

COMPUTER APPLICATIONS FOR THE MATERIALS LABORATORY/CLASSROOM: Illustrating Structure and Diffraction

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PREREQUISITE KNOWLEDGE: Introduction to crystallography and diffraction, as provided in a typical, lower-division materials engineering course.

OBJECTIVE: To utilize relatively sophisticated research equipment for undergraduate teaching.

EQUIPMENT AND SUPPLIES:

1. Scintag XDS2000 X-ray Diffractometer [or similar, contemporary diffractometer with computer control and data analysis capabilities].
2. Silicon Graphics Workstation with Molecular Simulations Software [or similar graphics platform with crystal structure simulation package].
3. Power Macintosh or PC with CD drive.

INTRODUCTION

Shackelford [1] has recently outlined the use of equipment available in the materials laboratories at a typical research university for the purpose of undergraduate teaching. The result is a set of three examples of the contributions that can be provided to materials engineering education by contemporary computers. First, the use of an x-ray diffractometer with computer control and data analysis in an undergraduate structures course is an excellent tool for demonstrating the role of computers in the materials laboratory. Second and closely related to diffraction is the use of computer modeling of atomic-scale structures, a major development in the field of materials science in the past decade. Commercial software packages are now available for this purpose. Using a graphics platform, these simulation packages can be used to illustrate structure in undergraduate courses, as well as predict diffraction patterns. Third, CD-ROM technology is providing a convenient supplement to current textbooks, e.g., a ready source of figures and tables. Ironically, there is some debate as to whether the CD-ROM may replace the textbook in the future.

X-RAY DIFFRACTOMETER WITH COMPUTER CONTROL AND DATA ANALYSIS

The x-ray diffractometer is a sophisticated piece of experimental equipment that is widely available in materials engineering laboratories. Although often acquired for support of research, a contemporary diffractometer is an excellent example of a computer-interfaced experimental system for teaching purposes. Both experimental control and data analysis are generally performed in conjunction with a computer. Table I summarizes a set of x-ray diffraction experiments used in EMS 132L, an x-ray diffraction based laboratory course on the structure of engineering materials. It is offered at the University of California, Davis in the junior year as part of a core-course sequence of basic materials science topics. The experiments represent long-established x-ray diffraction applications [2].

Table I List of X-ray Diffraction Experiments in a Junior-Level Introductory Course on the Structure of Materials

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EMS 132L Structure of Materials Laboratory

X-ray Diffraction Experiments

Introduction/Orientation, Radiation Safety
Phase Identification and Quantitative Analysis
Particle Size Measurement
Residual Stress Measurement

Our laboratory has a Scintag XDS 2000 diffractometer with an intrinsic Ge detector and a 486 PC and a MicroVax for computer control and data analysis. The most general application is the use of the Search-Match software based on the Powder Diffraction File of the International Centre for Diffraction Data (ICDD). The search of more than 60,000 powder diffraction files can be done in less than one minute. With the increasing interest in nano-scale sample preparation, the software packages for particle size measurement are highly useful. Both Scherrer analysis and Warren-Averbach analysis are available for determining particle size (and, in the case of Warren-Averbach, lattice microstrain) based on diffraction peak line broadening.[2] The Scherrer analysis can be carried out in about one minute, and the Warren-Averbach analysis can be carried out in a few minutes. Figures 1 and 2 illustrate experiments in which one powder sample is identified by its x-ray diffraction pattern and line broadening is used to identify the particle size of another.

