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APPLICATION OF Z-CONTRAST IMAGING TO OBTAIN COLUMN-BY-COLUMN SPECTROSCOPIC ANALYSIS OF MATERIALS

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ABSTRACT

Z-contrast imaging has been shown to be an effective method for obtaining a high-resolution image from a scanning transmission electron microscope (STEM). The incoherent nature of the high-angle scattering makes image interpretation straightforward and intuitive with the resolution limited only by the 2.2 Å electron probe. The optimum experimental conditions for Z-contrast imaging also coincide with those used for analytical microscopy, enabling microanalysis to be performed with the same spatial resolution as the image. The detection limits afforded by a parallel detection system for electron energy loss spectroscopy (EELS) allows column-by-column core-loss spectroscopy to be performed using the Z-contrast image to position the electron probe. Preliminary results from the study of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ illustrate the spatial resolution available with this technique and the potential applications for materials science.

INTRODUCTION

The electron microscope provides the ideal tool to investigate materials properties approaching the atomic scale. However, for conventional microscopic techniques, the spatial resolution of the analytical signal is an order of magnitude poorer than that of the image ($\sim 10\text{--}20$ Å compared with $1\text{--}2$ Å for a high-resolution image). Additionally, the coherent method of image formation in the conventional transmission electron microscope (CTEM) is very sensitive to operating parameters so that unknown structures cannot be directly interpreted in terms of atomic column locations and compositions.

The development of Z-contrast imaging [1] has facilitated a new approach to atomic-resolution microanalysis by the addition of a high-resolution imaging capability to the scanning transmission electron microscope (STEM), which is primarily used for nanometer scale microanalysis [2,3]. The VG HB501 UX dedicated STEM utilizes a focused 2.2 Å probe, which is scanned across the specimen while the integrated output from various imaging detectors is displayed on a TV screen, scanning at the same rate to form an image. This image formation process means that the spatial resolution of both the image and the analytical signal (when the scan is switched off) are limited only by the effective size of the probe. The detector arrangement in the STEM also has the advantage that the Z-contrast images can be recorded simultaneously with EELS and Energy Dispersive X-ray (EDX) signals.

EXPERIMENTAL TECHNIQUE

The Z-Contrast Image

As is illustrated in Fig. 1, the Z-contrast signal is collected from a high-angle annular detector. The annular detector collects scattered electrons in the range of $75\text{--}150$ mrad, where the dominant contribution to the detected intensity is from thermal diffuse scattering. In this high-angle regime, lateral coherence between the atomic columns in the specimen will be destroyed by detecting over a large angular range, and coherence between atoms in the same column will be averaged out by thermal vibrations. This high-angle diffuse scattering is, therefore, proportional to the electron intensity at each atom site, and as any coherent scattering of the outgoing electrons will also be averaged by the large angular range of the annular detector, the output signal is proportional to the integrated electron intensity at all atom sites under the beam. The detected intensity will, therefore, consist of a convolution of the probe profile and an object function which is strongly peaked at the atom sites. The width of this object function is typically ~ 0.1 Å and is dependent on the number of atoms in the projected columns and their atomic number Z . The spatial resolution of this signal is, therefore, limited only by the 2.2 Å probe size of the VG HB501 UX dedicated STEM. For a thin crystalline specimen in a major zone-axis orientation, when the probe is smaller than the

atomic column separations, a map of the location of the atomic columns can therefore be generated with the relative intensities of each column reflecting changes in composition [4].

