

## PROCESS FOR IDENTIFYING SINGLE CRYSTALS BY ELECTRON DIFFRACTION

This application claims the benefit of U.S. Provisional Application Ser. No. 60/333,583 filed Nov. 27, 2001, the entire disclosure of which is hereby incorporated by reference.

### BACKGROUND OF THE INVENTION

Electron diffraction is an identification technique for solid crystalline phases, particles, and surfaces observed in a transmission electron microscope (TEM) or other electron diffractometer. It is often used in conjunction with elemental analysis, which is often performed by fluorescence spectrometry (called EDS for energy dispersive spectrometry) on the TEM. Together these techniques are used by scientists to identify the chemical composition and structure of unknown materials of very small size, typically 10's to 1000's of nanometers (nm), in the fields of metallurgy, catalysis, analytical chemistry, mineralogy, forensics, and environmental studies.

Identification of a known single crystal phase by electron diffraction takes the form of interpreting a lattice net of spots produced in the diffraction mode of the TEM or electron diffractometer. Images can be recorded by (a) a fluorescent screen and photographic film, or (b) an electronic detector capable of converting diffracted electron impulses in two dimensional space to electronic signals which are converted, with their spatial positions, to digital form and stored in a computer file.

In case (a) the two minimum repeat distances ( $r_1$ ,  $r_2$ ) of the lattice net and their included acute angle ( $\phi$ ) are measured on the film. The corresponding maximum d-spacings, ( $d_1$ ,  $d_2$ ), in Angstrom units ( $\text{\AA}$ ) are calculated from each minimum repeat distance and the electron voltage or electron wavelength and the camera length (the distance between sample and recorder) of the diffractometer or TEM by Equation 1 (see below), or in case (b) the electronic file of converted signal impulses and positions ( $r_1$ ,  $r_2$ ), together with the electron voltage or electron wavelength and the camera length of the diffractometer or TEM is processed through computer programs or other calculations to produce the corresponding maximum d-spacings, ( $d_1$ ,  $d_2$ ), in Angstrom units by Equation 1 shown below:

$$r*d=C*\lambda \quad (\text{Equation 1})$$

wherein

$r$ =distance of spot from center in centimeters (also known as r-spacing),

$d$ =d-spacing in Angstroms ( $1 \text{\AA}=10^{-10}$  meter)

$C$ =camera constant in millimeter-Angstroms,

$\lambda$ =electron wavelength in nanometers,

which is determined from the electron voltage by conventional means, using the well known de Broglie Principle and related formulae.

Equation 1 is the well known application of Bragg's Law to electron diffraction (Reference 1). The two r-spacings ( $r_1$ ,  $r_2$ ) are the shortest and second shortest distances, respectively, to the center of the pattern (the direct beam), whereas the two d-spacings ( $d_1$ ,  $d_2$ ) are the largest and second largest d-spacings, respectively, of the zone of the pattern. The included angle,  $\phi$ , is both the acute angle between the lattice rows containing  $r_1$  and  $r_2$ , respectively, and the interplanar angle (acute) between the sets of parallel planes whose interplanar spacings are, respectively  $d_1$ , and

$d_2$ . These relationships as well as the terms, "d-spacing," "zone," "interplanar," are well known to those skilled in the art of crystallography.

An identification of a previously known material (or phase) is obtained when the values  $d_1$ ,  $d_2$ , and  $\phi$  are matched to measured or calculated values for a known material (References 2, 3).

The values of  $d_1$ ,  $d_2$ , of known materials are calculated from their unit cells through the well known formula for triclinic unit cells (Reference 4) by varying Miller indices ( $h,k,l$ ) from among those found in FIG. 1. These combinations ( $h_1, k_1, l_1$ ) and density (and low zone indices [U,V,W] (FIG. 1). These zones will also exhibit the highest spot symmetry in their electron diffraction patterns and will therefore be recognizable as the most desirable zones to be measured experimentally. The angle  $\phi$  is calculated from the well known formula for triclinic unit cells (Reference 4).

Candidate materials for a "hit" are found by matching the values of  $d_1$ ,  $d_2$ , and  $\phi$  determined experimentally to the values calculated from the unit cells of the known materials. Often the solutions above are not unique. In such cases, elemental analysis, for example by fluorescence spectrometry mentioned above, usually decides in favor of one or a very few possible, often chemically or structurally related, phases. Knowledge of sample history or other physical or analytical data might also be required for the final identification.

Prior art of comprehensive databases for electron diffraction is described in References 5, 6, 7, 8, and 9 and is summarized below.

The Powder Diffraction File, or PDF (Reference 6) of the International Centre for Diffraction Data (ICDD) is an x-ray polycrystalline diffraction database of d-spacings and other crystallographic data which is available in computer, microfiche, or book form. Its known disadvantage for use in electron diffraction is that it does not include d-spacings observed by double diffraction, because double diffraction is rare in x-ray diffraction.

Double diffraction is the phenomenon of a diffracted beam being rediffracted before exiting the crystal. The effect of this important phenomenon is that d-spacings which are unobservable ("extinct") by x-radiation appear in the electron diffraction pattern of the same material, as if there were no three-dimensional symmetry elements. These additional d-spacings due to double diffraction, which fill in x-ray extinct values, are included automatically if one calculates electron diffraction patterns from a reduced unit cell. This is the premise of ZONES. In this manner, no extra rings are calculated and none are missed. Further, there are no symmetry considerations.

Even more importantly, the PDF contains no interplanar angles ( $\phi$ ). One might use two d-values as  $d_1$  and  $d_2$  and calculate the interplanar angle from the Miller indices ( $h,k,l$ ) of each, which are usually on the PDF card for each material. This is a slow procedure of limited applicability to single crystal identifications which have very limited possible solutions.

The NIST/ICDD/Sandia Electron Diffraction Database (References 5, 6) is a polycrystalline computer database developed specifically for electron diffraction, incorporating both the PDF and NIST Crystal Data (described below). Since it contains no interplanar angles, it would have to be used for  $d_1$  and  $d_2$  only, requiring a separate calculation of  $\phi$ . Since no Miller indices are included in this database, it would be even more cumbersome to use than the PDF for single crystal electron diffraction.

Another database is available in book form only, the Elemental and Interplanar Spacing Index (EISI), available