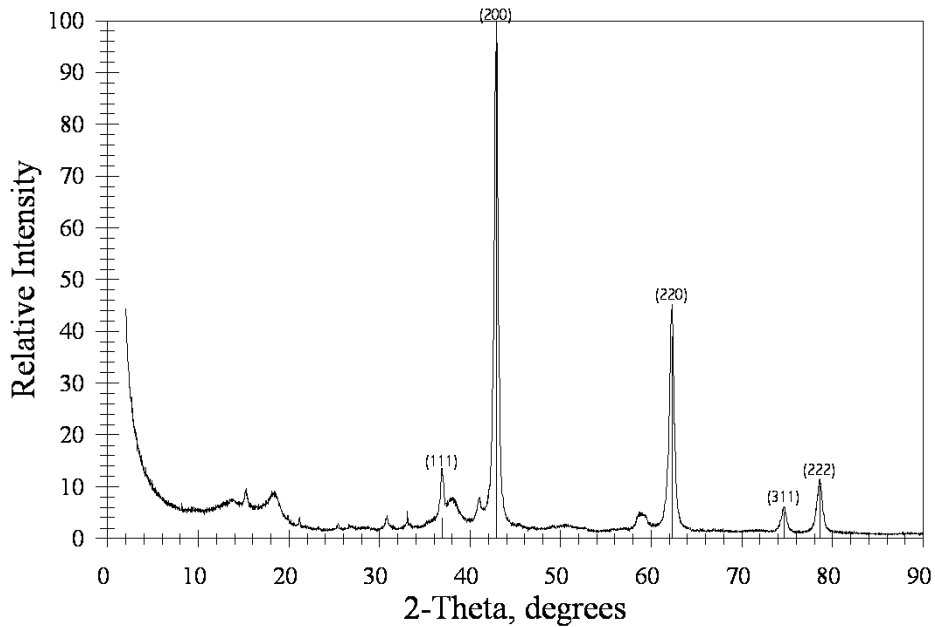


Figure 1 Experimental x-ray diffraction pattern of Buehler's Magomet polishing powder which is primarily MgO. The Scintag search match program was used to identify the peaks for the periclase phase, PDF file 45-0946. The periclase peaks are labeled using their Miller indices.

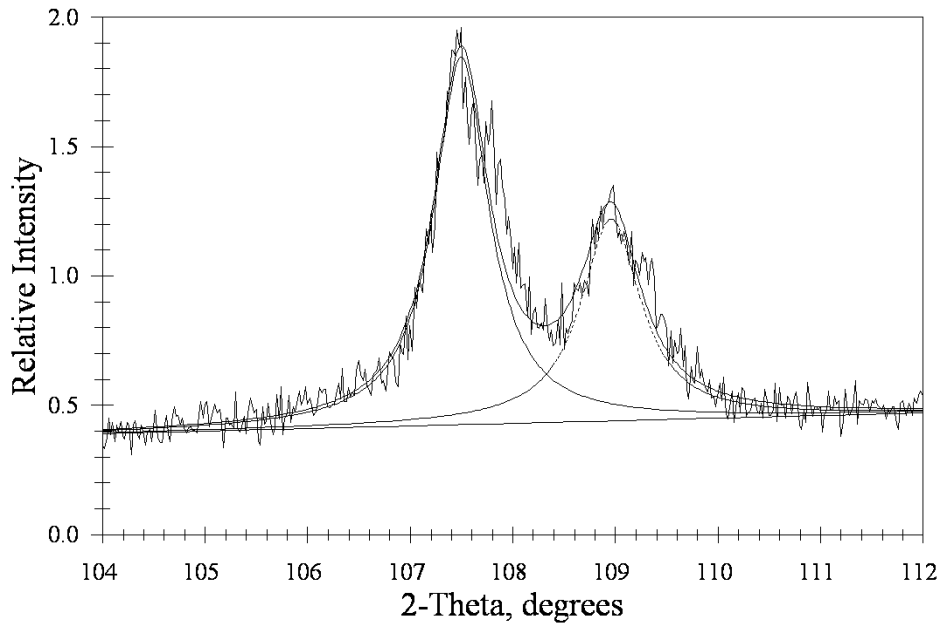


Figure 2 Example of diffraction peak line broadening in the x-ray diffraction pattern of nanocrystalline TiO₂ powder. An average particle size of 32 nm gives substantial broadening measured at the half-maximum peak height of each of two adjacent peaks.

