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Quantitative Electron Microscopy Workshop
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August 24–28, 1992

U. Dahmen and K. Krishnan, Editors

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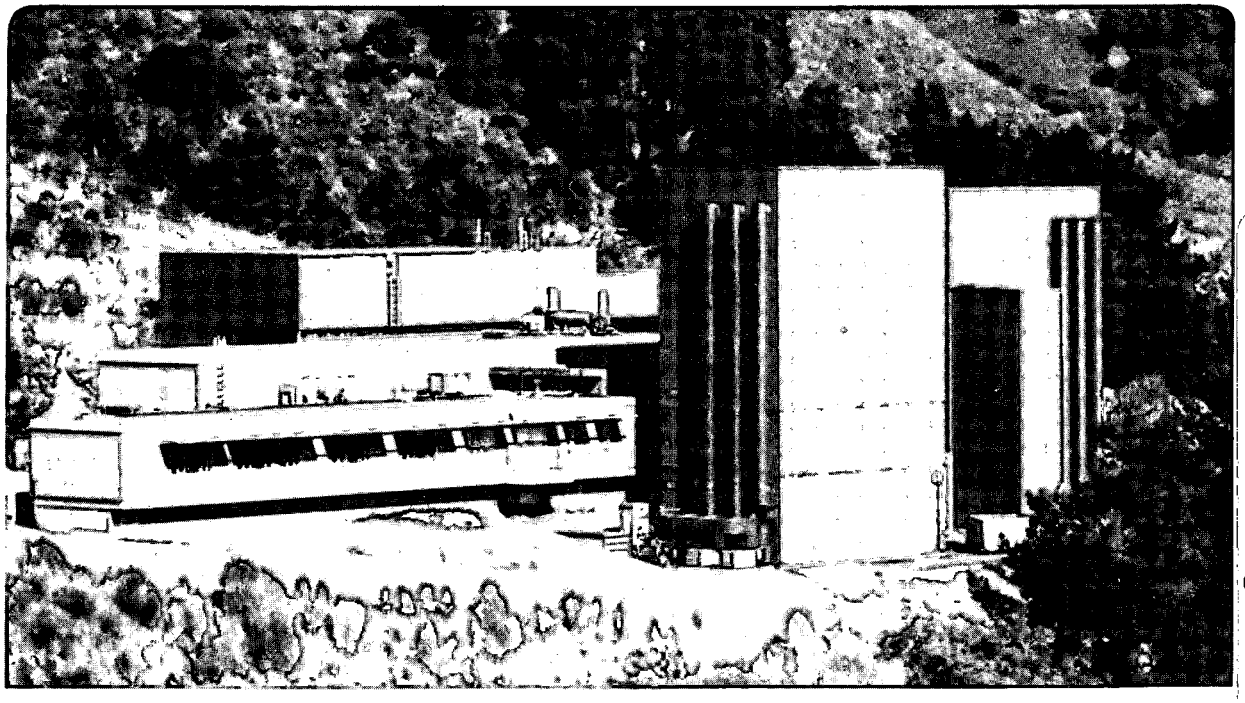

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Quantitative Electron Microscopy

Notes from an international workshop held at the National Center for Electron Microscopy Lawrence Berkeley Laboratory, University of California, Berkeley, August 24 - 28 1992

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PREFACE

For too long the field of electron microscopy has been viewed as a qualitative discipline, while its quantitative aspect has been neglected in favor of the artistic content of its images. It is true that electron micrographs have given us striking pictures of the microscopic and sub-microscopic world of microstructures and defects. And while the interpretation of images requires the expertise of the specialist, their aesthetic value has an appeal of its own. The images obtained directly on film speak to a wider audience than graphs. But perhaps because of its origin as a visual imaging technique, its quantitative side has not been developed to the same extent as is found for other techniques that do not have an "image problem." As electron microscopy matures into the major technique for micro-characterization of materials it is time to reassess its quantitative side.

It was the intent of this workshop to address this quantitative aspect of electron microscopy. The goal was to examine the state of the art or rather, the state of the *science*, of electron microscopy and to attempt to define the current limitations and future directions for the field. Its emphasis was on quantification: the numerical description and error limits of the information that can be extracted from micrographs, diffraction patterns, spectra or other signals.

We know of several previous efforts to address the subject of quantitative electron microscopy. The first was a workshop in 1964, held in Washington and organized by F. Bahr and E. Zeitler with proceedings published in *Laboratory Investigation*, vol. 14, number 6, part 2. The latest was a 1991 workshop in Schloß Ringberg/Germany, organized by W. Baumeister and again, E. Zeitler, with proceedings published as volume 46 of *Ultramicroscopy* in (1992). The tremendous progress that has been made in the intervening period is apparent from these proceedings. The main emphasis of these workshops was on quantitative electron microscopy in biology, although many of its conclusions apply to materials analysis as well.

A number of recent advances in instrumentation and computing power make this a very appropriate time to reexamine the field from the point of view of materials analysis. These advances include instrumentation such as CCD cameras and X-ray and energy loss detectors, field emission guns, energy filters, and of course enhanced computing power and computer control. All this has made it possible to readily obtain digitized maps of electron density, to process or transform these data maps and to compare them with models in automated cycles of parameter refinement. The result may be a lattice parameter, an atomic location or a composition. Such single

parameter refinements can be described easily and with well-defined error limits. Many other materials parameters cannot be expressed as a single number but may require a vector, vector field, a symmetry group, a geometrical shape, a power spectrum or other data sets for their description. The challenge to electron microscopy is to find adequate means of accurate data measurement and quantification for all these data sets. The magnitude of this challenge became clearly apparent in the course of this workshop.

Some of the conclusions of the workshop are summarized below. A most striking feature is the fact that many of the advanced techniques, algorithms and instrumentation for fully quantitative analysis are already becoming available now. However, since they are often cumbersome to use or insufficiently integrated, their application to the characterization of materials is lagging far behind. Much of the needed effort in bringing these advances to bear on the field of materials science is therefore that of integrating new techniques and instrumentation in a way to make them readily available to the materials community. This point is illustrated by the following partial list of conclusions discussed in this workshop:

- Improvements in microscope resolution from the resolution limit to the information limit can be achieved by focal series reconstruction. Extension beyond the information limit can be reached by combination with diffraction. To make this type of electron crystallography a routine procedure it is necessary to integrate microscopes with appropriate computer control and software for truly quantitative data analysis.

- For the determination and refinement of crystal structure and bonding in perfect crystals or at defects, inclusions or interfaces, a combination of TEM techniques is necessary. Coupling EDS (for composition) with HREM (for structure determination), CBED (for symmetry and structure refinement) and PEELS (for bonding and composition) will have to become routine for a fully quantitative analysis. All this is possible from specimen areas as small as a few unit cells in diameter but requires implementation of fast and simple procedures for quantification.

- Dynamic studies by electron microscopy have great potential due to microfabrication capability and specialty stages, ultrahigh vacuum, environmental cells, new electron sources, new imaging modes and recording devices. Instruments specially designed for specific experiments can be very effective in solving critical problems. The benefits of designing an electron microscope around an experiment are apparent from the recent work on the mechanisms and dynamics of Si oxidation.

- The quantitative elucidation of physical, chemical and magnetic properties and correlation with microstructure from the same area of a sample over length scales ranging from Angstroms to

microns will be invaluable in the study of magnetic materials. This will require novel approaches to instrument design, including the development of a special objective lens with minimum leakage flux in the specimen environment. For magnetic surfaces, the newly developed SPLEEM instrument holds enormous potential.

- Significant advances are possible in development and improvement of X-ray detectors for microanalysis at greatly enhanced sensitivity and resolution. Even though quantification procedures for EDS microanalysis are well established, related instrumentation development significantly lags behind that for PEELS. Particular attention should be paid to novel multiple detector configurations, new X-ray detectors and signal processing hardware.

- It is now routinely possible to obtain ELNES at sub-eV resolution. However, the quantitative interpretation of these fine structures, though well demonstrated for select systems, will depend upon a concerted theoretical effort in interpreting these solid state effects if the technique is to find more widespread application.

- In electron energy-loss spectroscopy the inner shell edges show many oscillations about the smooth atomic edge shape. These are mainly due to solid state effects. The interpretation of these fine structures is still a subject of controversy, and even the goals of quantification have not been fully defined.

- Increased attention must be paid to specimen preparation. Current limitations of quantitative analysis are mainly due to specimen noise, contamination or other artifacts. To allow observation of artifact-free thin foils, in-situ specimen preparation techniques or stages to transfer specimens prepared in separate preparation chambers must be developed. Cleaner sample surfaces will improve signal to noise ratios for structural as well as micro-chemical analysis. This applies to thin foils prepared from bulk materials, as well as to thin films and coatings which could be examined without the necessity for further thinning to electron transparency if thin films were deposited for the specific geometries necessary for observation in the TEM.

- Electron holography holds great potential for quantitative mapping of electric polarization fields, imaging of magnetic and superconducting materials and other novel applications, especially if combined with dynamic observation.

- Digital recording is essential in quantitative data extraction and analysis.

- Instrument stability should be enhanced by shielding from all electronic noise, possibly by fiber-optic coupling to control units.

- Energy-filtered imaging and diffraction should become a standard feature of future generations of instruments and will play a crucial role in quantitative data analysis, for diffraction contrast imaging, high resolution imaging, microanalysis and diffraction.

- Spectrum imaging holds great promise for future microanalysis with extensive spatial and compositional resolution. Advances in this area will depend greatly on improvements in the ability to acquire, store, handle, analyze and correlate large sets of data.

Many other conclusions from this workshop not explicitly highlighted here can be found in the body of this report which has been collated from the notes of the session reporters. It is the sum of their efforts that is represented in this document. After some discussion about the format, it was decided to leave the individual reports basically unchanged, with only a minimum of editing. This has resulted in a more colorful document that maintains some of the diversity and excitement, as well as some of the uncertainties, of the workshop.

U. Dahmen and K. Krishnan

Berkeley, California
December 1992

QUANTITATIVE STRUCTURE DETERMINATION

(M.A. O'Keefe)

Overview: J. Spence
Chair: A. Eades
Panel: J. Bentley, K. Downing, A. Fox, J. Silcox, S. Hovmöller

1. Scope

The session produced an *ad hoc* definition of "quantitative," then went on to describe the various CBED techniques available for the determination of crystal structure. Discussion focused on methods and procedures for using these techniques in order to interpret experimental results quantitatively, and thus to derive structural information about perfect (non-defect) crystal materials.

The session covered structure determination for inorganic crystals and did not attempt to treat the volume of work that exists for structure determination of surfaces, inorganics (polymers and biologicals), and amorphous structures (including radial distribution functions).

2. Problem

The problem under discussion was how to derive information that will lead to quantitative measurements of physical properties by examining the specimen in the electron microscope -- in this session the required property is the crystal structure of the perfect (defect-free) material.

"Quantitative" means measuring a property numerically to some given accuracy. Spence proposed to arbitrarily use a figure of 1 percent; i.e., a measurement is quantitative if it has an accuracy of 1 percent.

3. Structure Determination

Spence pointed out that quantitative structure determination is driven by available technology; recent advances in instrumentation, such as CCD cameras, energy filtered electron microscopy, and field-

emission guns (FEGs), have enabled electron microscopists to produce quantitative results. This is important, because "You don't understand something until you can measure it."

3.1 Strategies for structure determination

The strategy most suitable for structure determination depends upon the size of the unit cell of the perfect crystal under consideration. Information needed includes the positions of the atoms making up the unit cell, or the charge-density distribution within the unit cell.

3.1.1 Very large cells

Such cells include biologicals, polymers, and minerals; applications to minerals are described by Zvyagin [1]. Higher voltages are an advantage because of the flatter Ewald sphere, but require low temperatures to minimize radiation damage. Analyses of selected-area diffraction patterns can be carried out using the approximations of kinematic theory for thin crystals and a flat Ewald sphere, with a dynamic correction if necessary. Because of radiation damage, a large number of unit cells must be imaged and averaged over; hopefully the crystal does not bend too much within the illuminated area. Small amounts of bending are allowable for thin crystals under the projection approximation. Whereas x-ray structure factors can be used to produce a charge density map of the unit cell, the map produced from electron scattering factors is a "potential map;" the two are, of course, related by Poisson's equation.

3.1.2 Medium (>5Å) cells

Such cells include inter-metallic alloys. To find atom positions the preferred method is convergent-beam electron diffraction (CBED) using the method of Taftø and Metzger in which the illumination aperture is opened up to produce a large-angle beam so that the diffracted orders can overlap to produce useful information in the zero-order disk. This method has been used with great success in finding atom positions in intermetallic alloys.

3.1.3 Small (<5Å) centro-symmetric cells

Another large-angle CBED method uses the higher-order Laue zones to measure atom positions when the phases of structure factors are either zero or pi[2]. In a systematics orientation this method can be used to study the bonding between atoms; in this case a photomultiplier makes a better detector than a CCD or imaging PEELS, since the detector then has better statistics and the data we need is present in one line.

3.1.4 Small (<5Å) non-centro-symmetric cells

When the unit cell is non-centrosymmetric (acentric), we need two-dimensional data because the phases of the structure factors are not just zero and pi (positive and negative), and we need to measure them accurately in order to find the atom positions or to make a charge-density map. There has been no satisfactory method of measuring structure factor phases. X-ray measurements of inner reflection phases are accurate to only ±45° which is not sufficiently accurate for bonding studies.

3.2 Advantages of energy filtering

Energy-filtered CBED patterns exhibit much more detail than unfiltered ones. There is an optimum thickness for elastically-filtered patterns (patterns containing only the elastic signal) -- too thin no inelastic to worry about, too thick then all inelastic and nothing in elastic channel. Filtered CBED patterns exhibit oscillations in the rocking curve that are not visible in unfiltered due to the inelastic background. Low-order reflections tell us about bonding, high-order about atom positions. HOLZ lines tell us about strain -- accurate measurements of unit cell constants, and about Debye factors. From CBED patterns, we can get space groups and distinguish enantiomorphs (e.g., right- and left-handed quartz).

With a suitable computer program it is possible to refine parameters like crystal thickness, electron wavelength (i.e., accelerating voltage), structure factors, absorption potentials, Debye-Waller factor and atom positions. Spence uses a Bloch-wave program controlled by a least-squares refinement program (Simplex method using chi square) -- looks for global minimum in a function of many parameters. All parameters are treated equivalently in the program, just as in the Rietveldt method used in neutron scattering analysis. With this program, we can find bonding, atom positions, and cell constants -- from a volume of material only a few Å across if a we use a FEG to produce the CBED pattern with a suitable detector to provide a signal that is very accurately quantifiable.

