

Expunging Diffraction Contrast: EELS and HAADF in STEM

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Abstract. In 1975 the Scanning Transmission Electron Microscope promised to deliver point-by-point information, both structural and chemical, relating to problems of grain boundary segregation, nanostructured phases, glassy materials, and heterogeneous catalysts. Diffraction contrast, so important in TEM, for a while continued to play an important role. But the full utilisation of Crewe's ADF technique, developed for single atoms, but now applied to crystals, required the elimination so far as possible of diffraction contrast. Archie Howie recognised that elimination of Bragg scattered beams, whilst retaining incoherently scattered electrons at larger angles, could be achieved by modifying Crewe's annular detector. High Angle Annular Dark Field, HAADF, is now the most widely used imaging mode in STEM. 'HAADF' might with justification stand for 'Howie's Adaptation of Annular Dark Field'!

1. Introductions

The 'Howie-Whelan' equations for diffraction contrast are extraordinarily successful. The concept of 'diffraction contrast', that is, the observation in the image plane of the microscope of intensity variation due to electrons scattered out of the objective aperture by diffraction, owes its origin to the earliest interpretation of transmission electron micrographs [1]. Until then, contrast had been thought of as 'absorption contrast', like 'mass-thickness' contrast in X-ray images. Such a notion cannot produce the striking effects of thickness fringes, bend contours, stacking-faults and dislocation images. The development by Mike Whelan of contrast from stacking faults, using the simplification of only one diffracted beam multiply scattered back and forth from and into the primary beam, but suffering an abrupt phase change at the stacking fault, led him to a formulation of the contrast using Bloch waves. This he extended to the situation where the phase change is a continuous function of beam traversal. The resulting equations were disseminated in Summer School lectures in 1959. In 1960 Archie, in the course of writing his thesis, produced 'intuitively' the famous coupled equations directly written for the primary and diffracted beam amplitudes scattered in an imperfect crystal. At this point, Archie and Mike decided to collaborate to produce the magnificent papers [2] showing compelling agreement between theory and experimental details of dislocation images. The arrival in Cambridge in 1959 of Hashimoto enabled the three men to include absorption, especially 'anomalous' absorption, into the equations, to produce a relatively complete theory [3]. On this basis, many details of dislocations in many different materials could be studied, especially including extended nodes in networks,

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dislocation loops in quenched and irradiated metals, dipoles and forest interactions, etc. The equations, universally called the ‘Howie-Whelan equations’, now form a topic in most undergraduate lecture courses and in many standard texts.

In 1970 Archie and I both attended a summer school organised by Prof. Valdrè [4] and heard a series of lectures given by A. V. Crewe. It seemed to us that the future of electron microscopy lay in developing the ability to perform chemical analysis in the microscope, based on point-by-point acquisition of images simultaneously with spectra. Archie once said that once you have done something really fundamental – he was thinking of the development of diffraction contrast – it is difficult to change gear! However, under his leadership, the group nevertheless progressively overcame many technical and conceptual difficulties. It educated students, many of whom now lead the field and who apply STEM to a very wide range of problems. Ultimately, immediately after Archie and I retired, the group formed the nucleus of the SuperSTEM unit at Daresbury, which continues many of the lines Archie initiated. Studies of defects using diffraction contrast, once such a major activity, now play a minor role.

This paper is intended to provide a readable outline account of some of the developments along the way, for the benefit of new students who must wonder how the subject became what it now is!

2. Outline developments:

In addition to graduate lectures on electron microscopy, an important activity of the group was the weekly seminar. This was initiated under the banner of the ‘Metal Physics Group’ by Prof. Hirsch. It included both advanced presentations, often by visitors, but also by research students. Attendance at the lectures and the seminar was nearly obligatory. The seminars were held on Wednesday afternoons, to coincide with the one day of the week when there were no undergraduate laboratories in progress, and before the usual undergraduate supervisions began. This arrangement eliminated possible excuses for non-attendance. After about eight months’ work, first year students presented an outline of ‘progress so far’ – a daunting experience, used in part to assess whether they would progress to be enrolled as a graduate student for a Ph.D. Informal discussion was strongly encouraged, and often new ideas emerged and critical responses which had a palpable effect on the quality of the work.

