as a function of sample thickness, (c–g), reproduced from [31].](image)
Fig. 5. [110] Z-contrast STEM image of a nominal (Si,Ce)₃₄ superlattice showing interfacial ordering with simulated images of various ordered structures arising from the atom pump model. The [001] growth direction is toward the top of the image. Open circles represent Ge columns; solid circles, Si columns; and shaded circles, alloy columns. Simulation parameters are Cₓ = 1.3 nm, convergence angle = 10.3 mrad, and defocus = -69.4 nm. Reproduced from [39].

Fig. 9 shows the dramatic improvement in the ability of the HB603U to image single Pt catalyst atoms on γ-alumina after installation of the Nion aberration corrector [65,66]. Many materials advances rapidly ensued. For example, rare-earth sites in the intergranular phase of alumina were finally revealed [67,68], the origin of enhanced critical currents in Ca-doped YBa₂Cu₃Oₓ grain boundaries was elucidated [69], interfacial stacking sequences in complex oxide heterostructures could be resolved for the first time [70,71] and nucleation sites of quantum wells were imaged [72]. For numerous other applications see the review articles from that period [73–76].

Prior to this experience there were a number of misgivings about the potential usefulness of aberration-corrected STEM. For example, would the smaller probe lead to so much more beam damage it would not be practical? Would the reduced depth of focus become an issue? Well it turns out that having a smaller probe means that for the same beam current the peak intensity is higher, giving better signal to noise ratio, and for a given crystal spacing the contrast is improved, basically a win-win situation. So smaller currents can be used with aberration corrected probes and beam damage is less important. Similarly with the reduced depth of field, if channeling is not too strong a focal series becomes a series of images from different depths, giving information on the 3D structure of the material [77,78]. While the depth resolution did not match that of tilt-series tomography, the lateral resolution, being at the atomic level, was far superior. The 3D location of individual Hf atoms in a high-dielectric constant gate stack was able to be achieved, see Fig. 10, [79,80] explaining the high leakage current [81].

Another unexpected gain was in bright field phase contrast imaging. Prior to aberration correction, the collector aperture size for coherent bright field imaging needed to be very small, performing the function of the condenser aperture in HRTEM [82,83]. Hence bright field images used only a small fraction of the probe current and were very noisy. However, with aberration correction the collector aperture could be increased by an order of magnitude giving bright field images comparable to those that could be obtained by HRTEM. In STEM, however, coherent and incoherent images could be obtained simultaneously, with highly complementary characteristics, see Fig. 11 [75,84].

Even the traditional applications of STEM to microanalysis benefited substantially. The aberration corrector does not necessarily need to be used to produce smaller probes, it can also be used to provide more current into the same sized probe, with great benefits for the weaker analytical signals, as predicted explicitly by Ondrej, [85] and later demonstrated experimentally [86–88].

Of course, the CEOS corrector could also be used as a probe corrector [89,90] and they were in increasing demand from the large manufacturers, resulting in a rapid increase in STEM use. Another complementary imaging mode appeared, annular bright field (ABF) originally proposed by Rose [91], which is more efficient in imaging light elements [92–94]. In this way even H-column could be seen in VH₂ [95,96]. Although it is a phase contrast image, it is quite incoherent in nature since it integrates over substantial regions of the probe-forming aperture. It is especially useful for measuring octahedral tilts in complex oxides [97].

Ondrej’s choice to develop the aberration corrector for the STEM had really paid off. The STEM had finally overcome the historical noise issue that had plagued it for its entire history, and its inherent benefits could finally be exploited for applications, the interpretability of the incoherent image and the benefits of simulta-
neous analytical signals. But an incoherent image has other benefits too, it has an intrinsically higher resolution than coherent HRTEM [98, 99]. Over the next several years the STEM progressively broke resolution records to below 0.5 Å [91–94]. Only recently has the HREM method achieved similar performance, but requiring a 1200 kV acceleration voltage [100].

3. The UltraSTEM

Clearly installing correctors on old VG Microscopes columns was not optimum for demonstrating their performance, as the columns were never designed for such resolution. Peter Nellist joined Nion in 2000 to work on a 5th-order aberration corrector, which became incorporated in Ondrej’s new UHV column - the UltraSTEM [85]. Ondrej also appreciated that contamination was a major issue in many columns and designed his new column to be fully bakeable. At Oak Ridge the VG Microscopes columns were having increasing issues with failures and stability. DOE was again persuaded to invest in a new microscope, and an UltraSTEM was acquired, with newly improved stabilized power supplies. Ondrej provided the perfect test sample, monolayer BN, and we achieved the first atom-by-atom identification of B, C, N and O directly from the intensity in the ADF image, see Fig. 12 [101]. Finally, through aberration correction, a Z-contrast image was not just for heavy atoms. It was another good demonstration of the power of incoherent imaging since it was very difficult to distinguish these light elements based on coherent images due to the similarity in atomic scattering factors [102]. In the Z-contrast image however the scattering cross section of O is over double that of B allowing a reliable identification even in the presence of noise (Fig. 12c).