4. History of structure determination with electrons

- 1928 Arnold Sommerfeldt sets Hans Bethe the problem of explaining the intensities in Davisson's and Germer's diffraction results.
- 1930 Bethe produces the Bloch-wave theory of RHEED.
- 1932 Shinahara notices that Kikuchi lines were not quite at Bragg positions due to dynamical shifts.
- 1937 Möllenstedt builds his first electron diffraction camera in a wine bottle; it operates at an electron energy of 45keV (later 65keV and 750keV).
- 1940 McGillivary analyses Möllenstedt's pattern.

- 1945 For better interpretation, Blackman extends Bethe's work to the transmission case.
- 1957 Kambe solves the 3-beam case and shows that, while phases cannot be measured. sums of phases can be.
- During the '60's Goodman and Moodie develop CBED theory, as does Lehmpfuhl.
- 1965, Gjønnes and Moodie show that some absences in some beam directions remain invariant, even through dynamic scattering, for all specimen thicknesses and accelerating voltages, and can be used to identify screw axes and glide planes, as well as other symmetry elements.
- Using the critical voltage method in 1971, Gjønnes and Heuer find zeros in the pattern, and show that they depend on sums of phases.
- In the 1970's, Steeds' group and Buxton develop methods to apply CBED to a large range of problems in materials science, solid-state chemistry and solid-state physics; they also extended the theory of CBED.
- In the 1980's improvements in technology enable Cowley and Spence at ASU (also Brown at Cambridge) to advance nano diffraction techniques using a coherent (FEG) probe.

5. *Examples of Quantitative Structure Determination using CBED*

Advanced in instrumentation have made CBED a viable technique for structure determination -- in particular for structure factor measurement. It is important to measure structure factors quantitatively, since the crystal charge density determines the physical properties of the crystal -- e.g., the effects of dopants such as Mn in TiAl, which change the structure factors, and thus the material's brittleness at low temperature, via effects on the yield strength through the Ti sub-lattice. We need to measure structure factors to high accuracy because the bonding effects detectable in charge-density maps are only parts per thousand of the peaks due to atoms, yet the mechanical properties are governed by these bonding effects (also, we are looking for changes in only 10% of the bonding, since 90% of the bonding is simply charge overlap from adjacent atoms).

5.1 *Measurement of structure factors in BeO using CBED*

Spence fitted structure factors to experimental CBED measurements for BeO using automated refinement (his computer program for finding a minimum by using the method of steepest descent) to find the global minimum in a six- or seven-parameter n-space. The program, using about 100 beams calculated by Bethe's second-potential method, produced the same value for $|F^*(002)|$ when the minimization was started at two different points corresponding to CBED measurements from two different crystal thicknesses.

Magnitude measurements produced	$|F^*(002)| = 11.59 \pm 0.02$ volts
and the phase value was	$\phi^* = -1.190 \pm 0.0009$ radian

compared with an x-ray value of $\phi^* = -1.195 \pm 0.044$ radian

Thus the x-ray value has 50 times the error of the CBED value. Errors in the value from CBED include counting noise, crystal thickness measurement error, error in measurement of the accelerating voltage, and error in the value of absorption coefficients used for refinement.

Measurements of structure factors are important in determining the amounts of doping in silicon and intermetallics, and are *very* important in looking at dopants at grain boundaries since they determine the interface energy and thus the strengths of materials.

5.2 Determination of oxygen content in YBa2Cu3O7-d using CBED

The amount of oxygen (or the value of δ in $YBa_2Cu_3O_{7-\delta}$) can be found by accurate determination of the unit cell parameter. Spence used CBED on a 400keV FEG-TEM with a 20Å probe to look at two different positions within a sample of $YBa_2Cu_3O_{7-\delta}$. He found a shift in a HOLZ line indicating a change in lattice parameter from 3.8198Å to 3.8252Å. This indicates a change in b/a from 1.0187 to 1.0174 (with an error of 0.015%) and a shift in the δ value from 0.1 at one position to 0.27 at the second.

The best fit to the unit cell constants is found by measuring a large number (say 400) of line intersections and using a computer program to find the best-fit cell constants by minimizing the differences in the intersection positions of the experimental and computed patterns. Line intersections are used for accuracy rather than plain shifts, but take care to minimize dynamical diffraction effects (by avoiding zone-axis orientations) because these effects can also produce line shifts. Also, strain measurements in thin foils are subject to relaxation at the surfaces.

6. Quantification of Nano-Probe Patterns

Although such patterns have not yet been quantified, they point the way. Small probes are best since most specimens are perfect crystal for a sufficiently-small probe and we can then use perfect-crystal theory for interpretation. Small probes avoid defects, specimen bending, and variations in thickness. But diffraction patterns get bigger as probes get smaller. It is possible to demagnify the electron source sufficiently to coherently fill the condensor aperture, and produce a completely-coherent probe. Steeds showed that overlapping orders produced from a coherent probe can show interference effects that depend upon instrumental parameters such as spherical aberration, defocus, probe position, the electron wavelength, and instrument instabilities; the overlaps are thus as difficult to interpret as HREM images, and the "resolution" of the nano-probe diffraction pattern is limited by a damping envelope.

This method has been used on many systems to produce qualitative results for analysis and measurements of fault vectors, anti-phase boundaries, stacking faults and twins in steels, GP zones in aluminum copper alloys, catalysts consisting of small particles of Pt, Pd and Re. The method is particularly suitable for looking at inter-granular phases of only one or two unit cell width.

Nano-diffraction patterns (where the probe is smaller than the unit cell size) are closely related to HREM images. Shadow images, produced by focussing the probe above the sample, have resolutions approximately equal to the source size (i.e., the size over which it is coherent) and are identical to the HREM images produced by focussing the objective lens a distance from the sample equal to the probe-to-sample distance.

7. Discussion - Structure Determination in Real or Reciprocal Space?

Discussion centered on the benefits of reciprocal-space methods, such as CBED and nano-diffraction, compared with the benefits of real-space methods, such as HREM. The consensus appeared to be that the methods are complementary; quick structure determination is best done from images, but true structure refinement still requires diffraction information.

7.1 CBED Structure Determination

The most accurate structure refinement comes from HOLZ lines in CBED patterns. However, the influence of specimen geometry on CBED patterns is still difficult to include in auto-refinement; Spence's program assumes a parallel-sided plate specimen (which can be tilted) but not a wedge, so any wedgeness introduces error. Other errors occur because we measure the cell constants of the sample in the TEM; this sample is different from the bulk sample because of relaxation after thinning and oxidation of its surface due to ion-beam thinning. However, thickness variation is not a problem; in the work on $YBa_2Cu_3O_{7-\delta}$ the b/a ratio was measured at two positions, near and far from the interface and at different thicknesses, but the extinction distance for HOLZ is long, so the error is small.

To speed up refinement, Hough transforms could be used to characterize HOLZ lines in CBED disks in order to make identification of intersections automatic. Indexing of up to 400 lines is the most-time-consuming step, but auto-indexing software may be possible (even then, manual identification of the zone-axis and the expected symmetry will be necessary).

The original strain work was historically on Kikuchi lines since they are very insensitive to thickness because phonon scattering is generated throughout the bulk of the specimen, but HOLZ lines are so sharp that position measurements are more precise (but not necessarily more accurate);

accuracy improves if you go away from any major zone axis and use an energy filter. Then $\Delta g/g$ is sensitive since g is larger and very sensitive to strain.

It is necessary to calibrate the accelerating voltage; by matching a dynamical calculation to experimental HOLZ lines, it is possible to attain an accuracy of 14V in 100kV. Generally, the high voltage is stable, but varies by a few hundred volts every few months in a step function. Of course, one shouldn't change the gun bias between the calibration and the experiment.

7.2 Structure Determination from Images

High resolution electron microscopy and crystallographic image processing (CIP) can be used to determine atom positions to the TEM resolution limit. We can use either or both of the image and the diffraction pattern to sort out the phases. In solving the purple membrane structure, virtually all the phase information was obtained from the images, with diffraction data used only to get amplitudes not phases. Although images are affected by the CTF (and damping envelopes), these functions can be determined accurately and corrected for. The signal-to-noise ratio is much better in phases determined from images. CIP has successfully been extended from biological applications to high-voltage and inorganic structures; in making a determination of the structure of staurolite, images only were used to get phases and amplitudes, although the amplitudes were not very accurate[3].

CIP has the advantage of computing 500 phases in a few seconds[4] to an accuracy of 1°, compared with hours each from CBED. This yields the structure-factor phases to the resolution limit of the microscope, for at least the strong ones. In many cases the TEM resolution limit, of approximately 2Å, is enough to solve the structure. After using the image to get phases to 2Å, it is possible to use diffraction data to extend the resolution to 1Å, basing the diffraction spot phases on the model from the 2Å data[5]. An image obtained at 2Å resolution can give 0.1Å accuracy in atom positions if the symmetry is known. With diffraction information included, it is possible to refine the determination to 0.01Å accuracy with CIP. In comparison, CBED can produce a phase measurement accuracy corresponding to an atom movement of 0.001Å for a one-parameter structure such as CdS.

Shadow images are two-dimensional, just like HREM images, and do not contain the three-dimensional information of CBED patterns. HREM and shadow images are similar under a weak-phase object approximation, except shadow images are formed with spherical illumination compared with plane wave illumination for HREM images. Since only the overlapping disk portions form HREM-like shadow images, and interference effects wash out in the higher orders due to instrumental instabilities just as in the case of HREM envelope functions, shadow images are resolution-limited like HREM images.

In HREM imaging, the focus-variation method includes phases by combining several images. Since there is an analogy between the CBED shadow-image and HREM, a similar technique could perhaps be used in CBED shadow-imaging by limiting the field of view to the center of the pattern and varying the focus of the probe. It may be possible to use HOLZ lines in an image, forming an image including 3D information in the form of the phase difference between dynamical reflections, although this phase difference depends on specimen thickness and is not only a property of the crystal structure.

To get intensities and phases, perhaps we could take a pair of images; use a large probe to get the amplitudes from small disks, then a small probe to get overlapping disks with interferences showing the phase difference between adjacent beams. However, the excitation error will not be zero, and we really want the phase values at zero excitation error, i.e., at the Bragg conditions.

7.3 Super-Resolution

Both Rodenberg and Cowley have shown how, by taking a series of nano-diffraction patterns in a scanning mode then reassembling them, it may be possible to get below STEM resolution. This super-resolution method works in theory, but once instrumental instabilities are included, then the resolution is the same as the information limit. The Rodenberg approach solves the phase problem, just like the focus-variation method, but has the advantage of four-dimensional information, since it detects a two-dimensional diffraction pattern for each probe position within the two-dimensional projected cell. The diffraction distribution then yields the amplitude and phase of the specimen exit-surface wave, limited by any C_C damping.

7.4 Future Directions

The problem is to routinely carry out structure determination and refinement at high-spatial resolution with TEM, now and in the future. One way is to use CBED to find the space group, EDX to identify the elements present and to get their approximate ratios, then confirm the structure with a HREM image compared with simulations, using any *a priori* information available; the first crystal structure that was accepted by the IUCr based solely on an electron microscope determination, used EDX, HREM, and image simulation [6]. For CBED refinement, use Spence's refinement program from the EMSA EMMPDL.

We can conclude that, for structure *refinement* -- to refine bonding parameters -- we *do* need to have very accurate high-angle reflections, but to just *determine* the structure -- where the atoms are -- we just need the phases of low-angle reflections (say 20 phases) and that is where electron crystallography from images is a very effective technique. The two methods are complementary.

In the near future, structure determination and refinement will become more accurate and automatic. Both CBED patterns and HREM images will be recorded quickly and quantitatively with the use of detectors such as CCD cameras and photomultipliers; in many cases the patterns and images will be energy-filtered to improve signal-to-noise ratio and to facilitate interpretation. Focal-series processing of HREM images will extend the resolution of the image to the information limit of the microscope. By having image data in a digital form, we will be able to pass it to computer programs for crystallographic image processing and automatic comparison with simulated HREM images; similarly, HOLZ-line positions will be extracted for automatic comparison using programs like Spence's. Computer-intensive processing will become faster as processors become more powerful until on-line processing at the microscope becomes the norm. In the longer term, the promise of nano-diffraction, shadow images, and super-resolution may turn out to provide even faster and more-accurate ways to determine and refine specimen structures.

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QUANTITATIVE DEFECT STRUCTURE ANALYSIS

(A. Schwartzman)

Overview: S. Amelinckx
Chair: M. Tanaka
Panel: D. Joy, M. Mills, W. Coene, Z. Liliental-Weber

In his overview lecture, S. Amelinckx presented a comprehensive review of quantitative procedures for characterizing defects by TEM, combining diffraction contrast and high-resolution results. It covered a wide variety of defects, classified by their dimensionality. Zero-dimensional point defects include vacancies, interstitials and impurity atoms. One-dimensional line defects are only dislocations. Two-dimensional planar defects are of two types: (1) ones associated with a translation vector such as stacking faults, antiphase domain boundaries, discommensurations and crystallographic shear planes and (2) others that are defined by an orientation relationship, e.g., twin, domain and inversion boundaries. Finally there are the three-dimensional spatial defects such as cavities, precipitates and gas bubbles.

By quantitative TEM, one of two possibilities is meant. First, the result is specified by a number(s), such as stacking fault and antiphase boundary energies, composition profile across an interface, the Burgers vector of a dislocation, the displacement vector of a translation interface, the strain field of a dislocation or an atomic model for an interface. Second, a binary question is answered, for example, intrinsic versus extrinsic stacking fault, vacancy versus interstitial loop or stacking fault tetrahedron and single or double faults in hexagonal close-packed structures.

Point defects

Only clusters of point defects are visible in TEM diffraction contrast, such as dislocation loops, stacking faults, stacking fault tetrahedra and interstitial precipitates. They are visible due to their strain field and are more appropriately discussed under the heading of dislocations since they are no longer point defects.

In high-resolution electron microscopy (HREM), it is questionable that one can image the effects of vacancies on the atomic column spot brightness. However, what has been feasible in the quantitative analysis of point defects by HREM is to exploit the dependence of the spot brightness on the composition of the atomic column. Examples in the research literature encompass fabricated semiconductor structures, such as GaAs/AlAs multilayers, and antiphase boundaries in ordered long period structures. In the latter case, chemically sensitive imaging conditions are obtained by using the superlattice reflections and well-defined thickness and defocus values. Image simulations indicate a monatomic dependence of spot brightness on chemical composition for thin foils (40 nm or less), but not for thicker foils. Illustrations were given for the alloy systems, Au_4Mn, Au_3Zn, Cu_3Pd, CuAu and AlCu, as well as the YBCO high T_c superconductor. One exemplary quantitative result from high-resolution images of the Cu_3Pd alloy was the measurement of the occupancy along lines parallel to the antiphase boundaries at different distances. From this data, an experimental plot of the ordering profile was obtained and then matched to theoretical ones for determination of the correct long range structure.