Every year graduate lectures were offered on electron microscopy and spectrometry, including practical work. The lectures were given initially by me, then for many years by Archie, then by successive generations of postdocs. They were attended usually by ten to fifteen students from other departments as well as from physics. A look at the schedules over the years reveals many well-known names: Peter Ward, Mike Stobbs, Alan Winter, Bernard Buxton, Yuan Jun, John Rodenburg, Andrew Bleloch.

Something of the intellectual progress can be gleaned from the fact that in 1985 the name of the group was changed from ‘Metal Physics’ to ‘Microstructural Physics’, and then in 2000, just before it was disbanded, to ‘Nanostructural Physics’.

A research group in a department dedicated to science education is unlikely to have the resources to develop and construct entirely new instruments. The policy must be to purchase them, and then to add such modifications as seem timely and effective in the pursuit of research objectives. The table shows in outline how the group developed STEM after the first instrument arrived and the Physics Department (Cavendish Laboratory) moved to a new building. In addition to the line shown here, Archie used the acquisition of two front-line high resolution microscopes to investigate glassy structure, epitaxial thin films, and other microstructural problems. I continued investigations of defect structure in fatigued and irradiated metals, but added segregation studies at grain boundaries and in diamond.

3. Road to HAADF.

Early experience with dedicated STEM exposed us to many unfamiliar problems. High resolution analytical techniques included microdiffraction and EELS. Both yielded novel results rather quickly. But the acquisition of data was cumbersome, subject to errors such as drift of beam and specimen, as well as noise. As outlined in the table, significant

Table 1

YEAR	DEVELOPMENT	COMMENTS
1974/75	VG HB5 STEM ARRIVES: FIELD EMISSION GUN, TOP ENTRY SPECIMEN LOADING; INSTALLED IN NEW CAVENDISH	GRIGSON COIL SERIAL MICRODIFFRACTION ACQUISITION; MAGNET SCAN FOR SLOW SERIAL EELS COLLECTION; ADF DETECTOR
1974	ARCHIE COMMENCES STUDIES OF IN SITU EPITAXY IN VACUO	LECTURES ON EPITAXY AND DEFECTS BY J. W. MATTHEWS, M. J. STOWELL, W. M. STOBBS
1976	DRIFT TUBE ENABLES FAST HYSTERESIS-FREE ELECTROSTATIC SCANNING FOR EELS	PHIL BATSON (GLASGOW SUPPORT) COLLIEX STARTS ENERGY FILTERED IMAGING
1977	ARCHIE COMMENCES CATALYST STUDIES	
1977	EDX DETECTOR INSTALLED: X-RAY ANALYSIS OF CATALYSTS AND OTHER PARTICLES STARTS	LECTURES BY RUFUS RITCHIE ON PLASMONS AND INELASTIC SCATTERING
1977	PHIL GASKELL ARRIVES	
1979	CL DETECTION BY TAPERED SILVER TUBE	PENNYCOOK
1979	DIFFERENTIAL PHASE CONTRAST - SPLIT DETECTOR	JOHN CHAPMAN (GLASGOW SUPPORT)
1979	H.A.A.D.F.	HOWIE, TREACY, PENNYCOOK
1980	DENNIS McMULLAN ARRIVES	
1980	VIRTUAL OBJECTIVE APERTURE - CRAVEN DESIGN EFFECTIVELY REDUCES X-RAY BACKGROUND	CRAVEN GOES TO GLASGOW
1980	PHYSICS OF ELECTRON AND PHOTON DETECTION	LECTURES BY PENNYCOOK
1980	LECTURES ON STRUCTURE OF GLASSY MATERIALS	P. H. GASKELL, C. S. CARGILL
1981	HB501 ARRIVES FOR SURFACE STUDIES	CAROUSEL SPECIMEN LOADING - IMPROVED VACUUM AT SPECIMEN
1983	SECONDARY ELECTRON DETECTOR	IMESON/McMULLAN
1983	MICRODIFFRACTION CAMERA	RODENBURG/McMULLAN
1985	COINCIDENCE COUNTING	BLELOCH/MULLEJANS
1987	McMULLAN SPECTROMETER	CCD/EELS/ENERGY FILTERED MICRODIFFRACTION
1988	SP501 FOR BEAM WRITING	
1990	HOWIE BECOMES HEAD OF DEPARTMENT	
1991	STM PURCHASED	HOWIE
1992	ESEM PURCHASED (MP AIDS POLYMERS AND COLLOIDS GROUP GET STARTED)	DONALD
1994	PROF. RON BURGE ARRIVES	
1995	SPH. ABERRATION	KRIVANEK/DELBY