Perhaps the most significant benefit of the computer-aided diffraction experiment is the ability to do residual stress measurements. The use of the multi-angle specimen tilting technique has long been used to measure residual stress in metal alloys.[2] Lange, et.al. [3] have also shown the technique to be applicable to structural ceramics. The magnitude of stress is indicated by the amount of shift in the diffraction angle caused by the independent tilting of the specimen surface away from the normal configuration. Table II gives typical results for the measurement of surface stresses due to the fabrication of a steel spring. It is important to note that, prior to the computerization of such multi-angle tilting experiments, the experiment was extremely tedious and time consuming. With the system in our laboratory, undergraduates can carry out accurate and reproducible measurements of stress with five tilt angles between $\pm 30^\circ$ and a total experimental time of less than 20 minutes. One should also note that the steel sample was analyzed using Cu K α radiation. Traditional residual stress measurements on ferritic steels are done with Cr K α radiation for which the (211) plane gives a large diffraction angle (above $150^\circ 2\theta$). Such large angles maximize experimental accuracy.[2] The class experiment was carried out with Cu radiation to minimize disruption to research measurements. It is encouraging that good accuracy is possible with this much lower diffraction angle (in which the (211) line occurs just above $82^\circ 2\theta$). For calibration, Table II includes results for an annealed tungsten powder (essentially stress-free giving an essentially zero stress result within experimental scatter). Figure 3 illustrates a multi-angle plot of diffraction angle (2θ) versus the square of the sin of the tilt angle, with the magnitude of the slope representing the residual stress in the steel spring of Table II.

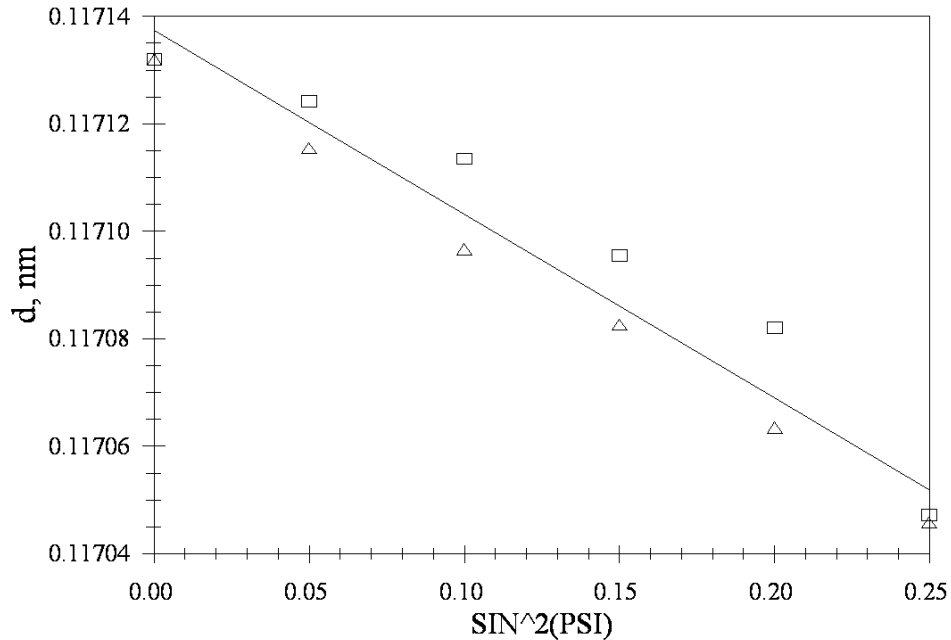


Figure 3 Experimental plot of the change in interplanar spacing of the (211) diffraction peak of a spring steel as a function of the square of the specimen tilt angle (psi). The shift in d values is a result of the residual stress in the surface of the steel sample as a result of its manufacturing process. The triangle symbol data represent negative values of psi (specimen tilted towards the x-ray source) and the square symbol data represent positive values. The slope of the plot indicates a compressive stress of 506 Mpa.

Table II Typical Residual Stress Data for a Steel Spring

Steel Spring Stress Measurement - Experimental Conditions

- C Cu K α radiation
- C (211) peak [at approx. 82.3° 2 θ]
- C Elastic constants*: $S_1 = -1.25$ and $\frac{1}{2}S_2 = 5.76$ [in units of $10^{-6} (\text{MPa})^{-1}$]

Sample	Stress (MPa)
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Steel Spring	-505.6 \pm 31.9
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Tungsten Powder Stress Measurement - Experimental Conditions

- C Cu K α radiation
- C (400) peak [at approx. 153.5° 2 θ]
- C Elastic constants*: $S_1 = -1.50$ and $\frac{1}{2}S_2 = 6.50$ [in units of $10^{-6} (\text{MPa})^{-1}$]