Line defects

Quantitative studies of dislocations establish the direction, magnitude and sense of the Burgers vector (**b**), the core structure, dissociation into partial dislocations, atomic configuration and glide plane. Each of these goals can be achieved with diffraction contrast analysis and/or high-resolution imaging. Diffraction contrast image effects have been simulated based on the well-established work by Head and Humble and are widely used in other quantitative diffraction contrast studies.

Weak beam and high-resolution imaging are the only direct means of determining the stacking fault energy by measuring the separation distance between the two bounding partial dislocations, assuming that the equilibrium conditions are satisfied and the elastic constants are known.

Dislocations are also examined quantitatively using HREM by directly imaging the displacement of atoms about the core. The main drawback is that high-resolution images are two-dimensional projections, thus resolving only the edge component when viewing in the zone axis parallel to the dislocation line. The direction, magnitude and sense of the dislocation's edge component are all obtained at once by doing a Burgers circuit on the high-resolution image. This Burgers circuit is an approximation, however, since it is not done in an otherwise perfect crystal.

This procedure has been commonly used for both mixed 60° and pure edge 90° dislocations in semiconductors. When looking end-on at screw dislocations, one should see no effect on the high-resolution image since the displacements are all parallel to the dislocation line. Due to the Eshelby twist, rotation of the atom columns, this is true to a first approximation only.

A few high-resolution studies have been performed in which the dislocation line is perpendicular to the zone axis projection of the crystal. This geometry has not been widely employed up to now. However, one example is lattice imaging of dislocations in lanthanum cuprate, in which the **g•b** criterion was used to determine **b**. Fringes that cross the dislocation and are deformed correspond to a nonzero value of **g•b** and those that are not deformed and remain straight to **g•b** = 0.

Planar defects

Inclined interfaces extending through the foil act as beam splitters in electron diffraction. Resulting fringe patterns due to interference between doubly transmitted and diffracted beams show up in diffraction contrast imaging and depend on both the foil thickness and the character of the inclined interface. Analysis of these fringe patterns leads to the quantitative nature of the planar defect.

Translation faults, for which the displacement vector **R** introduces a phase shift, **g•R**, are visible through alpha fringes. Orientation faults are visible through delta fringes where the boundary separates domains with slightly different deviation parameter. Delta fringes are commonly found in crystals that contain domains with different orientations of slightly a distorted crystal structure. Their contrast behavior is opposite to that of alpha fringes. As one illustration of many, this diffraction contrast technique has been used to study antiferromagnetic domain walls in NiO. One quantitative result was the deduction of the particular <111> axis that corresponds to the contraction direction for magnetostriction .

High-resolution imaging is a direct approach in analyzing planar defects. One measures the fault vector by the fractional shifts of the lattice fringes. Examples were shown for interfaces in polymorphic SiC and an intrinsic stacking fault and Frank loop in C60.

Discussion

Dahmen posed the general question of how quantitatively can electron microscopy map out a complete vector field of all kinds; for example, the whole displacement field of a dislocation and not just its Burgers vector or the electric polarization field about a domain boundary, and similarly the magnetization field about a magnetic domain boundary.

Displacement fields around dislocations

(Amelinckx): Mentioned Bourret and coworkers' research on atom position calculations for dislocations based on atomic models and elastic theory in which they determined the best model by matching simulated images with experimental ones; cautioned that analysis straight from HREM images is risky, the microscope's electron-optical lenses are not perfectly cylindrically symmetric, can have up to 1% error.

(Spence): Reiterated this last point with two examples, quasicrystals versus Pauling's multiple twinning model (only a 1° difference between the two possibilities) and Barry at ASU imaging a square as a rectangle due to projector lens distortions. Spence then posed the important question of precision in locating the atom columns from the image spots knowing *a priori* that we are dealing with single atom columns.

(Mills): Cited Bourret's group results, 0.2 Å, based on image simulations for different defoci, however, assumes a lot (perfectly aligned microscope and sample).

(Kilaas): Brought up the point that in high-resolution electron micrographs, very few of the peaks that represent atomic columns correspond to symmetric and nicely shaped image spots, it is model dependent and also can be affected by noise.

(Amelinckx): Agrees about noise being a problem, so he Fourier filters his images in order to reduce noise before performing any analysis of ordered alloys.

A general conversation ensued about sources of noise that adversely affect the ability to do quantitative analysis using HREM. In particular, what factors might cause the image spots to shift away from the atom column positions. The general feeling is that most critical is the systematic noise due to beam and crystal tilts, which can have an deleterious effect anywhere between 0.2 and 1 Å. After correction of the crystal and beam tilts, 0.1 Å accuracy is possible.

Eades pointed out the overriding effect of beam and crystal tilts give rise on the measurement of rigid shifts. Mills presented an example of how a rigid body translation across an interface changes with defocus and suggested that maybe it is due to a complex interplay between crystal and beam tilts.

This brought up the question whether crystal tilt renders displacement field mapping from HREM images useless. Coene remarked that the mathematical effect of crystal tilt is a common displacement which shows up as a phase shift in Fourier space and is easily factored out. Mills illustrated this point with HREM images of dislocations in Al, they change orientation in thin foils due to low Peierls stresses. Tried to estimate magnitude using embedded atom method calculations and image simulations, got little noticeable effect in experimental images, therefore feels that he can map out the displacement field with some confidence. However, due to a dependence on foil thickness, there is a need for caution.

(Baumann): Has a different approach, divided lattice image into unit cells, then centered each one via computer image processing algorithms before analyzing the information content, can center the unit cell within 0.1 Å. Gave the example of a strain field analysis of a 2% strained InGaAs 20 Å layer via lattice imaging, looked at the tetragonal distortion and plotted displacement over the whole quantum well structure, got 2% as expected.

(Spence): In response to the last example, favors HOLZ line measurement using a 5 Å probe. Wants to know what volume of the crystal contributes to the strain measurement, believes it is reciprocally related to the width of the HOLZ line by the uncertainty principle when measured in the direction normal to the HOLZ line, e.g., measure the HOLZ line width as 1/10 of the 5 Å probe, then looking at a volume corresponding to 50 Å. Can measure strains as small as 10^{-4} this way, but only if the strain is uniform.

While not as precise, Baumann's approach still gives better spatial resolution (3x3 $Å^2$) and therefore allows analysis of modulated structures.

Electric polarization fields about domain walls

(Joy): Using electron holography to investigate 90° domain walls in $BaFeO_3$, Joy and coworkers observed an offset in fringe structure which could be used to map out the variation in electric polarization across 2 to 3 nm thick domain walls. Because the accuracy in measuring the fringe shifts is $\pi/100$, he believes electron holography is well suited for accurate mapping of the

polarization field. These results are the first quantitative, spatially resolved measurements of electric polarization by both magnitude and direction.

Tanaka method for dislocation analysis

Eades raised the question of the use of the Tanaka method (large angle CBED) for dislocation analysis. Spence suggested that it is limited to perfect dislocations only, that you can't see dissociations. However, Tanaka maintains that the resolution is good enough to characterize individual partial dislocations. For instance, in the case of Si, with a LaB_6 electron source and accurate calibration of the magnification, 30 Å resolution is possible.

QUANTITATIVE HREM

(G. Campbell)

Overview: M. Mills
Chair: M. Mills
Panel: F. Baumann, D. Jesson, D. Luzzi, F. Ross, M.A. O'Keefe, R. Kilaas

The session addressed existing methods of quantitative HREM, issues facing further application of these methods, and issues limiting their accuracy. The objective of the methods is to determine where the atoms in a material are located and what type of atoms are on those sites. This objective is moving HREM from a qualitative to a quantitative discipline, where measurement can be made of a quantity of interest and error bars assigned. The approach is complicated by the sensitivity of high resolution images to a host of parameters. The methods used include correlation techniques for measuring atomic column position and intensity and simulated image optimization. Image simulation consists of two separate steps, phase reconstruction to recover the wave function of the electrons as they emerge from the specimen by through focal or holographic techniques and electron scattering simulation to calculate the exit wave function from the atomic structure of the specimen. Techniques used for atomic species identification include high angle annular dark field imaging in STEM and chemical lattice imaging in conventional phase contrast.

Correlation Techniques

Cross correlation of a Gaussian shape with an experimental image is a method of locating the center of a spot-like contrast feature in an image. It is a particularly useful technique for noisy images. It preserves spot position and intensity information. An example of its application is grain boundary expansion due to segregation. When Bi segregates at $\Sigma 3$ boundaries in Cu the grain boundary expands by 0.04 ± 0.005 *nm* compared with a $\Sigma 3$ boundary without Bi, as measured by this technique.[1] The technique has also been used with more complicated features, such as a grain boundary structural unit to map the position of its occurrence along a length of boundary. A drawback of the technique is that the image feature shape information is not used because the features are reduced to a single point. Therefore it is useful for only very simple images with well defined features.

A slightly more complicated technique, but giving more information, is chemical lattice imaging. It has been applied by the selective use of chemically sensitive reflections to form the high resolution image. It is applicable to composition variations on an ordered sublattice. To date, it has been applied very effectively to investigate the roughness and interdiffusion along interfacial planes at interfaces in the GaAs - AlGaAs system.[2] In this case, the method uses the (002) reflections which behave differently for the two materials as a function of thickness. Since the technique depends on the chemical sensitivity of an ordering reflection its application will be limited.

Simulated Image Optimization

Another approach to determine the atomic structure of a specimen is pixel by pixel comparison of simulated with experimental images. It has been applied to dislocation core structures, where image simulations using different models of the atomic structure of the core are subtracted from the experimental images and the differences inspected. The differences are minimized by varying the experimental parameters for the different dislocation models. It was apparent from the inspection that different models matched either the core region better or the surrounding strained region better. Hence, it indicated that a single residual quantity may not be instructive due to better matching in some regions of the image than in others. It was apparent that regions might have to be defined in which to consider the goodness of fit. The technique has the ability to discriminate among shape, position, and intensity of the contrast in the image. As it was applied, the technique is only a small step beyond visual inspection of the match between simulated and experimental images.

Another method implemented recently lets many parameters in the simulation vary, including the atom positions in the specimen, and uses a χ^2 goodness of fit parameter to evaluate the match between the simulated and experimental images. With this method many local minima are found for χ^2, but there is always one minimum which is best. Well defined error bars are associated with the best fit image.[3] A key to the success of the method is the acquisition of a focal series of experimental images and, if the conditions for the χ^2 minimum of each image differs by only a change in focus with the other parameters (such as thickness) remaining constant, then the method is consistent.

These methods have many complicating factors, including crystal tilt, beam tilt, surface effects, amorphous layers on surfaces (specimen noise), inelastic scattering, and defect alignment.

The accuracy of alignment of crystal tilt is typically given as 1 - 2 mrad, but this is very hard to achieve in practice. Beam tilt can be corrected in principle to 0.1 mrad, but this is also difficult in practice. It has been found that these tilts may alter the apparent positions of the center of intensities, for example in boundaries. Amorphous contamination or oxide layers on the sample surfaces introduce noise which can distort images, especially in thin sections. Noise reduction necessitates image averaging, a severe limitation for studies of isolated defects, but possible for bulk crystals and periodic grain boundaries. One solution to this problem is to make the specimen free of an amorphous surface layer (although this removes the material on which to correct the astigmatism during microscope operation). However, outside an ultrahigh vacuum microscope with in-situ sample cleaning capability this is extremely difficult, if not impossible, to achieve.

Inelastic scattering is handled in a number of ways by the simulations. The Debye-Waller factor describes the attenuation of the Bragg reflections due to phonon excitation by changing the shape of the potential (blurring). Values of the Debye-Waller factor are available from x-ray measurements, but they may not be entirely accurate for electron scattering. The absorption coefficient accounts for scattering outside the objective aperture due to phonons and low angle scattering due to plasmons. But this is strictly an approximation, included as an imaginary component of the crystal potential in the transmission function. It leads to a reduction of contrast in the images. A more insidious problem is multiple scattering due to small angle plasmon scattering combined with Bragg scattering. It can lead to high resolution detail. This is more of a problem at greater thickness and at larger defocus because the electrons suffering an energy loss will be brought to a more optimum contrast transfer condition. As a minimum for detailed comparisons, clean samples and well aligned defects are needed.

Simulation optimization can also be carried out in reciprocal space for perfect crystals. It may also be possible for planar defects composed of periodically repeating structural units. But it is impossible for isolated defects such as dislocations. In real space it may be possible to artificially limit the field of view to the cell of interest, whereas this is not possible in reciprocal space.

Elemental Analysis

The discrimination between atomic species by HREM appears to be a very difficult problem. The technique of "chemical lattice imaging" has already been mentioned. Another technique is Z-contrast imaging in STEM using a high angle annular dark field detector, which is very sensitive to the scattering potential (approximately as Z^2). But there are other sources of intensity variation which complicate the interpretation, such as surface contamination or thickness variation. An

amorphous surface layer broadens the probe and decreases the compositional sensitivity. The images are noisy and have not yet been quantitatively evaluated in a rigorous manner. But good results have been obtained for Si-Ge interfaces which is not possible in phase contrast imaging.[4]

Testing the Methods

A test has been proposed for evaluating high resolution image simulation and matching to experiment by using small MgO cubes imaged along [110].[5] It is a simple experiment to perform because the cubes are easily made by collecting the smoke of burning magnesium. The cubes have a symmetric 90° wedge along the beam direction so that the thickness is known exactly as a function of position. The challenge is to match the simulated images to the experiment. The simulations will need to consider absorption, ionicity of the atoms, correct ionicity of the scattering factors, the focus, spherical aberration, and the Fresnel fringes on the edge of the wedge. Because the experiment is so well controlled, the simulations should match exactly, provided the correct assumptions are used and that the microscope parameters are accurately measured.

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QUANTITATIVE AEM I

(F. Hofer)

Chair: P. Batson
Panel: M. Disko, D. Joy, O. Krivanek, J. Silcox, P. Rez, M. Tanaka

This session addressed both experimental and theoretical issues of fine structures in electron energy-loss spectroscopy (EELS). Recent results on near-edge fine structures (ELNES), extended energy-loss fine structures (EXELFS) and low-loss fine structures have been discussed.