	CORRECTION	
2000	VOLTAGE STABILISER FOR SPECTROMETER	McMULLAN
2000	FUNDING SECURED FOR SUPERSTEM AT DARESBURY	GOODHEW, KIELY, BLELOCH, BROWN, BRYDSON
2001	RETIREMENT OF HOWIE AND BROWN	GROUP MERGES WITH PCS GROUP

improvements were made in the first few years. In addition, the group lacked experience in high vacuum and field emission. A crucial development was Archie's bold venture into studies of 'supported' catalysts, usually heavy metal particles of nanometre size dispersed in a matrix of much lower atomic number. He set Mike Treacy the task of looking at these. The problem soon encountered was the variable scattering due to diffraction effects from particles and matrix. A version of the annular detector pioneered by Crewe was provided with the microscope. The detector was positioned on the electron exit end of the specimen cartridge, giving an effective lower collection angle of about 12mr, with the upper angle limited by the bore of the cartridge to about 50mr. The resulting images were very poor, scarcely visible particles on a background made patchy by variations in thickness as well as diffraction contrast. Archie recognised that increasing the outer collection angle would at least partially eliminate the diffraction contrast. But how could one do this neatly? The cartridge bore seemed an impermeable obstacle.

As shown in Table 1, at the same time, Pennycook was developing methods for the collection of cathodoluminescence (CL) from single defects. He had designed and used successfully a tapered internally reflecting silver tube, the narrow end of which could be placed close to the source of light in the specimen, and the wider end of which could be matched to a quartz light guide, thence to a photomultiplier detector. With Treacy, he recognised that the CL collector could be modified by placing a small annular glass scintillator close to the specimen, thereby avoiding the bore of the cartridge. Fig. 1 shows the configuration. The inner angle of collection could be increased to about 100mr, and the outer angle to 400mr, essentially infinite so far as scattering theory is concerned. The resulting images were much improved, now useful, enabling size distributions of the particles to be obtained. The image could be further enhanced by dividing the HAADF signal by the energy-filtered low angle signal to eliminate some of the variation due to thickness in the substrate. This image is a version Crewe's 'Z-contrast' image, now made useful for crystalline specimens. Although HAADF stands for High Angle Annular Dark Field, it seems appropriate to refer to it as Howie's Adaptation of Annular Dark Field. Fig. 2, reproduced with permission from Treacy's thesis [5], shows images of Pd particles in a charcoal substrate. In Fig. 2(a) is a bright field image, energy filtered to remove losses greater than about 5eV. The thicker substrate at the top of the image transmits few zero-loss electrons. Fig. 2(b) shows the ADF image, which clearly suffers from confusing diffraction contrast and mass thickness contrast from the substrate. Fig. 2(c) shows the HAADF image, now showing the particles with greater and much more reproducible contrast, although residual substrate scattering is present. Further images of Pt on alumina show similar effects.