The UltraSTEM used a VG Microscopes gun, with modified electronics, but represented a new trend in atomic resolution imaging: The use of lower acceleration voltages, which Ondrej termed “Gentle STEM” [103]. With graphene for example, 60 kV was well below the knock-on damage threshold and intrinsic defects could...
Fig. 10. A sequence of frames from a through-focal series of Z-contrast images of a Si/SiO$_2$/HfO$_2$ high-k device structure showing an individual Hf atom coming in and out of focus (circled). Results obtained with the aberration-corrected HB603, adapted from [79].

Fig. 11. Comparison of incoherent and coherent imaging of SrTiO$_3$ in the ⟨110⟩ projection using a 300 kV VG Microscopes’ HB603U STEM with Nion aberration corrector. (a) A through focal series with 4 nm defocus steps in which the phase contrast images show complex variations in contrast while the incoherent ADF image contrast slowly blurs. All images are raw data and show some instabilities. (b) Under optimum conditions, the phase contrast BF image shows the O columns with high contrast while the ADF image shows the Sr columns brightest, the Ti columns less bright and O barely visible. Microscope parameters are optimized for the smallest probe with, nominally, a probe-forming aperture of ~ 22 mrad, $C_5$ = - 0.037 mm and $C_7$ ~ 100 mm. Adapted from [171].

Fig. 12. (a) Raw ADF image of BN taken at an accelerating voltage of 60 kV. (b) Image corrected for distortion, smoothed and deconvolved to remove probe tails. (c) Line profiles between the indicated arrows shown on (b). Note that O atoms show over twice the intensity of B atoms. Reproduced from [101].

Fig. 13. Controlled nanofabrication of MoSe$_2$ nanowire network from a MoSe$_2$ monolayer by electron beam nanofabrication, adapted from [108].

be studied more easily. Even so, atoms at edges and defects are more weakly bonded and could be knocked into metastable configurations. However, this provides information on the stability of the metastable configurations and has provided much insight into atomic dynamics of nanostructures [104–112], and even allows nanofabrication by electron beams, see Fig. 13 [108].
of oxygen vacancies, which were found to form ordered arrays as a strain relief mechanism but with dramatic effects on film properties, see for example Fig. 14 [118–122].

Ondrej also designed his own gun, using an innovative design to cover both low and high accelerating voltages up to 200 kV, which was delivered to Oak Ridge in the form of the UltraSTEM200. Easily capable of sub-Å resolution, it gave much better images of thicker materials such as CdSe solar cells, clearly revealing the atomic structure and Cl dopant segregation, see Fig. 15 [123–125]. Its higher energy beam also gave sufficient energy transfer to allow the direct imaging of atomic diffusion inside crystals, see Fig. 16 [126]. Quantitative matching of image contrast showed the diffusing Ce atoms to be inside the AlN crystal while density functional calculations revealed the energy barriers.

This was an exciting time for the Oak Ridge group and its many visitors, as we found new applications at both low and high beam energies. We also found new physics, for example, that the energy loss fine structure was dependent on probe position [127] necessitating incorporation of probe position and full solid state bonding effects into the matrix elements [128,129]. Also that large momentum transfer losses at low energy could show atomic resolution, again confirmed by density functional theory [130].

Ondrej’s next project was his monochromator, an innovative design coupling the power supplies for the monochromator and the spectrometer for improved stability [131]. A spectacular energy resolution of only 9 meV was obtained using the Rutgers UltraSTEM, including a redesigned EELS filter, power supplies and detector in addition to the new monochromator. This simultaneous monochromator and spectrometer development allowed vibrational spectroscopy to be achieved in the STEM [132]. Again the EELS signal comprises high and low resolution components with theoretical predictions of atomic resolution being possible [133,134].