Overview of the problem:
Different fine-structure features can be found in the EELS-spectrum:

1. core-loss fine structures: ELNES and EXELFS
2. low-loss fine structures

The qualitative and semiquantitative analysis of fine structures can provide insight into the structural, electronic and hence chemical properties of the atoms undergoing excitations. However, full theoretical interpretation of fine structures is a difficult task and for the moment can only be achieved in particular systems.

1. Experimental constraints

For fine structure studies an energy-resolution of about 0.3 to 0.5 eV is desirable, which can be obtained with microscopes operated with a FEG and a PEELS-spectrometer. The accuracy of the energy-scale (e.g., for identification of valencies) is also very important and sometimes more useful than a very high energy resolution. It has been pointed out that in many practical applications of fine structures LaB_6-sources and PEELS-spectrometers are sufficient (with optimized illumination conditions).

2. ELNES

Typically ELNES can provide information on chemical bonding like coordination, valency and interatomic distances. However, because near edge fine structures depend on the compound-

type (system) it is difficult to derive general guidelines for full quantitative interpretation. While oxide compounds lead to edges with typical fine structure details, metals or related compounds often exhibit no significant edge fine structures.

One approach to understanding near edge structures is to collect "fingerprints" from elements in similar environments (compounds) and try to identify common features. The other approach is to calculate the near edge structures using appropriate theory and identify those features which show sensitivity to a property of interest.

Fingerprinting

As the ELNES exhibits a structure specific to the arrangement and type of atoms in the first coordination sphere, it can be often used as a so called fingerprint. Several examples for the identification of chemical compounds by using the ELNES as a type of fingerprint have been presented:

Carbon compounds are routinely identified by using the ELNES of the C K edge even with an energy-resolution of 1.5 to 2 eV (e.g., amorphous carbon, graphite, diamond, carbonates, carbides, acetylides). With better energy resolution and combined with band structure calculations, more detailed information of the specimen can be obtained: This has been demonstrated by the investigation of the atomic arrangement in BC_3 and in the investigation of the electronic structure of carbon in $YBa_2Cu_3O_{7-\delta}$ with very high energy resolution (0.2eV). The ELNES of the L_{23}-edges of Si and Al can be also used as fingerprints. This has been demonstrated in the measurement of the local stoichometry of thin-oxide injectors between Al and Si layers.

Fingerprinting using the K-edges of the light elements is now in wide use and in many cases it can be theoretically supported.

For a quantitative interpretation of the near edge structures, complicated models are necessary. The fine structures up to 30eV above the ionization threshold can be interpreted either as the result of interference of waves scattered from neighboring atoms or in terms of the local projected conduction band density of states. Methods of calculating near-edge structures are based on these viewpoints: a. XANES cluster calculations and b. band theory methods

a. The XANES method works best when there is strong scattering and the symmetry allows for an obvious partioning into muffin tins. This is the case with compounds containing

oxygen, because oxygen is a strong scatterer and therefore these compounds often provide fingerprints typical for the coordination of the excited element. Then the first coordination shell mainly determines the fine structures such as has been demonstrated for the O K edges of MgO, CaO and SrO or for the B K edges in boron minerals (octahedral and tetrahedral environments). However, XANES calculations have been less successful for the less densely packed semiconductor structures and for layer materials like graphite.

b. A self-consistent pseudo-atomic-orbital band-structure-method has been used to calculate accurate projected density of states. The calculations are in good agreement with the near edge structures of the K edges of diamond, silicon, cubic and hexagonal SiC and Be_2C and with the near edge structures of the L_{23}-edges of silicon and SiC.

While there are no problems with the background subtraction in the near edge region of K and L_{23}-edges, problems may arise in case of delayed M_{45}-edges. It has been argued that 1% accuracy will never be obtained with near-edge structure interpretations.

3. *EXELFS*

Like EXAFS experiments conducted with synchrotron radiation, the corresponding energy-loss modulations can be used to measure interatomic distances. The EXELFS methods is limited to a smaller range of edges, but the information can be obtained from very small specimen regions.

In addition to nearest-neighbor-distances, short-range order and local thermal vibrations can be measured by EXELFS and its temperature dependence: Recent work showed that the temperature variation of the EXELFS amplitude can be analyzed in order to obtain a localized measurement of the Debye temperature (θ_D). Measurements have been performed on the Al K edge of metallic Al in the temperature range 86 K to 236 K within sample volumes of approximately 0.01 μm^3.

EXELFS has been also used to study the short range chemical order and local thermal vibrations of the Al atoms and the Fe atoms in chemically disordered and ordered Fe_3Al. The mean square relative thermal displacements (MSRD) between the excited atoms and their coordination shells have been determined from the damping of the 1 shell EXELFS oscillations as a function of temperature. From this the vibrational entropy difference between chemically disordered and DO_3-ordered Fe_3Al has been determined.

4. Information of the low-loss region

The low-loss region has long been used to study the optical properties of a wide range of materials. It has the advantage of a wide-energy range which ensures an accurate Kramers-Kronig analysis of the energy-loss function to recover the optical dielectrical function.

The low-loss region can be very useful in case of free electron-like materials exhibiting strong, well-defined plasmon losses. Elemental compositions can be derived from the composition dependence of the energy of the plasmon-peak centroid. However, this method is limited to some special alloy systems.

Low-loss studies with very high energy resolution (58 meV) were presented: Data obtained from C_{60} and GaAs were compared with optical measurements and band structure calculations and the band gaps of these materials have been determined from the low-loss region.

The valence-loss data are difficult to analyze and can be complicated by interface and surface plasmons. Other problems are the high background due to the vicinity of the zero loss peak and hence the extremely high dynamic ranges in this energy-loss region. Therefore, it has been proposed to prefer the core edges, because the detection limit for states in the band gap can be better for ELNES.

QUANTITATIVE AEM II

(V. Dravid)

Chair: A. Romig
Panel: F. Hofer, T. Malis, J. Bentley, J. Wittig

This session covered the quantitative aspects of microanalysis with x-rays and EELS, including theoretical, experimental and practical concerns. The topics included experimental and theoretical determination of cross-sections, spatial resolution, analytical sensitivity, trace analysis, segregation studies and specimen-electron-microscope environment interactions.

Overview

Energy dispersive microanalysis (EDS) has reached a mature stage where quantitative analysis of local composition can be performed routinely and with reasonable accuracy invoking the Cliff-Lorimer K-factors. Microchemical x-ray analysis using K-factors is the most widely used analytical technique in physical and life science applications. In contrast, the experimental, practical and theoretical aspects of EELS microanalysis are still not well established for routine applications to problems of interest. Some of the topics of current interest, common to both EDS and EELS microanalysis, include the proper definition and determination of detectability limits, spatial resolution and accuracy of quantification. Other concerns that keep on coming up in the discussion include the effect of radiation damage and specimen-microscope environment interactions. Radiation damage and/or contamination/etching remain as the major stumbling block for extending the limits of microanalysis for problems of real interest.

Major Issues

In his keynote talk, A. Romig touched upon several important issues concerning quantitative (x-ray) microanalysis. These include:

- Electron-Optics: Instrumental parameters

• Electron scattering:	The basics of x-ray generation in thin foils in the microscope environment
• Definitions:	Spatial resolution, detectability limits and their determination
• Deconvolution:	Especially for interface segregation problems
• Specimen:	The ideal specimen for microanalysis

Optics

Microscopes are rareley tuned for x-ray microanalysis. In most cases, microanalysis is taken as an added convenience to the main imaging function. However, the current generation of cold field emission TEM/STEM is an important step forward. The advantages are twofold, (a) a small intense/bright source eliminates the need for any significant demagnification for small probe formation on the sample. This reduces the spurious signal (hole count). (b) appreciable current in a small probe that provides acceptable signal from small interaction volumes. However, the x-ray detector configuration, geometry and hardware developments are far behind the progress seen in EELS instrumentation in recent years.

Theory

There was a consensus that not much progress has been made in the area of cross-sections in the recent past, especially for x-rays. The sensitivity factor (K-factors) approach, though sometimes time consuming, still remains the best alternative. There have been a few studies on cross-section calculations and measurements in EELS. Hofer illustrated that both Egerton's hydrogenic model and Leapman & Rez's modified Hartree-Slater calculations yield similar results for quantification for K-, L_{23} and M_{45} edges. However, the accuracies of analyses differ such that K-edges are can be accurate to <10%, L_{23} < 20% and M_{45} < 50%. There is a long way to go for N and O edges of heavier elements. In any event even < 10% accuracy is clearly not acceptable for most applications. Thus even in EELS microanalysis the standards approach analogous to K-factors in EDS is preferred. Quantification with relative accuracy of better than 10% can be obtained by a careful combination of standards, choice of energy window and careful background subtraction routines. It was pointed out that in addition to the problem of cross-section, varying fluorescence yield for low atomic number elements is still an unresolved issue, largely due to a lack of funding support for theoretical research.

Spatial Resolution

Spatial resolution in x-rays (as well as EELS) may be taken as the smallest distance between two analysis points whose signal volumes do not overlap significantly. Despite the recent

claims of very high spatial resolution with x-rays, beam broadening remains as the major stumbling block for higher spatial resolution in EDS. This is aggravated further by the need to have better S/N ratio in EDS which requires more beam current in thin areas which results in beam damage or thicker specimens, which leads to more beam broadening. The issue of fast secondary electrons (FSEs) and their effect on spatial resolution was discussed by Al Romig. His Monte-Carlo simulations for a C-C interface indicate a very small effect of FSEs on the spatial distribution of x-ray generation. It was pointed out that the problem of FSEs would be severe across an interface between two very different atomic number phases (such as the carbon-copper interface) where the x-ray spatial profile is broadened at higher voltages. Peter Rez suggested the use of transport theory instead of parallel processed Monte-Carlo simulations and disagreed with the problem of FSEs indicating that their cross-sections would be very small. In response, David Joy pointed out the fact that the FSEs can ionize low Z elements nearby quite easily. Thus it is not the cross-sections of FSEs that is a problem, but the ionization probability for low Z.

Spatial resolution in EELS is determined by the probe size and delocalization effect. Delocalization is inversely related to energy loss. Thus for most edges of interest above ~300-500 eV, delocalization is not a serious threat. John Spence pointed out that even for valence losses (low loss) careful manipulation of detector geometry and momentum transfer, one can still minimize the delocalization.

Accuracy and Sensitivity:

In reference to John Spence's "quantitative" criterion of 1% accuracy of analysis, Jim Bentley conceded that it may not be possible to achieve it for most microanalyses with EDS or EELS. Thus began the discussion on sensitivity and detectability limits for microanalysis with EDS versus EELS. Jim Wittig reminded that the counting statistics are the limiting factor in EDS. Other problems in EDS include setting up appropriate nonchanneling conditions for analysis and most importantly radiation damage, contamination and spurious signals. Joanna Batstone indicated that semiconductor dopant analysis requires accuracy in the ppm range which is clearly a formidable task. Peter Rez reminded the audience that Leapman et al can approach close to 1-10 atom detection with EELS and that EDS can at best be in the vicinity of 50 atoms, of course depending on the element(s) detected and the matrix containing them. The difference mode of EELS is very useful for detection of trace elements. EELS detection of K-edges and L_{23} white lines can approach <0.1 wt% but the accuracy of quantification still remains ambiguous. Jim Bentley outlined the problem of chemicalanalysis of radioactive specimen with EDS where the detector

response would be very unpredictable. EELS, on the other hand, can still handle radioactive specimens and does offer very good sensitivity for a large number of elements in the period table.

Combined Spatial Resolution and Analytical Sensitivity

With reference to combined high spatial resolution and sensitivity, Al Romig and Jim Bentley illustrated examples of segregation profile determination by EDS and EELS. It was conceded that a lot of information about segregation profiles is needed for deconvolution since both EDS and EELS do not offer through thickness chemical profiles. Convolution of interaction volume and expected segregation profile can be fit to the experimental data to extract segregation information. David Seidman pointed out these major limitations of segregation analysis with EDS or EELS. Clearly, in a multi-phase space of internal interfaces, local segregation profile is greatly influenced by a large number of interfacial relaxation phenomena. Atom probe FIM provides a useful tool for detailed analysis of segregation profiles.

Specimen Related Problems

Tom Malis discussed specimen related problems in microanalysis. An ideal specimen remains quite elusive. Virtually all the specimen preparation techniques have their own problems. Some are likely to change the defect structure (e.g., ultramicrotomy) others may change the composition (e.g., electropolishing) and some can change both (e.g., ion beam thinning). Although a good specimen is a clear prerequisite for better analysis, specimen preparation still remains the most limiting factor in electron microscopy. Nevertheless, he pointed out that a careful choice of specimen preparation techniques and better control of microscope environment (i.e., better vacuum, LN_2/heating holders) can circumvent the problems in some cases. The quality of analysis today depends more on the problems of radiation damage, surface films, contamination and etching, rather than electron microscopes themselves.

Food For Thought

It is admitted that more discussions to get to the bottom of the issues are required. Surprisingly, there was clear consensus on some of the issues of microanalysis. Detector hardware development for EDS clearly lags behind that for EELS. Despite the fact that EDS detectors have not changed significantly over the years and that the collection efficiency for EDS detectors is miserably low, EDS analysis remains as a very user-friendly and widely used analysis technique. Developments in EELS instrumentations have been rapid and we have reached a stage that further developments are going to improve the performance very slowly. The same cannot be

said for EDS instrumentation. It is high time that scientists, technologists and manufacturers come up with better detector design with particular attention to its geometrical configuration in an AEM.

The issues of sensitivity, accuracy and detection limits remain to be defined rigorously. Their values vary considerably from system to system and from one researcher to another. A well-defined set of parameters to describe these important terms would be valuable. EELS with parallel detection appears to overshadow EDS in almost every issue. However, considering that EELS instrumentation has reached a mature stage but has not-so-trivial problems in quantification, and that EDS instrumentation development has not even started, I wonder what the status of EELS versus EDS would be in a few years.

Finally, specimen preparation and artefacts of electron-specimen interactions such as radiation damage, contamination, etching, etc., would require a very careful and systematic approach. After all it is the quality of the thin specimen which would dictate the validity of the analysis and not the fancy microscopes which come later!