The principle of HAADF can be understood simply. Atomic motion, either zero point motion or thermal agitation, has the effect of producing a diffuse background in the diffraction pattern, but more importantly, of reducing the intensity in the Bragg peaks. When the amplitude of the motion exceeds the spacing of the Bragg planes, coherent interference between the scattered waves is lost. The atoms scatter independently, or incoherently. The higher order Bragg reflections, scattered to larger angles from the more closely spaced Bragg planes, are most affected. The trick of HAADF is to eliminate from the image those beams from the lower order reflections. If the scattering is truly incoherent, it is caused by Rutherford scattering from the atomic nuclei, with intensity proportional to the square of the

atomic number, Z . Crewe's Z -contrast is achieved by dividing the HAADF signal by the inelastic signal, proportional very approximately to the number of electrons.

As first emphasised by Pennycook and Boatner [6], because they are formed from incoherently scattered electrons, HAADF images display intensity much less dependent upon foil orientation, thickness, and microscope defocus than images resulting from diffraction contrast or phase contrast. Atoms of higher atomic number than the background appear bright. It becomes possible to interpret the images intuitively. It is largely for this reason that HAADF imaging has become so popular. However, as pointed out clearly by Treacy, Howie and Pennycook [5], the Bragg scattering is never totally suppressed. For example, long wavelength phonons contribute to the root mean square atomic vibrations, but leave the relative motion of atomic near neighbours highly correlated. The effect of long range strain is to change the background intensity in the image, and the effect of electron channelling down atomic columns enhances coherent scattering and localised intensity. A review by Nellist [7] is recommended.

In spite of these complications, HAADF is by far the most utilised imaging mode in STEM. It is compatible with EELS, and transmits over an angular range large enough to acquire useful convergent beam diffraction patterns. A search through Google throws up 100,000 references of all sorts, still much less than a similar search for diffraction contrast, which yields nearly 6 million. It is fair to say that without HAADF, STEM would be far less widely practised than it is.