Fig. 1. STEM schematic showing the simultaneous acquisition of Z-contrast image, EELS, and EDX

This incoherent nature of the Z-contrast image makes it an ideal reference signal on which to base atomic-resolution microanalysis. The effect of increasing thickness is initially to scale the intensity as more atoms contribute to the image, although eventually the contrast reduces as the beam gets depleted by scattering effects. The effect of changing focus is also intuitively understandable as the focus control effectively alters the probe profile (Fig. 2). Changing the focus away from the Scherzer incoherent condition [5], the probe either broadens for lower defocus causing the individual columns to be unresolved or narrows with the formation of more intense tails for higher defocus causing a sharper image but compositional smearing. The optimum focus condition, therefore, represents a compromise between high-resolution (narrow probe profile) and the desire for a highly local image (no significant tails to the probe). As can be seen from Fig. 2, changes in focus do not cause contrast reversals, making the optimum condition experimentally straightforward to identify. These easily interpretable thickness and focus changes allow the unambiguous identification of the atomic column sites.

Fig. 2. Probe profile as a function of defocus. The central profile corresponds to the Scherzer condition.

Electron Energy Loss Spectroscopy (EELS)

In order to achieve atomic-resolution analysis, the range over which a fast electron can cause a particular excitation event must be less than the interatomic spacing. This range is described classically by the impact parameter, b , an approach which has been shown to be valid for applications in STEM imaging [6,7]. A root-mean-square impact parameter, which gives the effective spatial range of the inelastic scattering signal, can be defined [8] as

$$b_{\text{RMS}} = \frac{\hbar v \theta_{\text{max}}}{\Delta E \left[(\theta_{\text{max}}^2 + \theta_E^2) \ln \left(1 + \frac{\theta_{\text{max}}^2}{\theta_E^2} \right) \right]^{1/2}} \quad (1)$$

where ΔE is the energy loss and $\Delta E \ll E$, v the electron velocity, θ_{max} is the aperture limited cut-off angle, and $\theta_E = \Delta E/2E$ (E = incident beam energy). In the STEM, the experimental spatial resolution limit is therefore given by adding the probe size and the impact parameter in quadrature (Fig. 3). For energy losses above ~ 300 eV and a collection angle of 30 mrad, the spatial resolution of the energy loss signal approaches the probe size.

Fig. 3. The effective spatial resolution for various energy losses as a function of collection angle.

The detection limits of the system are of critical importance in atomic-resolution studies. The signal count rate for EELS is given by [9]

$$S = J N_A n_{\Delta} \sigma \quad (2)$$

where J is the number of electrons/m², N_A is the number of atoms under the beam, n_{Δ} is the efficiency of collecting a given event over a finite range of energy and angle, and σ is the total scattering cross-section. Typically, for Z-contrast applications, the beam current is ~ 0.01 nA, the probe diameter is 2.2 Å, and the collection angle is limited to ~ 30 mrad by the inner angle of the dark field detector. The other factors are dependent on the particular energy loss, but for example, the oxygen K-edge ($\Delta E = 530$ eV) at the maximum useful quadrupole dispersion (0.1 eV/channel), where σ is $\sim 10^{-24}$ m², $n_{\Delta} \sim 6 \times 10^{-4}$, and $N_A \sim 100$ atoms gives a count rate of

$$S \sim 100 \text{ electrons / channel / second} \quad (3)$$

The dark current of the CCD is only ~ 0.05 electrons for a multiphase pinned (MPP) chip, which is negligible when compared to the fact that each incident fast electron produces 10 CCD charges. For this chip, the signal-to-noise ratio (expressed in equivalent fast electrons) is ~ 10 . Using the criterion that the signal-to-noise ratio should be at least 4 for a signal to be observable above random noise, the CCD is working within reasonable limits for this low current operation. For more practical conditions, i.e., 0.2 eV/channel dispersion and a 5-second acquisition time, the signal-to-noise ratio is ~ 32 , indicating that as well as elemental identification, it should be possible to observe the spectral fine structure.

As for the Z-contrast image, by collecting the scattered signal up to a fairly large angle, ~ 30 mrad, the scattering is effectively localized at the atom cores in the core loss region of the spectrum, and the large angular range averages any coherent effects on the outgoing electrons. For relatively thick specimens, as in the above example where the atomic column consists of 100 atoms, elastic scattering of the energy loss electrons outside of the angular range of detection may reduce the detected signal intensity. However, the detection limits of the system are such that even if this signal is depleted by as much as a factor of 5, it is still observable above the random background noise.