QUANTITATIVE AEM III

(D. Jesson)

Chair: M. Scheinfein
Panel: J. Silcox, J. Batstone, O. Krivanek, M. Otten, N. Yamamoto, J. Hunt

The purpose of this session was to cover analytical electron microscopy techniques which had not been discussed in previous sessions. The discussion was initiated by M. Scheinfein, who introduced the topic of electron coincidence spectroscopy, in which two measured signals are combined to extract a specific piece of information uniquely. The example cited was to utilize single-pulse counting on an EELS spectrometer simultaneously and together with high-efficiency secondary electron detection on the MIDAS instrument to obtain information on the origin of secondary electrons. This is achieved by measuring the time differences between events to create histograms which reveal the correlation signature in multiparticle cascade events. Coincidence spectra were presented for an amorphous carbon film exhibiting the correlation between an energy loss event at a specific energy and a particular secondary electron energy. In the case of a [111] oriented Si crystal, it was observed that the bumps and most of the intensity in the total secondary emission correlation spectrum are at a higher energy than the plasmon energy, implying that the bulk of secondary electrons produced are not from plasmons. It was subsequently claimed that secondaries originate from single-particle events and bumps in the spectrum were tentatively linked to band structure effects in Si. It was concluded that in order to perform difficult experiments such as determining where multiparticle cascade events originate, it is necessary to resort to extreme techniques which are slow, inefficient, and statistically unfavorable! However, it was pointed out that a fast (30 ns) electron beam resistant, UHV-compatible scintillator compared with the current 150 ns peak width YAG scintillator would improve the detection efficiency by a factor of 5.

The second topic, introduced by Dr. Yamamoto, involved the study of Cherenkov and transition radiation using a 200kV TEM equipped with a CL detection system. Cherenkov radiation is produced when the electron velocity exceeds the velocity of light in a particular medium, which therefore gives a threshold value for the accelerating voltage of the electrons. An ellipsoidal mirror positioned either above or below the specimen was used to detect the light emission, and by comparing spectra shapes, it was possible to confirm that the spectrum collected

in the lower position corresponds to Cherenkov radiation on specimen thickness and accelerating voltage. Studies of transition radiation from silver and silicon were also presented. The light could be detected with both the upper and lower mirror settings, and there was no observed accelerating voltage threshold. Furthermore, the light intensity decreased monotonically with decreasing accelerating voltage indicating that the observed light is transition radiation, which is generated when an electron crosses the specimen surface. Intensity modulations in the spectra were attributed to interference between transition radiation emitted from the top and bottom surfaces of the specimen. It can be concluded that although the physics of Cherenkov and transition radiation in TEM is certainly very interesting, considerable developments are required before the technique could routinely contribute to AEM.

The topic of cathodoluminescence (CL), applied to the determination of dopant/impurity distributions in semiconductor materials was introduced by Dr. Batstone. It was demonstrated how the technique was extremely sensitive to the presence of Cu impurities in ZnSe, for example, although it was not possible to quantify the amount of Cu present using the technique. It was stated that the quantification was related to several problems, which in this case included the 1-3% radiative efficiency in a wide band gap semiconductor. A study of Al dopants in high quality epitaxial ZnSe again demonstrated the sensitivity of the technique to dopant atoms. It was pointed out that the chief advantage of a CL system in a SEM is that spectral features can be correlated with spatial features. In particular, it is possible to form monochromatic images at different wavelengths. In this way, by forming an image using the Al-bound exciton, for example some information on dopant uniformity can be obtained, although alternative recombination routes through the presence of defects can greatly complicate the interpretation. Also, it is possible to directly locate a probe over a grain boundary or defect to investigate its luminescent properties. In a TEM, luminescent features can be correlated directly with the defect structure in the material. To detect impurity atoms such as B or As in Si, it was suggested that phase-sensitive detection methods would be necessary owing to the indirect nature of the bandgap. Finally, it was concluded that the signal generation volume limits the spatial resolution of the technique. In an SEM, this is around 0.2 μm, and in a TEM, the useful minimum thickness is limited by the loss in signal due to specimen surfaces acting as nonradiative recombination sites. It can therefore be concluded that CL is a sensitive way of detecting impurities with moderate spatial resolution although the signal is inherently difficult to quantify, particularly in the presence of defects.

ALCHEMI (atom location by channeling enhanced microanalysis) is a well established technique for determining the site occupancy of a particular atomic species. A comparison of energy-dispersive x-ray spectra obtained in channeling (axial or planar) and non-channeling

orientations enables the location of a particular element to be determined. Dr. Otten pointed out that to successfully apply the technique requires a-priori information—namely the presence and location of a suitable reference atom together with strong channeling atomic planes or columns which discriminate the atomic sites of interest. Although these requirements were recognized as fundamental limitations to the applicability of the technique, delocalization was identified as one of the major factors limiting quantification. In particular, the need for additional theoretical and experimental studies of signal localization was emphasized. Subsequent discussion revolved around the recent ideas proposed by Rossouw for analyzing ALCHEMI data. It was pointed out by Eades that Rossouw's methods treat the data in a most statistically efficient way, although they cannot influence the important systematic errors inherent in the technique. Bentley pointed out that anti-site defects and channeling discrimination between atomic planes or columns of a similar composition are also important limitations. It can, therefore, be concluded that future work should concentrate on overcoming the systematic errors of the technique, although the fundamental limitations seriously limit the applications to specific classes of materials.

The topic of spectrum imaging, namely obtaining a complete spectrum (e.g., energy loss or x-ray), for every pixel in the image was introduced by Dr. Krivanek. He discussed the energy-filtered CTEM approach to spectrum imaging which is most suited to tasks where only a few sections in say the energy spectrum are required for the whole image. Such applications include energy-filtered CBED as well as high spatial resolution elemental mapping using energy windows in the vicinity of high energy loss edges. It was pointed out, however, that considerable care is required when interpreting lattice images formed by the latter technique since elastic scattering contrast can be shifted to the inelastic channel by subsequent inelastic scattering. The practical spatial resolution limits of the technique relating to the acquisition of weak signals in the presence of specimen drift and/or radiation damage were suggested as interesting areas for future research.

The alternative approach to spectrum imaging is to obtain a whole spectrum pixel by pixel. This dedicated STEM approach is most suited for sophisticated spectrum processing as explained by Dr. Hunt. Indeed, the concept was extended to include the storage of all spectroscopic data from every pixel. The obvious limitation to such an approach is the very large data size involved. For example, a single EELS spectrum at every point of a 256 x 256 pixel image would generate around 256 M Bytes of data. Hunt has performed experiments using around three times this data size and pointed out the advantages of being able to perform time-consuming processing on data independently of acquisition time and the capability of detecting unanticipated effects. Al and Li compositional determinations in alloys using plasmon centroids were discussed. Through a detailed statisitical analysis, it was possible to quantify Li compositions to say 25±0.2 atomic

percent and infer absolute Al and Li concentrations by estimating the thickness at each pixel using standard techniques. Another study showed how by obtaining 126 EELS spectra from regions of a silicon-silicon dioxide-silicon nitride sample it was possible to construct individual reference spectra. These fingerprints could then be used to probe the composition and chemistry of the sample by forming an image map of elemental Si for example However, it was pointed out that the linear addition of spectra in this way may not always be valid. The session ended on an interesting philosophical discussion involving Drs. Hunt, Eades, and Batson, which essentially focused on how an electron microscopist should utilize, preselect, and interact with the potentially vast amounts of raw data available at his or her disposal.

INSTRUMENTATION I

(R. Kilaas)

Overview: O. Krivanek
Chair: D. Joy
Panel: M. Otten, D. Shindo, M. Tanaka, A. Eades, J. Wittig

This was the first of two sessions on instrumentation. The emphasis of this session was on detectors and sources, current status and future enhancements. The discussion was preceded by an overview by O. Krivanek of Gatan, Inc.

Sources

The key issues regarding sources were brightness, energy spread, total current stability, vibrational stability, ease of use and cost.

Because of the coupling between brightness and energy spread one cannot increase brightness and decrease the energy spread at the same time, i.e., it is necessary to sacrifice energy coherence for brightness. One could argue that the current limitation is radiation sensitivity and not source brightness, thus claiming that there is no need for increased source brightness However, the consensus was that increased brightness of the source is desirable. This is particularly true as one is moving towards energy filtered imaging where the use of monochromators will require higher source brightness in order to produce reasonable signals.

In comparing stability of filaments, the reproducibility of the CFEG after flushing was questioned. In general, with thermionic filaments the brightness will go down over its lifetime. The Schottky emitter was claimed to have very good short term (~seconds) stability coupled with excellent long term stability (lifetime). Drift was quoted at about 1%/h and emission data was reported not to have changed over the time of operation.

Energy spread was quoted to be 0.17eV for a cold field emission gun and about 0.5eV for a Schottky FEG. Smaller filaments will have larger instabilities. P. Batson commented on some of

his work on zirconia-treated tips which produce the same current for lower electric fields because of the lowering of the work function. However, emission stability was reported to be poor, possibly because a smaller work function is more sensitive to changes due to imperfections and contamination.

The microscopy community is looking forward to the day when the addition of the FEG does not double the cost of the microscope.

Detectors

There were two groups of detectors discussed as part of the session. X-ray detectors and electron detectors. The most interesting development in this area has been the emergence of slow scan CCD cameras for recording images and diffraction patterns in the electron microscope.

Because of the linearity of the CCD cameras, their large dynamic range, the ability to do channel to channel gain compensation and the ease to which the data can be directly stored in a computer for comparison with theory, the slow scan CCD camera is widely seen as the best detector in TEM. The emergence of the slow scan CCD camera is closely related to the current focus on quantitative comparison between theory and experiment in both imaging and diffraction. Slow scan CCD cameras are not, however, wholeheartedly embraced by everyone and should be compared to other detectors as well. Shown below are various remarks and claims comparing detectors:

Linearity:	Slow Scan CCD:	1% is easy to obtain
	Photodiode:	10%
	PMT:	Highly linear up to saturation

Charge Spill Over: In photodiodes and TV rate CCD cameras, extra signal is drained
In slow scan CCD cameras, extra charge flows over to neighboring pixels.

Dynamic range: Slow Scan CCD; 2^{14} -> 2^{16}. Dynamic Range can be increased by several exposures (Gatan gets 10^5:1). Going to 14 bits eliminates the concern about gray scales, etc.

Performance of slow-scan CCDs

A CCD camera that is fiber optically coupled to a single crystal Yttrium-Aluminum-Garnet (YAG) gives a signal of about 300 electrons at the CCD per electron incident on the YAG. Since noise is typically about 25 electrons at about -35°C this gives single electron detectability. The noise would decrease further by cooling. It was argued that single electron detection is good for weak signals, but for strong signals it increases processing times unduly.

To optimize a CCD detection system it is necessary to match the pixel size to the generation volume. Resolution (half width) in a YAG scintillator is about 30μm for 100 keV electrons so that only large pixel size CCD cameras are useful in TEM. Typically the pixel size should be of the order of 20-27μm. Smaller pixels require demagnification from the scintillator and coupling which creates loss in efficiency.

Channel to channel gain variation is about 1% for CCD and linear photodiodes, but can be normalized to much better that the statistical noise in the signal. This is one of the advantages over film and imaging plates since gain normalization can only be done on devices that allow two successive readouts from the same "detector area."

The Detection Quantum Efficiency (DQE) of the CCD camera is defined as $(S/N^2)_{out}/(S/N^2)_{in}$, where S/N is the ratio of signal to noise. Although one would expect DQE smaller than 1, an interesting result is that the measured DQE can be typically of the order of 8. This can be understood from the point spread function of the CCD. Because of the spread of charge over neighboring pixels, the camera effectively acts as a low pass filter, reducing noise. By characterizing the point spread function (impulse response function), one can perform a deconvolution to restore un-smoothed output, giving rise to a DQE of the order of 0.5-0.85.

There is an inherent danger in deconvoluting noisy data in a system where the response function of the detector goes through zeros or close to zero. It was pointed out by Spence, only by characterizing the point spread function and by applying that to the calculated spectra and comparing with experiments, were they able to get agreement between experiment and theory.

Although the CCD camera is more suited than the photographic film for recording quantitative data, there are still many that argue that film is a better recording medium, capable of storing more information than the CCD camera. The following estimate compares encodable information for CCD cameras and film.

- A 1024x1024 pixel CCD with 14 bit pixel size will contain $2^{10}*2^{10}*2^{14} = 2^{34}$ bits of information.
- By going to 2048 by 2048 CCDs one should be able to push the CCD to 2^{36} bits.
- A 10cm by 10cm film with 2μm grain size (on-off grain: 1bit) contains 2^{32} bits of information

However, as was pointed out, the 14 bit range in digitization rarely is fully used to carry information. In recording typical images, the contrast levels only cover a very small region of the dynamic range available and thus the argument that the CCD records more information than film is meaningless in this case. Contrast levels in typical HRTEM images are generally in the order of 5-10%. Its only during the printing process that the images come out with the solid whites and black. However, diffraction patterns do require a much larger dynamic range.

Further comparisons were made between slow scan CCD cameras and film. It was mentioned that film has smaller grain size than the CCD pixels and that the film cannot be gain normalized.

Imaging plates were also discussed and it was pointed out that the imaging plates are sensitive to x-ray production in the column and thus prone to fogging. Also no grain to grain gain normalization can be carried out and the image cannot be read out directly for use in computer assisted autotuning, etc.

Prospects of going to larger format CCD cameras will depend on the trend in astronomy because the microscopy community is benefiting from advances made in low light level recording for astronomy presently focused on 2K by 2K cameras. There are some larger size CCD cameras, but they generally have small pixel sizes and could only be used if the image were demagnified. Thus because of loss of image intensity, they would only be useful if the number of electrons is large enough. In response to a comment that one could make use of demagnification coupled with an optical image intensifier to overcome this problem, it was argued that this will give limited dynamic range. Also one gets distortions and loss in the Modulation Transfer Function. It works well in TV cameras, but not for slow scan CCD cameras.

X-Ray Detectors

The area of x-ray detectors was singled out as one of the few areas where there are still orders of 10 in improvements to be made in the foreseeable future. Most of the x-rays are not

recorded by the detectors. In fact, only about 1% of the produced x-rays are seen by the detectors due to the geometry of the detection process. In addition, there is also absorption of x-rays by the windows used in front of the detectors themselves. By going to thinner windows it has been possible to increase the efficiency, such that with current windows efficiencies of ~35% for boron and nitrogen and 50-70% for carbon and oxygen can be obtained. There has been research in the use of Ge instead of Si as a detector material. Ge has increased sensitivity to high energy x-rays, but poorer low energy sensitivity. A suitable solution may be to use both types detectors. In terms of energy resolution, the idea of using wavelength dispersive spectrometers was brought up. Currently, none are available commercially, but one company is developing one. A potential problem is that the solid angle could be worse and the quantum efficiency may be worse for wavelength dispersive spectrometers than energy dispersive spectrometers.