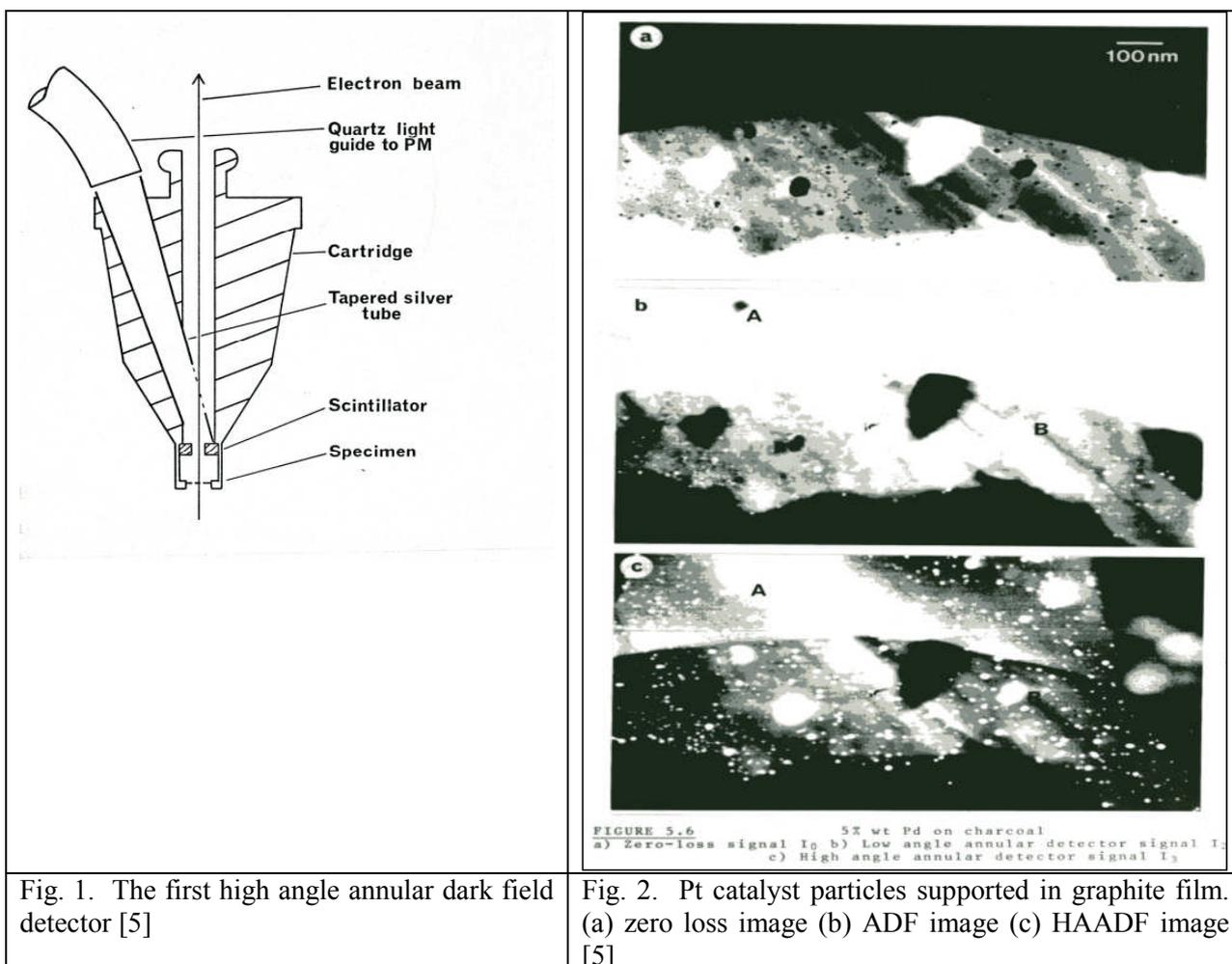


Fig. 1. The first high angle annular dark field detector [5]

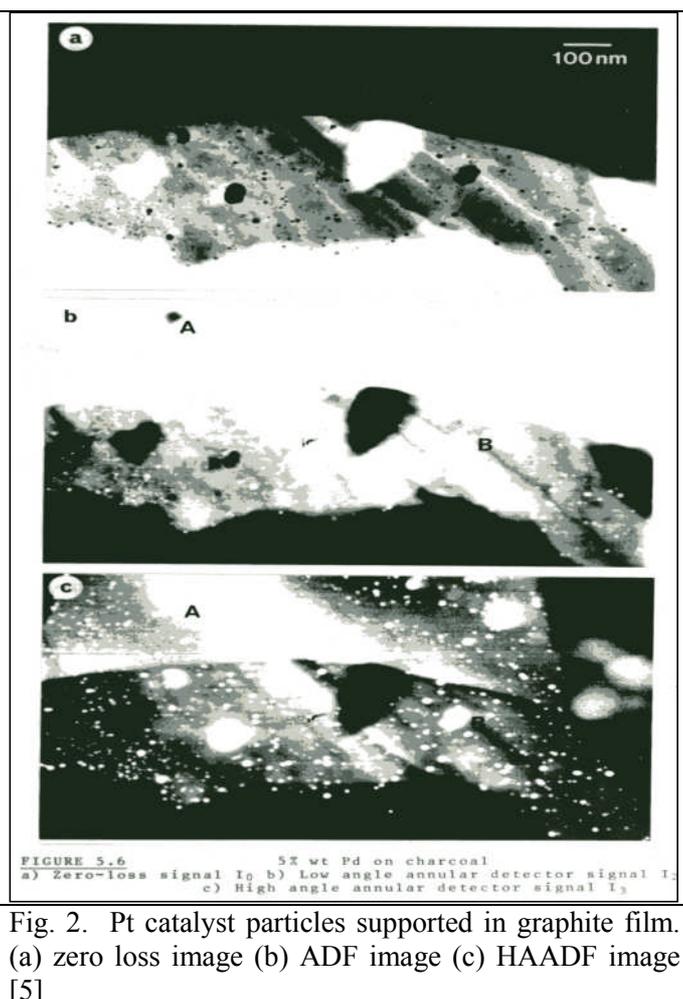


Fig. 2. Pt catalyst particles supported in graphite film. (a) zero loss image (b) ADF image (c) HAADF image [5]