Sample	Stress (MPa)
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Annealed W powder	-12.5 \pm 29.4
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* Note that $S_1 = -\langle \epsilon \rangle / E$ and $\frac{1}{2}S_2 = (1 + \nu) \langle \epsilon \rangle / E$

COMPUTER MODELING OF ATOMIC-SCALE STRUCTURES

Computer modeling has become a highly effective tool in materials research in the past decade, stemming from the refined understanding of interatomic potentials which allows precise modeling of atomic-scale structures.[4] The application to biological chemistry has allowed such modeling to replace substantial amounts of experimentation in the preliminary stages of drug design. The leading commercial software package for structural modeling, Molecular Simulations, Inc., grew out of BIOSYM Technologies, Inc., which, as the name implies, grew out of the biomolecular simulation market, e.g. pharmaceutical design. An inorganic package is now available, appropriate given that Molecular Simulations, Inc. is now a subsidiary of Corning, Inc. In our laboratory, we are using the Molecular Simulations Insight II software on a Silicon Graphics Indigo 2/XZ platform. Figure 4 gives a simple example of the use of a similar simulation package to produce an illustration of the crystalline structure of rock salt, which applies to a number of important ceramic oxides. Nearly all crystal structure illustrations in the fourth edition of Shackelford's introductory materials science text were produced in this way.[5] In more advanced materials courses, the software package can be used to simulate x-ray and electron diffraction patterns and nmr spectra for given crystal structures.

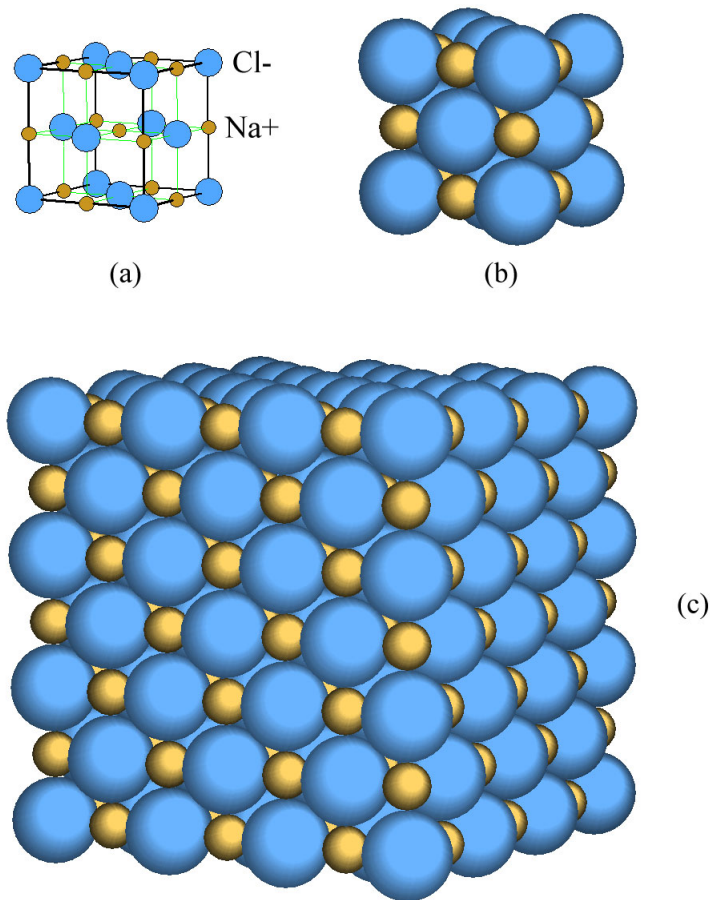


Figure 4 Illustration of the sodium chloride (and related oxides) unit cell. Parts (a), (b) and (c) were generated with a commercial computer simulation software package.