The energy resolution in x-ray detection is only about 130-150eV which is largely due to the limited counting statistics (the number of electrons generated is small) and also by the energy gap which is used in the detection of x-rays. In silicon this gap is about 1eV. By going to superconductors with smaller gaps (~meV), we may be able to get down to 5eV energy resolution. Astronomers have been investigating this path and have achieved 50eV resolution by using a dilution refrigerator, since the system must be cooled to temperatures below liquid helium in order to eliminate thermal signals.

On a general note on energy resolution, one could in principle go on forever, down to μeV. However, a practical limit may be of the order of 0.1eV due to life time broadening.

With computers becoming more important in both data acquisition and interpretation, there were some general comments made about the status and future of the computing power required in EM. The commercial interest in speech recognition and image compression is causing personal computers to become increasingly powerful. As an example, Apple computer will be introducing the MacCyclone with a Digital Signal Processing (DSP) chip making the computer capable of performing calculations at the rate of 50 Million Floating Point Operations per Second (MFLOPS) in the spring of 1993. It is felt that desktop computers presently have the sufficient power for 1D and 2D applications. For 3D problems there is still a need for increasing power. With tomography emerging as a growing area of interest, this is becoming more apparent. Instead of a single multipurpose computer for all tasks, individual computers specialized for certain tasks networked together will become more commonplace. 1K by 1K images can now be transferred over Ethernet in about 2-3 sec. With computers for auto-tuning and full control of the microscope, one can easily envision controlling the microscope and viewing images from one's desk at the office. In

order for this scenario to work smoothly on a range of computers, there will be an increased emphasis on platform independent software.

General Discussion

A general question was raised with respect to 3D reconstruction and the feasibility of performing accurate crystal-tilt while controlling the position of the specimen on current specimen holders. A computerized fully eucentric stage has not been developed until now because specimen holders for HRTEM were optimized for maximum stability and tilt and stage control were considered secondary. Various views and ideas were raised such as the difficulty of designing stages that can be controlled without backlash, the need to track movements (possibly through laser interferometry), the use of piezo-electric crystals for controlling movements of the stage (good for small movements, useless for large distances).

Finally, as an interesting observation it was pointed out that the microscopy community had to wait for the astronomy community to develop the slow-scan technology and advance the technology in x-ray detectors.

INSTRUMENTATION II

(B. Zhang)

Chair: I. McFadyen
Panel: D. Joy, H.Poppa, M. Tanaka, T. Yoshida, E. Weimer, J. Wittig

The status of instrumentation for the characterization of magnetic microstructures was summarized by Dr. McFadyen. At the moment there are no objective lenses in the market that are truly optimized for these applications, i.e., good imaging performance with minimum leakage flux in the specimen area. The fields that can be tolerated depend on the materials being studied. Estimates range from 100-200 G for hard magnets like samarium cobalt alloys to < 1G for soft permalloys. Presently, best performance is being achieved in a dedicated STEM with the objective lens turned off, relying on the high brightness of the FEG source and using a DPC detector for imaging. The resolution is then determined not by the C_S of the lens but by the demagnification of the source. 20 nm can be routinely achieved. Two new designs by Philips and JEOL, have been recently introduced for such applications. Whilst these instruments reflect major improvements they are modifications of existing designs and are nowhere near what is possible. A design of a new objective lens is imperative and should be pursued more vigorously. Aberration correctors being developed by Rose et al. could also be incorporated in such instruments. Ability to perform dynamic experiments in the presence of applied fields would be important and this would impose additional constraints on the polepiece gap.

For DPC imaging, commercially available back scattered detectors with appropriate modifications to enhance the magnetic contrast are used. Simple solutions include using an anular detector and/or a configuration of inner and outer quadrants. There was some discussion related to the use of a general purpose detector, such as a CCD camera, as opposed to a dedicated special-purpose detector for such applications. It was felt that even though the detector requirements for this application was nothing more than an ability to identify the edge of a bright field cone, a random access device with rapid readout would be desired. Such detectors and the related software are not currently available.

The second lead-off presentation on holography raised three issues. In typical applications a fringe spacing of 0.1-0.2Å has to be resolved. For micron size pixels this requires a magnification of ~20,000,000 X. This is well beyond the direct magnifications available in most commercial instruments and it was suggested that they be reconfigured for higher top end operational magnifications. Rf noise (high frequency ~MHz) also significantly affects holography. In addition to the viewing ports a common source of such problems are the exposed leads that connect the lens windings to the outside. It was also suggested that such microscopes be installed in screened rooms (typical cost $35,000) with all the electronics placed outside (remote operation). Fiber optic coupling is recommended. However, special attention should be paid to the ground wire (source of electromagnetic noise) and the whole situation be evaluated periodically.

Two other presentations on holography highlighted recent applications. Of particular interest was the work being carried out on the imaging of stationary and dynamic movement of flux lines in superconductors. It was also pointed out that the a recent PRL paper by the Hitachi group has clearly resolved the In and P sublattices in InP by holographic methods.

The presentation by Dr. Poppa on the newly built, fully bakeable UHV spin polarized low energy electron microscope (SPLEEM) was very interesting and provoked much discussion. This demonstration instrument uses a GaAs spin polarized source operating at 2V and is capable of a resolution of 150Å for imaging of surface magnetic structures. Magnetic structure information is obtained by switching the polarization of the source by hand, recording the images and subsequently extracting appropriate difference images. The lifetime of this novel source deteriorates with time in vacuum, but fortunately it can be reactivated with a well known recipe of cesium and oxygen. The technique is particularly efficient for it is a global imaging capabiltiy as opposed to the alternative scanning electron microscopy with polarization analysis (SEMPA) method being pursued at the National Institute for Standards and Technology (NIST). Some important numbers that emerged in the discussions were: in SEMPA where an unpolarized incident beam is used, the spin dependent scattering is ~1-2%; for the GaAs source about 20-30% of the incident electrons are spin polarized, leading to an order of magnitude improvement in sensitivity for SPLEEM. This sensitivity could be further improved by coating the source with europium oxide/sulphide in which case 90-100% of the electron are polarized. However, this will require an operating temperature of 4 K! A the moment the prognosis for the use of such sources at medium voltages (100 - 300 kV) seems to be rather poor. Fine probe geometries allow complementary microanalysis experiments. Pursuit of smaller sources should eliminate the need for the demagnification of the source as currently practiced and make the signal detection very much more efficient.

This part of the session concluded with some discussion of the length scales of relevance in magnetic materials. It was mentioned that typically magnetic domains in bulk materials are of the order of μms, there are interesting questions in the 1-10Å range such as spin density waves, antiferromagnetic coupling in dense alloys, etc., and therefore design of instruments with spatial resolutions of 10-100Å may not be relevant. However, it was also pointed out that in many applications (such as particle recording media and granular films exhibiting giant magnetoresistance) the domain sizes are precisely in the 10-100 Å range. Moreover, the structure of domain walls and their pinning mechanisms are also in this range. Further, many applications such as hard magnets where the microstructural features are relevant to the understanding and control of coercivity, require an elucidation of the magnetic, physical and chemical microstructure at this level of resolution.

Two other topics were briefly presented and discussed. The SHEEBA machine, a hybrid MBE/TEM is nearing completion at the University of Illinois and combines 4 evaporation sources with both transmission and reflection imaging capabilities. This differentially pumped machine with a C_s of 0.1 to 1m (!) and 20Å resolution has not yet become fully operational but may be first in a series of dedicated instruments capable of novel dynamic experiments. The development of the omega energy filters from the manufacturer's point of view was discussed. Greater interaction with non-commercial laboratories was solicited for future instrumentation projects.

INTEGRATED ANALYSIS TECHNIQUES

(N. Thangaraj)

Chair: K. Downing
Panel: P. Batson, J. Bentley, D. Seidman, J. Spence, M. Tanaka

This session addressed the important area of analysis that involves more than one specialized technique to extract the quantitative information necessary to understand critical properties of materials and their defects. First, an overview was presented of what quantitative analysis may mean for different features in materials, pointing out that while a single number may be sufficient for some problems, others need to be specified by a vector, a field, a group, a shape, etc. This overview was followed by a number of short presentations on specific new, unusual and combined techniques for quantitative analysis.

Overview of quantitative analysis of defects in materials

The concept of quantitative TEM analysis is more complex than it might at first appear. The quantities of interest in a material range from crystal or electronic structure to point and volume defects and may be described by a single number such as an order parameter, an array of numbers such as a vector or a transformation matrix, or even by a spatial distribution of quantities such as a composition or displacement fields. Quantitative electron microscopy must be able to describe the desired features with measurable accuracy. For different features this may involve very different procedures.

Even in single phase materials defects such as point, line, planar and volume defects need different descriptions. Point defects, composition, order parameter, etc. may be given by a single number. Line defects are characterized by their line directions, displacement vector and displacement field. Planar defects are defined by a displacement vector and a plane normal. Volume defects such as stacking fault tetrahedra require in addition the description of their shape and orientation.

For multiphase materials and grain boundaries in single phase materials the problem is even more complex because of the presence of interfaces. For planar interfaces, 8 geometrical parameters (orientation relationship, inclination, rigid displacement) must be specified. In

addition, other features of an interface may need to be characterized. These include, for example, interface roughness (*amplitude, fractal dimension, power spectrum*), the type and degree of reconstruction (*symmetry group, order parameter*), segregation (*composition gradient*), faceting, dissociation (*reaction equations*), ledges and ledge motion (*step vector, displacement vector or field, rate*). For second phase inclusions, there are additional characteristics such as shape and distribution. The following specific examples of techniques for quantitative defect analysis were discussed:

Displacement field at dislocations

A technique was described for quantitative mapping of the displacement field around a dislocation in a high resolution electron micrograph. This technique utilizes the moiré effect to magnify displacements near defects by comparing the HREM image with an undistorted reference lattice. This can be done in real space by overlaying a reference grid on the image, or in reciprocal space by shifting the first Brillouin zone from the origin to the reciprocal vector of interest and inverse transforming. It is possible to obtain the displacement field for each diffracting plane separately. By separating the deviatoric from the symmetric part of the displacement field gradient it is possible to distinguish lattice rotations from distortions. Theoretical calculations based on the anisotropic elasticity also agree qualitatively. Th technique was illustrated with an example of a Frank partial dislocation in edge orientation bounding an intrinsic stacking fault in a ZnTe thin film. The strain contours extracted by this technique qualitatively agreed with the theoretical predictions although the observed strain field was much more extended than that calculated. The difficulty of this technique, like that of all defect analyses by HREM lies in its sensitivity to imaging conditions, alignment and thin foil relaxations.

Fresnel technique for interface analysis

This technique uses Fresnel fringes to analyze the composition of an intergranular layer, or more generally the composition change across an interface. A through-focal series of images of an edge-on interface showing out-of-focus Fresnel contrast is digitized and averaged along the interface. The measured fringe profile and contrast values are compared to 1-dimensional multislice calculations using the mean inner forward scattering potential of the material.

Extracting quantitative data is very straightforward because:

(a) the width of the fringes gives direct information about the width of the intergranular layer.

(b) the contrast levels give direct information about the composition of the central layer.

(c) the variation of contrast with the amount of defocus provides information about the interface diffuseness.

Accuracies of 2Å are attainable in both the width of the layer and the sharpness of the interface. However, there are disadvantages to using this method:

(a) the difficulty of including inelastic scattering in the very simple calculations used, which leads to inaccuracy in the determination of layer composition.

(b) contribution of diffraction contrast in an on-axis orientation; the method works best for crystals tilted off a strong diffracting condition (or amorphous materials).

(c) the difficulty of relating the measured forward scattering potential to the composition of the material, especially in systems containing several elements.

The first problem is the most restrictive and the advent of energy-filtered imaging will lead to great improvements in the determinatinon of composition using this method.

Characterization of non-periodic boundaries

Periodic interfaces are described by their macroscopic geometrical parameters plus a rigid body shift. Localized relaxations are characterized by structural units. Since structural units in periodic boundaries have the periodicity of the boundary they are easily detected and averaged to reduce noise.

For non-periodic grain boundaries, rigid shifts cannot be defined and structural units are no longer periodically spaced. This presentation described the detection of structural units in a non-periodic boundary by a cross correlation technique. A template of a locally relaxed structural unit is compared with similar units in the boundary. Similarity is defined as the height of the cross correlation peak. Units thus identified as identical can then be averaged for noise reduction. To assess the level of specimen noise the root mean square displacement of centroids of image intensity from a perfectly periodic lattice is measured in the crystal lattice adjacent to the boundary.

Optimization technique for HREM image simulation

Comparisons between experimental HREM images and images simulated from models are commonly done by visual comparison. Although quite successful in many cases, this procedure is qualitative and does not make use of the full range of data contained in an HREM image. In this contribution, an algorithm was presented that uses a χ^2 goodness of fit parameter to refine a model of a $\Sigma 5$ (310) <001> symmetric tilt boundary in bcc Nb. Successive simulated images are compared with the experimental image and the atomic positions in the model are optimized by non-linear least squares fitting.

This scheme requires extensive treatment of experimental data by digitization, flat-field correction, correcting the negatives for electronic exposure, normalization to incident beam intensity and image averaging.

The optimization requires the spherical aberration coefficient C_s, the Debye Waller factor, the lattice parameter and the accelerating voltage as inputs. Any systematic errors such as spread of defocus, semi angle of convergence and beam tilt can be easily adjusted. Parameters for optimization at the third level are defocus, beam tilt, atomic positions and astigmatism. Future development should include multiple defoci and crystal tilts.

3-D image reconstruction for crystal structure determination

This technique relies on combining images of the specimen obtained in several different orientations. The number of projections required is dependent upon the crystal symmetry of the structure, as well as its packing which dictates the number and directions of useful projections. The technique has been successfully applied to the mineral staurolite to determine the location of all the atoms, including oxygen atoms. In the staurolite case, the use of Scherzer images in five projection directions was sufficient to produce enough structure factors to fill a large proportion of three-dimensional reciprocal space to 1.6Å resolution. By processing five-member focal-series in each projection direction (a total of 25 images), the accessible volume of reciprocal space was extended to 1.38Å[+] . In some three-dimensional projections, one might be able to identify a contribution from a single atomic column, where contributions from large portions may not be significant. Future development should include 3-D analysis of precipitates in a crystalline matrix. In this case, one may require the large tilt angles of a high-voltage HREM.