4. Development of EELS

The early acquisition of spectra by scanning the magnetic field in the spectrometer was slow, noisy, and suffered from hysteresis. The rule was: the same spectrum must be obtained three times, and the features observable in all three were probably real! Many visitors played a role in improving the system, starting with Phil Batson's design of the 'drift tube' which enabled fast electrostatic scanning, and ending with Dennis McMullan's design for the parallel acquisition of spectra using CCD detection and optical coupling to the spectrometer output. Early work by Howie and his students confirmed that the spatial resolution achievable is very great, fundamentally limited by the impact parameter [8]. This permits atomic resolution for core transitions greater than about 100eV. At about the same time, it was demonstrated that lattice fringe contrast is preserved in images using only electrons which have lost energy to plasmon excitations with energies around 25eV, although the resolution is degraded by the increased scattering angles [9]. This latter observation promoted much discussion as to which comes first as the electron traverses the specimen, the inelastic scattering or the elastic diffraction! But the impact parameter for the plasmon is large enough that either way contrast is preserved. An extraordinary development of these ideas is the recent intense interest in the excitation of valence losses – mainly plasmon losses – in particles of nanometre size. It is possible to excite the losses when the probe is positioned not inside the particle, but near it (the so-called 'aloof' mode of excitation) and to observe energy losses due to various resonance modes. Howie has reviewed the fully relativistic theory [10, 11] which can treat edges and corners of particles, as well as interfaces. The interested reader is recommended to view recent spectacular recent images of excitations in triangular metallic nanoparticles [12]. This is a far cry from the diffraction contrast of nearly 60 years ago! Over that period, Archie and his group have been leaders in the remarkable progress in electron microscopy, witnessed by successive EMAG conferences.

5. References

1. Hirsch, P. B., Horne, R. W., and Whelan, M. J. 1956 *Philos. Mag.* **1** 677-684, also Whelan, M. J., Hirsch, P. B., Horne, R. W., Bollmann, W., 1957 *Proc. Roy. Soc. Lond.* **A240** 524-538.
2. Howie, A., Whelan, M. J., 1961 *Proc. Roy. Soc. Lond.* **A263** 217-237 & **A267** 206-230.
3. Hashimoto, H., Howie, A., Whelan, M. J., 1962 *Proc. Roy. Soc. Lond.* **A269** 80-103
4. Crewe, A. V., 1971 in *Electron Microscopy in Material Science*, U. Valdrè, Ed., Academic Press, N. Y.
5. Treacy, M. M. J., Howie, A., and Pennycook, S. J., 1980 *Electron Microscopy and Analysis 1979* T. Mulvey, Ed., Conference Series No. 52, Inst. of Physics, Bristol and London; p 261; also Treacy, M. M. J., 1979, *Electron Microscopy of palladium and platinum catalysts*, University of Cambridge Ph. D. thesis.
6. Pennycook, S. J., and Boatner, L. A., 1988 *Nature* 336 656-567
7. Nellist, Peter D., 2011 Ch. 5 in *Aberration-Corrected Analytical Transmission Electron Microscopy*, Rik Brydson, Ed., John Wiley and Sons, Chichester.
8. Craven, A. J., Gibson, J. M., Howie, A., and Spalding, D. R., 1978 *Philos. Mag.* **38** 519-
9. Craven, A. J., and Colliex, C., 1977, *Electron Microscopy and Analysis 1977* D. Misell, Ed., 271 – 274.
10. Howie, A., 1999, Interpretation of spatially resolved valence loss spectra, Ch 6 in *Topics in Electron Diffraction and Microscopy of Materials*, P. B. Hirsch, ed., Inst. of Physics, Bristol.
11. Howie, A., Aizpurua, J., García de Abajo, F. J., and Rafferty, B. K., 1999, *Jpn. J. of Electron Microscopy*, **48**, 673-679.
12. Nelayah, J., Kociak, M., Stéphan, O., García de Abajo, F. J., Tencé, M., Henrard, L., Taverna, D., Pastoriza-Santos, L., Liz-Marzan, L. M., and Colliex, C., 2007, *Nature Physics*, **3** 348-353.

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