RESULTS AND DISCUSSION

A typical Z-contrast image of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ oriented with the c-axis perpendicular to the beam is shown in Fig. 4. The barium columns and the copper columns in the copper-oxygen chains are clearly resolved. The yttrium columns and the copper columns in the copper-oxygen planes are more difficult to resolve due to the poor signal-to-noise of the image. However, the image does provide a map of the atomic structure of the material and can be used as a reference for positioning the probe. By setting the quadrupole dispersion so that both the Ba $M_{4,5}$ and the Cu $L_{2,3}$ edges are present on the same spectrum (780 and 930 eV, respectively), the relative peak intensities can be measured as the probe is positioned on different atomic columns in the unit cell. Figure 5 shows the relative peak intensity of the barium edge to the copper edge as the probe is positioned on different atomic planes. The result clearly maps out changes in composition on the scale of a few Ångströms, with a change in the intensity ratio by a factor of ~ 3 in moving from the barium planes to the copper planes.

Fig. 4. Typical Z-contrast image of $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$.

Fig. 5. Ba/Cu edge intensity ratio as the probe is moved across three unit cells on the image.

While the result shows a spatial resolution which is on the sub-unit-cell scale, it is not the atomic-resolution spectrum expected from the calculations. For the ideal probe profile, an order of magnitude change in intensity ratio is expected in moving from the copper to the barium planes. The complete disappearance of one of the edges when the probe is centered on the other plane is unlikely due to the contribution to the spectral intensity of the probe tails (Fig. 2) on the surrounding columns. The extent of this contribution will be dependent on the atomic spacing of the material and also the composition of the column as the energy filtering of the spectrometer means that only surrounding columns containing elements with core-edges in the same region of the spectrum will affect the result. The calculations of spatial resolution for the energy loss signal also assume a very thin sample and ignore any beam broadening effects. For thicker specimens beam broadening effects have been observed experimentally for EELS by measurements on specimens in random orientations [10]. However, for a zone-axis orientation, the Z-contrast result [1] shows that if the scattering event takes place in close proximity to the atom cores, the effect of beam channeling preserves the spatial resolution of the signal (Fig. 6) (this non-broadening of the beam in specimens on or near zone-axis orientations has been observed in the x-ray measurements of Furdanowicz et al. [11]). While these factors, and the presence of an amorphous layer on the surface caused by the thinning technique, may degrade the resolution slightly, the overriding factor in this case is the mechanical shutter on the CCD which, when opening to acquire the spectrum, causes mechanical vibrations that move the probe during acquisition. Even with this mechanical vibration, which can be corrected by employing an electrical shift to move the beam off the CCD, rather than a shutter, the effective spatial resolution of the signal can be estimated, with reference to the image, to be ~ 5 Å.

CONCLUSIONS

Atomic-column spectroscopy can aid the understanding of materials at the fundamental atomic level. Using this technique, it will be possible to unambiguously locate the atomic columns in the complicated interfacial structures present in real materials, to measure

Fig. 6. Spatial resolution in the zone-axis orientation (a) is maintained by electron channeling effects, whereas for an amorphous or randomly oriented crystalline material (b), beam broadening occurs.

individual column composition and to determine local band structure. This capability will have applications in all fields of materials science. For example, the mechanical properties of steels, high-temperature intermetallics and nanophase ceramics are all controlled by segregation to dislocation cores at grain boundaries. Local changes in hole doping and atomic structure can now be studied simultaneously in the high-temperature superconductors on the same scale as the coherence length. This ability to study phenomenon at the atomic level will also provide a test for the atomistic simulations of interfaces and dislocations now being developed (ab-initio, molecular dynamics and Monte Carlo).

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