Crystallographic image processing

Most experimental HREM images suffer from noise, distortions and instrument misalignments such as beam or specimen tilt. Therefore, symmetries that are characteristic of a crystal may be partially obscured in an experimental image. The technique of crystallographic image processing searches for the most likely projection symmetries and imposes them on the

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[+] "3d structure determination from electron-microscope images: electron crystallography of staurolite," H.-R. Wenk, K.H. Downing, Hu Meisheng, and M.A. O'Keefe, *Acta Cryst.* A**48** (1992) 700-716.

image to obtain a less noisy and more faithful density map. Similar to lattice averaging which utilizes only the translational symmetry of a crystal, crystallographic image processing uses rotational, mirror and space group symmetries as well. From the Fourier transform of the experimental image the most likely phases for selected reflections are calculated by refining the origin of the unit cell. In most cases this allows unambiguous determination of the two-dimensional plane symmetry group of the crystal and recovery of the projected potential with an accuracy of ±0.1Å for heavy atoms. As its name implies, the technique is applicable only to perfect crystals. At present, the CRISP software is also restricted to two-dimensional analysis, i.e., combination of data from different zone axes of the same crystal is not yet part of the routine.

Determination of crystal thickness from HREM images

The accurate determination of crystal thickness is a critical but largely unsoved problem in high resolution imaging. A technique was described which uses an analytical description of the linear image contrast in an HREM image to derive a simple relationship between defocus conditions that yield characteristic image patterns and specimen properties. With this description it is possible to determine the specimen thickness from the local defocus. At interfaces between different materials it is possible to determine even the local defocus value from the difference between defoci belonging to characteristic image patterns in the two crystals. Examples of a GaAs/AlAs interface were presented.

Chemical mapping in energy filtered TEM

Energy filtering can be used in a variety of TEM techniques such as diffraction, weak-beam imaging, REM, RHEED and PEELS, etc. In the case of RHEED, surface plasmon and phonon scattering can be filtered to get very sharp diffraction peaks. New information is buried under the inelastic scattering. Chemical mapping by PEELS was illustrated with energy-filtered images of C-N-O ceramics.

Atom probe field ion microscopy

In an Atom Probe Field Ion Microscope (APFIM), pulsed field evaporation of a sample tip allows atomic identification in a time-of-flight mass spectrometer with single atom sensitivity. When combined with structural analysis by TEM, the relationship between structure and composition at interfaces can be studied with unprecedented accuracy. Because pulsed field evaporation permits removal of material one atomic layer at a time, the composition can be measured error-free in a single atomic layer. Combined techniques of analysis such as TEM/APFIM provide unique advantages for improved characterization of materials.

DYNAMIC EXPERIMENTS

(C. Allen)

Overview: R. Sinclair
Chair: D. Howitt
Panel: J. Batstone, I. McFadyen, F. Ross, K.H. Westmacott

This session included presentations and discussion of a wide variety of phenomena observed in situ, including interphase interface structure and migration, oxidation of Si, irradiation-induced and irradiation-enhanced phenomena, fracture toughness, magnetic structures and various experiments for determining quantities such as surface energy and diffusion coefficient. These involve several techniques including HREM, HVEM and SPLEEM (spin polarized low energy electron microscopy). In addition there were a number of remarks about the current state of instrumentation, specifically the notable lack of specimen holder development.

The keynote overview presentation summarized very succinctly a number of requirements and methodologies to ensure that the results of in-situ TEM experiments involving phenomena associated with bulk behavior are credible. In every instance in which dynamic observations of thin foils are employed to study a solid state phenomenon of interest for bulk material several questions must be asked. In addition to those regarding the technique of observation itself and artifacts deriving from the technique itself, there are questions of possible thin foil effects, of electron beam heating, charging or displacement damage during observation, and of control and accurate measurement of environmental parameters such as the temperature of a specimen. High resolution imaging at elevated temperatures demonstrates that at least single tilt heating holders are available commercially with both satisfactory mechanical and thermal stability. Unfortunately the same cannot be said for specimen cooling holders and most double tilt holders in general. The accurate inference of specimen temperature is a perpetual problem, exacerbated for specimens having poor thermal conductivity or inferior physical contact with the specimen holder. Ultimately it is the lack of adequate stability and controllability of specimen holders in dynamic experiments which limit our present capability for dynamic observations at high and even moderate spatial resolution to relatively few experiments in a small number of institutions.

There are both advantages and disadvantages associated with in situ TEM studies. It is very advantageous to be able to directly observe atomic mechanisms at play in a particular phenomenon and to record, usually in real time, sequential events. In some instances, information cannot be acquired by any other means. In situ techniques allow a rapid survey of a particular reaction phenomenon to be made, for instance, in order to quickly determine temperature range of interest for subsequent detailed investigation. On the other hand, however, in situ TEM experiments are time-consuming and often rather difficult in that special care must be taken in design and preparation of the specimen; also it may be necessary for several people to be on hand to accomplish the variety of tasks which may have to be performed virtually simultaneously during the experiment. In addition, the specter of thin foil effects is present, except, of course, when the phenomenon is to be studied in a thin film, for which case that dimension of the specimen may be of the essence of the result.

Several clear guidelines can be given for judging both the qualitative and quantitative validity of dynamic TEM experiments in general for the case in which bulk phenomena are of interest. In order to convince oneself and others that conclusions drawn from in-situ observations are correct, cross-checks with known bulk behavior must be made wherever possible, such as the net activation energy for a particular phenomenon determined in situ and ex situ, and, for example, the known nucleation sites for reactions such as at grain or interphase boundaries. In foil specimens severity of thin foil effects may also be assessed by comparison of the kinetics of a phenomenon in thin and thick regions of specimen. Other thin foil effects which may be troublesome for dynamic experiments include interface grooving at the free surfaces and the effects of surface contamination, including native oxides. For some phenomena such as diffusion-induced grain boundary migration the influence of the surface morphology can totally dominate the process in thin specimens. Finally to assess the possible role of secondary displacement phenomena, kinetics should be the same whether the electron beam is on or off during the events of interest. (The effects of subthreshold electron irradiation are discussed elsewhere in this Workshop.)

The major points stressed in the overview presentation were illustrated by several example studies involving cross-section TEM specimens (XTEM). From a classic HREM study of solid phase epitaxial regrowth of Si at ~480–580°C, an activation energy for interface migration of 2.7 eV was determined, indicating expected interface-controlled growth, which compared well with results obtained by RBS and HVEM studies. For such observations, interface migration rates of ~0.1 nm/s are very convenient experimentally; the actual rates were 1–70 nm/min. Specimen temperature may be checked by incorporating into the cross-section specimen a material within which some dynamic phenomenon occurs with well established temperature dependence.

A study of the interfacial reaction of Pt and GaAs to form Pt|PtGa|GaAs and then PtGa|PtAs|GaAs illustrated the Kirkendall effect and diffusion-controlled growth of the reaction products (thickness of the product layers increased as the square root of reaction time for 180–220°C). From video recordings of the reaction at 300–400°C the atomic mechanism of the initial growth process was clear: the replacement of Ga by Pt in the GaAs. In any such study the spatial resolution of the TEM, of course, must be better than that required for the particular level of detail to be observed. In this case, 0.3 nm point-to-point was adequate in a 0.2 nm instrument.

Two studies were presented to illustrate the power of in situ TEM experiments in elucidating physical mechanisms of phenomena, for which conventional spatial resolutions are quite adequate. In XTEM multilayer specimens of Al|Si|Al|Si... in which the starting Si was non-crystalline, Si was observed to crystallize within adjacent Al layers at very low temperatures (170–180°C). The diffusion model derived from the in situ observations predicted a crystallization rate of 2.5 Å/s at 200°C, in good agreement with the observed values 3–5 Å/s. Finally a video showed the reaction "between two materials" under moderate resolution conditions, in which the ledge mechanism of growth was clearly evident.

Discussion turned to the importance of developing much more stable specimen holders for a variety of experimental purposes, including capabilities such as heating and cooling, in situ V-I and other electrical measurements, stressing, UHV, environmental control and controlled magnetic fields. Today's heating holders, for example, are virtually identical in design to those of the 1950's. Other possibilities for such holders include those with laser heating or electron beam heating (an example of the latter is the 2200 K top entry cartridge at the UHVEM Center at Osaka University). Improvements in heating holders imply accurate temperature measurement and control. There have been such significant improvements in recent years, in image recording for instance, which have had a profound positive effect on in situ studies, that improved specimen holder designs are long overdue.

Several in situ TEM studies were presented, representing a variety of physical phenomena. In a study of the etching of Si by oxygen, the kinetics and detailed mechanism of the process could be determined quite precisely, employing real time video recordings of images. In another case, a technique was described for handling dynamic experiments involving time-varying elemental changes, utilizing short interval x-ray energy dispersive spectra (EDS spectra) acquired sequentially. The example cited was the decreasing Cl concentration in NaCl under the action of the

electron beam of the microscope. In a similar manner the reduction of TiO_2 to TiO has been followed by parallel electron energy loss spectroscopy (PEELS).

There are a rather large number of methods for extracting quantitative information, which were introduced perhaps 20–30 years ago, but which are still not being widely applied. For example, in conjunction with the shrinkage of faulted dislocation loops at elevated temperatures, in a high stacking fault energy material the shrinkage rate of large loops is governed by diffusion of vacancies to the free surfaces of the TEM foil; from the uniform shrinkage rate, one can deduce the stacking fault energy. In addition, however, because the stacking fault energy is not a sensitive function of temperature, the activation energy for self diffusion can be determined with high accuracy from the shrinkage rates determined at several temperatures. Similarly, the shrinkage of voids, produced from condensation of quenched-in vacancies which results in an uncontaminated internal surface, can be employed to deduce surface energy, at least of elemental materials, and activation energy for self diffusion. If such a foil is lightly deformed so that dislocations link the voids to the foil surfaces, the void shrinkage rate allows determination of activation energy for pipe diffusion. Another example of this same type of quantitative in situ experiment is the dynamic dissolution of precipitates. If the dissolution reaction is interface controlled, the interphase interface energy can be determined; if the reaction is diffusion controlled, a diffusion coefficient can be determined. Such dissolution may result in significant shape changes of precipitates. In fact, in some cases a well defined transition temperature corresponding to isotropic interfacial energy $\Leftrightarrow$ anisotropic interfacial energy may be identified. In the activation energy determinations, of course, the specimen temperature must be known with some accuracy and differences in temperature with high accuracy. The starting microstructures involved in any of these experiments may be the result of thermal-mechanical treatment or may be artificially tailored by using other techniques such as photolithography.

In TEM, electrons, of course, are employed as the medium for information transfer. But radiation by electrons, ions, photons or other particles may be used for creating material systems deviating in various degrees from equilibrium and even from non-equilibrium conditions produced by other means. For example, electrons of sufficient energy will produce point defects in crystalline solids and in many alloy phases may even cause transformation from the crystalline state to a non-crystalline state, particularly at low temperatures. An irradiation experiment of this sort which results in production of metastable phases might be done by someone interested in exploring a part of free energy-composition space which is otherwise inaccessible, for instance. Similarly ion irradiation which generally produces much more severe localized damage (displacement cascades) may drive a system further away from equilibrium, as in radiation-induced segregation in alloys, or

may drive a system toward equilibrium, as in irradiation-enhanced crystallization above a temperature range below which just the opposite effect would have occurred. Another example of an ion irradiation-enhanced phenomenon is grain growth which in Au, for instance, has been shown to occur even at 20 K under 1.5 MeV Kr bombardment under conditions for which the average temperature rise of the specimen is less than 1 K. All of these processes can be observed in situ, for electron irradiation in HVEMs, of course, and for ion irradiation, in facilities such as the HVEM-Tandem Facility at Argonne or at ten such installations in Japan or one in France. This variety of installations offers ion energies as low as 200 eV (Kyushu—Kasuga campus) to about 4 MeV (Argonne). For phenomena such as irradiation-induced amorphization and grain growth, rather unexpected mechanisms may be observed which are not deducible from a macroscopic property measurement. One advantage of such an in situ observation is always that a local event is followed, not just some grand average event and quantitative results are often more directly correlatable to fundamental models as a consequence, as was demonstrated in the overview talk.

There are still many mysteries involving the radiation-response of alloys, especially to neutron irradiation, which are of great practical as a well as fundamental importance. For understanding the basic phenomena associated with neutron irradiation, in-reactor experiments are a nightmare in which the reactor temperature cycles, the particle flux cycles, the experiments require months and years to conduct and the specimens are difficult to instrument for dynamic analyses. The relicensing of existing power reactors is a multibillion dollar question, for which ion and combined ion and electron simulations of material behavior remain an achievable goal. A strong effort exists in Japan, for example, in such "irradiation correlation," in large part involving quantitative TEM analyses and application of several of the TEM-ion beam installations, including several with dual ion capability, to more adequately taylor the recoil spectrum. The role of HVEM is still very important for production of low energy events resulting in freely migrating defects at controllable concentrations.

The stress intensity factor for dislocations in Si has been determined in conjunction with the ductile to brittle transition in Si. Under Mode I loading, for example at 700°C, determination of the local bending of lattice planes near dislocations emitted from the tip of a crack circumvents the problem of knowing the applied load. In principle the local strain could be determined by convergent beam electron diffraction (CBED) but too fine a probe would be required to achieve the necessary spatial resolution.

Other observations in CTEM employing in situ specimen heating, which were presented for discussion included the disappearance of dislocation contrast "just below" the melting temperature

of Sn, which may be evidence for grain boundary melting, possibly due to solute segregation in the boundary. A related situation was described for $AuCu_3$ in which disordering at both symmetric and asymmetric twin boundaries was observed in CTEM to occur 15–20°C below the bulk disordering temperature of the alloy. While disordering in bulk $AuCu_3$ exhibits first order kinetics, it is possible that at these interfaces disordering is second order as it is at free surfaces. Again the question of local composition may be raised as well.

The concluding presentation turned to the imaging of magnetic structure changes of Co islands on W during annealing by spin polarized low enrgy electron microscopy (SPLEEM). Images are acquired in one-second intervals utilizing 2–3 eV electrons. The Co islands were 6 monolayers thick initially. Studies of magnetic materials involving electron microscopy have been noticeably few and far between over the past twenty years or more.

The foregoing constitutes a representative slice through the world of dynamic experiments involving several electron microscopies, both as essential analytical tools and as host instruments within which experiments are performed. The discussions illustrate the level to which physical behavior can be quantitatively evaluated during such experiments and the importance for the observer's focus of attention on highly localized events, from which new insight into mechanisms of phenomena may be achieved and physical models derived.

Finally this session also emphasized the experimental limitations imposed by measurement and control of environmental parameters during such experiments, with the conclusion that considerably more attention needs to be devoted to this aspect of development.