CD-ROM TECHNOLOGY

Another interesting aspect of computer technology in engineering education is the increasingly wide use of the CD-ROM. The enormous memory storage capability of the CD-ROM has had an especially significant impact

on the technology of the textbook. A good example is the CD-ROM "Materials Science - A Multimedia Approach" by J.C. Russ. It includes a set of interactive HyperCard stacks and QuickTime visualizations. This CD is marketed as a supplement to Askeland's introductory materials science textbook.[6] Another example is the CD-ROM entitled "Materials Science on CD-ROM", published by Chapman and Hall, which takes more of a tutorial approach complete with interesting simulations. An alternative approach is a complementary CD-ROM which is a straight reproduction of the figures and tables of Shackelford's introductory text [5] and is provided with the Instructor's Manual. This configuration allows the instructor to produce laser-quality reproductions of any figure or table from the text. Figure 5 is an example of such a print out. Perhaps the most intriguing question associated with the CD-ROM is whether it will continue to be a supplement to the textbook or become its replacement.[7]

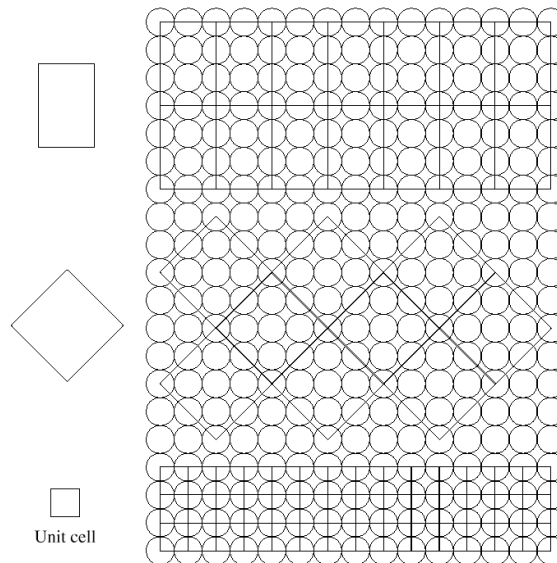


Figure 5 A visual representation of the crystallographic unit cell. This illustration was taken directly from the CD-ROM supplement to reference 5.

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REFERENCES

- [1] J.F. Shackelford, "Computer Applications for the Ceramic Engineering and Materials Engineering Curricula," in Innovative Ideas in Ceramics and Materials Curricula, ed T. Stoebe and W. Huebner, American Ceramic Society, Westerville, OH, 1996.
- [2] B.D. Cullity, Elements of X-ray Diffraction, 2nd Edition, Addison-Wesley, Reading, MA, 1978.
- [3] F.F. Lange, M.R. James, and D.J. Green, J.Amer.Ceram.Soc., **66** C16-C17 (1983).
- [4] H.W. Kroto, et.al., "New Horizons in Carbon Chemistry and Materials Science," MRS Bulletin, **19** [11] 51-55 (1994).
- [5] J.F. Shackelford, Introduction to Materials Science for Engineers, 4th Edition, Prentice-Hall, Upper Saddle River, NJ, 1996.
- [6] D.R. Askeland, The Science and Engineering of Materials, 3rd Edition, PWS, Boston, MA, 1994.

[7] P. Hood, "Books: The Next Big Thing," Newmedia, 4 [4] 8 (1994).

BIOGRAPHICAL SKETCHES

James F. Shackelford has BS and MS degrees in Ceramic Engineering from the University of Washington and a Ph.D. in Materials Science and Engineering from the University of California, Berkeley. He is currently a Professor in the Department of Chemical Engineering and Materials Science and the Associate Dean for Undergraduate Studies in the College of Engineering at the University of California, Davis. He teaches and conducts research in the areas of materials science, the structure of materials, nondestructive testing, and biomaterials. A member of ASM International, the Materials Research Society, and the American Ceramic Society, he was named a Fellow of the American Ceramic Society in 1992 and received the Outstanding Educator Award of the American Ceramic Society in 1996. He has published over 80 archived papers and books including Introduction to Materials Science for Engineers now in its 4th Edition and The CRC Materials Science and Engineering Handbook now in its 2nd Edition.

Michael L. Meier has a BS degree in materials science from North Carolina State University, Raleigh and MS and PhD degrees in materials science from the University of California at Davis. He is currently a lecturer in the Department of Chemical Engineering and Materials Science at the University of California at Davis. He teaches and manages the central departmental laboratories and is developing the undergraduate laboratory teaching program, is a member of TMS and ASMI and is a member of the executive committee for the Golden Gate Chapter of ASMI.