Fig. 14. (a) High resolution Z-contrast image of an LCD film showing dark stripes with an average modulation length of three perovskite blocks. EELS line traces vertically averaged within the green box show reduction of O from the dark stripes, green, La M₄ edge, red, O K edge. (b) EELS fine structure across the O-vacancy superlattice. Co L₃/L₂ intensity ratio calculated by using a Hartree-Slater cross-section step function (dark blue points), and also using the second derivative method (cyan dots). The top HAADF image shows the area where the line scan was acquired, blue arrows marking the O-deficient planes. Reproduced from [122]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the rapidly increasing interest in 2D materials the UltraSTEM was highly sought after, its simultaneous efficient ADF and EELS imaging providing quantitative insights into vacancies and defect configurations [113–117]. It also produced numerous new insights into the properties of complex oxide thin films, particularly on the role

Fig. 15. Atomic structure and elemental distribution at a grain boundary in a CdClₓ-treated CdTe solar cell. (a) STEM Z-contrast image showing a Σ₉ grain boundary with symmetric and asymmetric segments indicated by yellow and green dashed boxes, both comprising the same structural units, Cd₆Te₁₂ dislocation cores (white dashed circles). The small blue and large yellow solid circles indicate single Cd and Te columns, respectively. (b) An EELS line scan was taken along the yellow arrow, and (c) the resulting composition profiles show strong Cl enrichment and Te reduction confined to a 1–2 nm range at the GB. Reproduced from [125]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Fig. 16. Selected frames from a sequence of 30 Z-contrast images of a w-AlN single crystal doped with Ce viewed along the [11\bar{2}0] axis. (a–g), Frames 1, 4, 5, 6, 10, 16, 20, respectively, show the locations of a single Ce dopant as marked by the arrowhead in each panel. (h), Frame-averaged Z-contrast image. The observed Ce trace is overlaid and the Ce positions in each panel (a–g) are indicated. The scale bar is 3 Å. Reproduced from [126].

Fig. 17. The relaxed Si (001) surface atomic structure viewed along the (a) [10\bar{0}] and (b) [001] directions. The green-, red-, and blue-colored Si atoms are positioned at the top-, sub-surface and bulk layers, respectively. Simulated focal-series ADF STEM images with (c) α = 30 mrad at 200 kV, (d) α = 60 mrad at 300 kV and (e) α = 100 mrad at 300 kV. Note the changing relative intensity of the arrowed atoms. The focus range is –10 to 35 Å with 5 Å steps. Z-contrast intensity profiles obtained from the (f) X-X' and (e) Y'-Y' regions shown in (b) for the 100 mrad illumination with defocus of –5, 0, +5 Å. The scale bar in (e) is 2 Å. Reproduced from [170]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
4. Reflections

It has been a very rewarding journey with Ondrej seeing the STEM finally achieve what physics has long said was possible, in principle. By far the majority of aberration correctors sold today are for the STEM, and we are seeing continual further developments, applications and improvements in instrument performance. Notable are the increasing use of quantitative imaging to count the number of atoms in a column [135–147]. Mathematical methods are increasingly being used for noise reduction or image reconstruction [148–155] and tilt-series STEM tomography has finally achieved atomic resolution [145,156–159]. Increasingly accurate atomic positions allow ferroelectric properties to be mapped unit cell by unit cell [160–166].

Pixelated detectors seem set to replace the scintillator detector, allowing the imaging mode to be selected after the data has been collected to optimize contrast. In addition, other modes can be constructed such as differential phase contrast to reveal electric or magnetic fields [167] or ptychography [168,169] for high efficiency phase contrast imaging. Particularly intriguing for me is the possibility offered by depth sectioning with high convergence angles. As the depth resolution goes as the square of the aperture angle, with the 60 mrad probe semiances being achieved today sub-nm resolution along the beam direction seems to be in reach. The potential is indicated in Fig. 17, where a focal series of the Si (001) surface reconstruction shows that the different layers of the reconstruction can be distinguished clearly [170]. Of course, real microscopes have chromatic aberration which will blur the depth resolution somewhat, and the noise problem may surface again. However, noise reduction techniques should allow a focal series to be acquired in the time normally taken for a single image. It may be that resolution would be improved by tilting off axis, so that atoms do not lie right behind one another. Perhaps we would no longer need to tilt crystals onto a major zone axis. Perhaps we would not need tilting holders, and we could make even smaller gap pole pieces for ultimate resolution.

Even today, it would be fair to argue that the impact of the aberration corrector on the STEM has brought about a transformation of the field of electron microscopy. Indeed, it is bringing about a transformation in the way materials science is undertaken. We are now able to see the complexities of structure and chemistry at the atomic scale like never before, follow and understand the reaction and transformation pathways that create the materials we desire. Such understanding leads to crucial insights into fabricating new devices with improved properties. Trial and error synthesis is being replaced by sound scientific methodology based on informed knowledge of the actual atomic processes and energy barriers involved.

Truly it has been an exciting and rewarding journey, and one that shows no sign of slowing down in the foreseeable future.

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