CRITICAL MATERIALS ISSUES

(D. Howitt)

Chair: G. Thomas
Panel: A. Berkowitz, D. Chemla, D. Clarke, R. Gronsky

Many of the critical issues of the next decade will remain unsolved unless things change, was the essence of G. Thomas's opening remarks. The approach to the new challenges has to be mission-oriented which is ironic as the erosion of the multidisciplinary support continues. There has to be an expansion in our base of learning, that is also seeing tremendous cuts and we are at risk of losing the cooperative and integrated facilities that we need to move forward. In the field of Materials Science, we are seeing a fragmentation and only a few groups now remain which have the theoretical base integrated with facilities for synthesis, characterization and the determination of properties and performance.

In these difficult times, we may also be losing sight of the needs of the Nation and perhaps as researchers we must pay more attention to the current expenditure in advanced materials research. The imbalance of 245 million for biomaterials research and 5 million for magnetic materials, for example, draws attention to the disparity of the research base to the industries that most strongly support the economy of the Nation.

D. Chemla reviewed the status of semiconductor research and looked to the direction of research and technology for the 90's. He drew attention to the single atomic layer processing of AlGaAs/GaAs quantum well waveguides and layers in VCSEL arrays down to 10nm as examples of current microdevice technology and talked about x-ray microscopy with zone plates at 30nm to study devices and circuits. The development of line widths at 100nm, 5nm gates and complex structures with polysilicon and metal silicides are not far in the future, and the evolution of optical materials and devices in and beyond the visible spectrum is very rapid. New alternative device technologies including nanometer scale magnets and biomaterials for drug and virus recognition are also fast developing and the typical stacked layers will soon include semiconductor / metal / superconductor / polymer / insulator. Our ability to characterize such devices in terms of state

specific information, that is composition and coordinate variance across these interfaces as well as the signatures of the magnetic and electrical need to keep pace with these technologies.

That the properties of magnetism and electron spin polarization where not successfully characterized to the extent that will soon be called for led naturally to A. Berkowitz who discussed the magnetic recording and permanent magnet needs for the next decade in much the same vogue. Spin polarized methods and the need for the microscopes to keep pace with the smaller and smaller storage volumes were to be recognized. Looking to the future, the structures and compositions of surfaces and interfaces on an atomic scale will be invaluable if it includes the interatomic spacings and coordination that so influence magnetic properties. The atomic positions at the interface between an antiferromagnetic film and a ferromagnetic substrate is just one example of the kind of interfacial and surface information required. The next generation of recording media based on giant magnetic resistors, i.e., multilayers of magnetic and non-magnetic materials which show very large changes in resistivity in the presence of an applied field, will also look to high resolution electron microscopy. The extension beyond planar interfaces is also called for because the same resistive behavior is exhibited by small clusters of copper cobalt or silver cobalt and the exploitation of these structures by precipitate reactions is potentially so much simpler. Structures one to two nanometers in diameter are the prize, and the tools needed to characterize them must combine structural with magnetic and compositional information. This challenge in magnetics of course extends to the deciphering of nanocrystalline structures as well as to the thin film interfaces in the new multilayers such as NiO, CoO/Co,Ni,NiFe and $Fe_3O_4Fe_2O_3$/Co,Na polyphosphate; emphasizing again the need to be determine coordination and interatomic separations.

D. Clarke's perspective was a more personal one beginning with a career chronology to justify his assertions that Materials Science is an enabling technology and that the critical materials issues are those that leverage the present or future technology. He maintained that the elitist image of the microscopist is unfortunately rather well deserved and all too common. There are few exceptions, where TEM is used as a rapid diagnostic tool, but there is a misconception amongst microscopists that their technique somehow has intrinsic value. What we must do is to pay more attention to the industries critically dependent upon materials advances, and he listed them in order that reflected their contribution to the balance of payments. Aerospace at the top, structural materials in the middle and semiconductors at the bottom. D. Clarke emphasized the large number of fundamental challenges in the aerospace industry and distinguished them from the plethora of development opportunities in the industries further down the list. A 1% reduction in weight is in real terms equivalent to doubling the storage capacity of a device and he pointed out that perhaps too many areas of materials are very poorly served by microscopy at present. An example of a

different kind was magnetic materials where despite tremendous progress in developing and applying high resolution microscopy to microstructural observations, there is little that has been gained. We need techniques and instrumentation that can determine local magnetic and electrical properties and there are far too few of us working as true experimentalists and designing and manufacturing the tools that we need for such analyses. Perhaps the needs of the semiconductor industry are distorting the direction of microscopy and people should no longer operate under the microstructure property relationships paradigm. He finished with an example of some recent in-situ analysis of crack propagation to persuade us that we should also be devoting more effort to performing experiments inside the microscopes.

R. Gronsky directed his attention at near term materials problems in the light of developing technologies. He quoted A. Bromley (Director of OSTP) from the recent address to Congress about the Advanced Materials and Processing Program (AMPP) "This is a coordinated interagency effort to exploit opportunities in materials research and development to meet significant national goals and to extend U.S. leadership in this area. Increased investments in materials science and technology should result in major contributions to this Nation's quality of life, national security, industrial productivity, and economic growth."

Drawing attention to how we clearly underutilize advanced materials, titanium now accounts for at least 33% by weight of the airframes in military aircraft, but only 10% in the Boeing 777. Ti-6-22-22 comprises over 66% by weight of the new Advanced Tactical Fighter (the F-22) and yet we are still without the far less sophisticated alloys for automobile applications where 35% weight savings could easily be achieved over steel.

The fiber coatings which facilitate low-temperature processing in composite materials have the potential to optimize the performance for process integration and the same understanding of the relationship between microstructure and microchemistry needs to be applied to oxide superconductors and functional materials, for example piezoelectrics for actuators, where the new science is understanding the electric and magnetic behavior of materials with complex ionic structures. We now have "Intelligent" materials, "Smart" materials and "Adaptive" materials, but we still need to understand the atomic structure of grain boundaries and continguous regions, the role of organic capping molecules, the association of boundaries with the amorphous state and the crystallization of glasses. The determination of the nature of grain boundaries and nanophase microstructures during processing of consolidated materials is also a substantial but achievable goal.

We must not lose sight of the fact that quantitative TEM in Materials Science from an Engineering perspective in the near term, is a Diagnosis of Process Control. This includes Multimaterials Systems Development in both Functional Materials and Engineered Composites. The discovery of new materials is a long-term application in Solid State Chemistry, microstructural control and atomic level engineering.

The information and ideas in this session came so freely that they were difficult to keep up with, but it nonetheless was very clear that the California perspective (Chemla, Gronsky and Thomas @ Berkeley, Clarke @ Santa Barbara and Berkowitz @ San Diego) is that we need to look to a firmer foundation in the organization and direction of our research than our geology affords.

FUTURE NEEDS AND DIRECTIONS, PROJECTS AND INITIATIVES

(F. Ross)

Chair: E. Zeitler

Panel: C. Allen, J. Bentley, W. Coene, K.M. Krishnan, M.A. O'Keefe, D. Jesson, J. Silcox

The panel leading this session represented several National Laboratories and universities as well as one of the microscope manufacturers, and the discussion was therefore of a particularly broad scope. The emphasis in this session was on the needs and desires of electron microscopists at present and in the future, and the projects and initiatives which are being undertaken to fulfill these needs.

To summarise the discussion, there are two main areas in which we would particularly like to see progress. The first is the achievement of sub-Ångstrom resolution, with its potential for examining both new and more traditional materials in different projections to give a three-dimensional view of their atomic arrangement. Secondly, the construction of specialized microscopes will enable us both to study particularly difficult materials (such as magnetic and ferroelectric materials) and also to perform *in-situ* experiments. These aims can not be achieved without simultaneous advances particularly in both specimen preparation and the design of specimen holders, as well as pole piece design, aberration correction and real time image processing (such as focal series restoration). These areas are at present in very different stages of development.

One of the most ambitious proposals for an initiative in these areas has been made to the NSF by a Panel focusing on Atomic Resolution Microscopy. The Panel consists of a number of distinguished microscopists in both the TEM and scanning probe microscopy areas; it was set up in January 1992 and will present its final report to the NSF in October 1992. Many of the points raised in discussion in this Workshop are also emphasised in the Panel's report. In the scanning microscopy field, the most urgent need was seen to be in the understanding of the interaction between the tip and the specimen. In the area of TEM, the report emphasises the need to extend the available resolution towards 0.6Å, to develop aberration correctors and to improve the cold FEG.

This ambitious program will require advances in optical design, stability and image processing, as well as in specimen preparation and stage design. A further point made was that future designs of instruments must be user-friendly and must yield results in a short timescale, if they are to be useful in the materials science community. The Panel also noted that the present system does not reward instrument builders (or experts in specimen preparation), and this situation will have to be rectified if we hope to see improvement in these important areas.

The report calls for a hopeful $10M over five years, to be distributed equally between the areas of TEM and scanning probe microscopy. The TEM funds will be used to construct approximately 15 new machines, of which at least one will be used to assess spherical aberration correctors, and others will address areas such as analytical STEM. This program represents a major initiative in the development of microscopy, and we hope that Congress will agree with us on its importance.

The Brite EURAM project is an ambitious and exciting project which is much further along the road to realization. The project is a collaboration between Philips and the universities of Tübingen, Delft and Antwerp. Its aim is to achieve sub-Ångstrom resolution at only 200-300kV, by using an FEG combined with through focal series reconstruction or holographic methods to reach the information limit of the microscope. Real time image processing and automated through focal series acquisition and analysis form an essential component of the system. At present, a resolution of 1.4Å has been achieved with a FEG at 200kV (C_S = 0.5mm) and a recently installed FEG which can operate at 300kV is expected to give sub-Å resolution (with a C_S of 0.7mm). One problem raised here was drift and the dose to the specimen; the long (20-30 image) through focal series needed take 75 seconds, of which the specimen is illuminated for 30 seconds, and the importance of sputtering and (for example) Frenkel pair formation, which both take place well below the displacement damage threshhold, was discussed. It is possible that very fast acquisition of images will provide a solution; a poor signal to noise ratio is not so important for single members of a through focal series.

A similar approach to the improvement of resolution is the Quantitative Sub-Ångstrom Microscope proposed for the NCEM at Lawrence Berkeley Laboratory. The idea here is to extend the range of use of a FEG towards 400kV. The information limit of the microscope will be reached by processing series of images, making use of the high coherence of the source. Improvements in specimen and microscope stability, focal series reconstruction and source coherence, rather than an increase in accelerating voltage, provide the best route to higher resolution. To analyze images of increased resolution, a more quantitative approach to image matching is under development, based on the use of R-factors rather than a personal judgment of the best fitting image.

As mentioned above, the development of *in situ* microscopy and the extension of microscopy to traditionally "difficult" materials such as magnetic materials will be of great importance in the future. Several specific ideas for new instruments were described during the discussion. One proposal submitted to DOE is for the HVEM Tandem Facility at Argonne. This machine will operate at 2MeV and will be specialized for *in situ* ion beam experiments. The design features a large polepiece gap with several ports, and a resolution of 1.2Å at 2MeV and >5Å at 150kV. Radiation effects can be reduced by doing the initial analysis of a specimen at a lower voltage (<300kV).

The Magnetic Materials Microscope, proposed for the NCEM at Lawrence Berkeley Laboratory, is intended to be a user facility for the examination of the microstructure of magnetic materials. As such, its design aims for a compromise between high resolution and the need for a spacious, magnetic field-free specimen environment. Probe sizes of 1nm in normal operation, or 3nm for magnetic materials, are envisaged, with facilities for holography, a DPC/STEM detector, and microanalysis using PEELS, CBED and BSED. This will enable both the physical and magnetic microstructures of the specimen to be examined at the nanometer scale. The main design constraint is of course the objective lens; at present, magnetic lenses have too small a gap to fit in the necessary microanalysis facilities and field-compensating coils, and electrostatic lenses do not operate at sufficiently high voltage and are also of poorer optical quality. The best solution may be a lens in which the specimen position is varied between microanalysis and magnetic experiments.

For many *in situ* experiments, high resolution is not necessary and this enables the specimen environment to be optimized around the use of other techniques. The SHEBA machine, nearing completion at the University of Illinois, has a very large specimen chamber differentially pumped to 10^{-10} Torr, in which specimen heating, evaporation and growth of different materials and techniques such as AES and RHEED can be carried out. The value for C_S is of the order of 0.3m, but the attainable resolution is still about 3nm, enabling observations of, for example, the behavior of steps during surface reactions.

The combination of other analytical methods with TEM is of course extremely powerful in solving materials problems. At ORNL, one approach which has shown great promise in the study of segregation at grain boundaries, for which high spatial resolution chemical information is required, is the combination of TEM and atom probe analysis. Grain boundaries near the tip of a needle shaped specimen are characterized firstly using TEM and later with the atom probe. A 300kV FEG with TEM and STEM capabilities, a dual objective lens (for imaging and analysis) and

an imaging energy filter is envisioned at ORNL to continue this research; the advanced design of this machine makes it a project for the distant future!

Finally, we discuss the exciting advances anticipated in the area of Z-contrast STEM, which parallel the proposals for developing conventional TEM. This technique has been very successful in chemical interface analysis at only 100kV and in the future the use of a 300kV dedicated STEM, achieving higher resolution, can be used for chemical analysis of (for example) the dumbbells in GeSi alloys, as well as new projections and new materials. *In situ* Z-contrast microscopy will be able to examine chemical reactions and growth mechanisms in real time. Although *in situ* STEM does not suffer from the polepiece space problems described above, its present frontiers are the improvement of our understanding of the image forming mechanism, as well as the usual specimen preparation problems.

In summary, the areas in which we most eagerly anticipate progress are firstly the achievement of sub-Ångstrom resolution, and secondly the construction of specialized microscopes, either to study particularly difficult materials or to do dynamic *in situ* experiments. The limits of high resolution do not appear to be λ or C_s, α, or C_c, which can be solved using aberration correctors, field emission guns and energy filtering; instead they are in the areas of stability (of both the specimen and the microscope), specimen preparation, contamination and thin foil effects such as relaxation. The limits are not even being approached in the area of *in situ* electron microscopy, particularly in the design of experiments which combine information from TEM with other analytical techniques. Innovative polepiece designs which allow more space around the specimen without compromising the resolution too seriously, environmental cells, and specimen holders which allow combinations of heating, cooling, biasing, straining and so on, make this one of the most rapidly advancing areas to be in. The future of microscopy as an exciting science is assured.

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