

1

## PROCESS FOR IDENTIFYING POLYCRYSTALLINE MATERIALS BY ELECTRON DIFFRACTION

This application claims the benefit of U.S. Provisional Application No. 60/333,551 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 polycrystalline (meaning many crystallites in the electron beam simultaneously) phase by electron diffraction takes the form of interpreting images of concentric circles (rings) produced in the diffraction mode of the TEM. Images can be recorded on film, or more recently, collected electronically by an area detector for display on a computer monitor screen.

An identification of a previously known material (or phase) is obtained when the radii of the rings are matched to measured or calculated ring radii for a known material. As a practical matter, since ring radii also depend on instrumental parameters, a "d-spacing," which is dependent only on the crystal structure (instrument invariant) is calculated for each observed ring using Equation 1:

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

wherein,  $r$  = radius of a ring in centimeters (also known as r-spacing),  $d$  = d-spacing in Angstroms,  $C$  = 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). All references relating to the pattern of rings or concentric circles that will be alluded herein and in practice will be through the derived d-spacings (having the usual meaning to those skilled in the art of crystallography) in Angstrom ( $\text{\AA}$ ) units ( $1 \text{\AA} = 10^{-10}$  meter).

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.

The prior art of comprehensive databases for electron diffraction is summarized in Reference 4. The Powder Diffraction File (Reference 4) of the International Centre for Diffraction Data (ICDD) is an x-ray polycrystalline diffraction database of d-spacings. Its known disadvantage (Reference 6) 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

2

important phenomenon is that d-spacings which are unobservable ("extinct") by x-radiation due to the presence of symmetry elements appear in the electron diffraction pattern of the same material. This fact makes for incomplete and uncertain matches of most electron diffraction patterns to the Powder Diffraction File.

NIST Crystal Data, currently in Release J of 1997 on CD-ROM, began in the mid-1980's as a large computer file (first available on tape) of crystallographic and related data obtained from several other original sources such as ICDD (then known as The Joint Committee for Powder Diffraction Standards—JCPDS), The Cambridge Crystallographic Centre (U.K.), The Metals Data Center (Ottawa, Canada), The Inorganic Structural Data Center (Germany), and the open literature. Today, the database contains information on 237, 659 organic, inorganic, and organometallic phases (of which 79,136 are inorganic) and is available on CD-ROM from NIST or ICDD (References 2,3,4). For each phase (also called a "known material", as defined above), the data is organized into sixteen different types of several related fields each (Reference 2). The CD-ROM contains a single flat text file of these types for each phase, plus a coded literature reference file (one of the fields), and various special use files, not used here. Since d-spacings are not among the data, a reduced unit cell must first be determined from the d-spacings before searching this database. The quality and extent of typical electron diffraction patterns is inadequate to determine a unit cell, consequently the database can only be used in reverse mode. That is, guess a known material from the elemental composition of the unknown, calculate the known diffraction pattern from the database unit cell and compare to the experimental pattern. Such a process is too dependent on past experience and involves repeated calculations.

The NIST/Sandia/ICDD Electron Diffraction Database (References 3,4,6,7,8) is a collection of ring diffraction patterns (mostly calculated from NIST Crystal Data, but also obtained from the Powder Diffraction File and related phase information along with search software (EDSEARCH) and utility programs for electron diffraction. It is available through the ICDD. Developed in the mid-1980's, the system was written for a PC with limited disk storage (approximately 10 Mb), limited memory (approximately 640K), limited other general use PC software (e.g. for relational databases), and relatively slow speed (less than 50 MHz) in mind. Consequently, it sacrifices user convenience and flexibility for code optimization and data storage considerations. The results from the EDSEARCH option must be examined by hand in great detail for realistic solutions ("candidate materials") to the problem. Usually, the correct solution(s) are found among many other solutions which are equally or nearly equally ranked by its "Figure of Merit" (FOM) index, defined below. Recommended values for FOM minimum and number of input rings are 80 and six, respectively.

The FOM is defined in EDSEARCH as:

$$\text{FOM} = 200 \sum_{i=1}^N W_i / \{N(N+1)\} \quad (\text{Equation 2})$$

wherein  $N$  = number of experimental r-spacings,  $W_i$  = weighting factor, either  $N+1-i$  or zero, depending on whether the  $i$ -th R-spacing is a hit or a miss. R-spacings are numbered consecutively beginning with the smallest. Interpretation of the FOM is as follows.  $N(N+1)/2$  is the sum of  $N$  consecutive integers. Hence the formula is a percentage of