Syllabus, MSNE/PHYS 435/535, Spring 2019

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Crystallography and Diffraction – Study of crystalline and other condensed matter by x-ray, electron and neutron diffraction. Includes basic diffraction theory as well as methods for characterizing structure, composition and stresses.

This course is required for all MSNE undergrads and most MSNE grad students. It may also be appropriate for students in CHEM, CENG, PHYS, GEOL, etc. For applications in biology there are BIOC 482/552 and 535.

- **Instructor:** Peter Loos **on campus:** ME 215 ploos@rice.edu
- **Office hours:** after class, by appointment, and other times TBD
- **Teaching Assistant:** Lucas Isenhart lci1@rice.edu availability: TBD, probably Tue. or Thu. afternoons
- **Class Meets:** MWF 10:00-10:50 am in MEL 254.
- **Prerequisites:** MSNE 301 & 303 are required pre-requisites for undergrads. Familiarity with the seven crystal systems, fourteen Bravais lattices, and Miller indices is assumed. An understanding of geometry and trigonometry is essential. Differentiation, integration, complex arithmetic, and linear algebra are also used.
- **Text:** ***Elements of X-ray Diffraction***, 3rd ed. by Cullity & Stock (2001). Available from abebooks.com, bn.com, amazon.com, www.campusbooks4less.com, directtextbook.com, etc. but not Rice Campus Store. Cost of the international edition is about $20. Cullity's 1978 2nd edition can also be used along with a cross-reference list. The numerous 3rd editions have numerous errors but 2nd edition has none. See errata list. If you will be using 3rd edition, print out a copy and keep it with your book. On the Web one can find complete PDF copies of the 1956 first edition, some of which have a first page identical to the cover of 3rd edition. **The 1956 edition is NOT suitable. Students using the 1956 edition will have their homework graded as wrong.**
- **Grading:** 45% homework, 40% tests, 15% quizzes. There will be approximately two tests, two quizzes and eleven homework assignments. 535 students will be assigned several more homework problems than 435 students. Points may be deducted for assignments turned in late and for bad or missing references.
- **References:** Whenever quoting or giving data from a source other than the class lecture slides or textbook, a proper reference must be given. Use the ACS format per pubs.acs.org/doi/pdf/10.1021/bk-2006-STYG.ch014 or in simpler form**:** http://library.williams.edu/citing/styles/acs.php**.**
- **Absence Policy:** Students are expected to attend class unless they have a communicable disease, a job interview which could not be scheduled outside of class hours, or they are incarcerated in jail or hospital. Missed quizzes will have to be made up right away.
- **Tests** are take-home, unlimited time, open book, and open notes but limited to your own books and your own notes, the class lecture slides, information found at links given in those lecture slides, and other resources provided on the class Canvas page. Answers and work turned in must be your own. Students are NOT permitted to communicate with anyone other than the instructor about any aspect of tests, past or present. Students are NOT permitted to examine or use information about tests previously given in this class, except for ones a students has taken himself or herself. The **Rice Honor Pledge** must be included on every test.
- **Homework:** may be ***discussed*** with others, but you must NOT examine or borrow from anyone else's written or typed homework solutions.
- **Quizzes** are limited time (about 15 to 25 minutes at the end of class), closed book, closed notes, no electronic devices of any kind. Answers and work turned in must be entirely your own. Students are NOT permitted to communicate with or copy from others who are currently taking or have already taken this class. Students are NOT permitted to look at or use information about any quiz previously given in this class, except for ones a students has taken himself or herself. The **Rice Honor Pledge** must be included on every quiz.
- **Software:** PowderCell is used to create models of crystal structure unit cells and to calculate the corresponding x-ray powder diffraction patterns. This software is available free as described below under Resources on the Web. CaRIne has many similar features and can also compute and display reciprocal lattices. A free demo version is available. Spreadsheets will be used extensively. The Crystallography Open Database and AFLOW will be presented and used in class.
- **Lab:** MSNE 437 is required for the BS MSNE and is also open to a limited number of other students.
- **Disabled Students:** Any student with a disability requiring accommodations in this course should contact Instructor after class, by email, or during office hours. Additionally, students will need to contact Disability Support Services in Allen Center.

Topics to be Covered

- Production, discovery & applications of cathode rays & x-rays.
- Properties of x-rays. Emission, absorption, detection & safety precautions.
- Crystal lattices and their symmetry. Point groups and space groups.
- The reciprocal lattice and stereographic projection. Ewald construction in reciprocal space.
- Diffraction, constructive & destructive interference, derivation of Bragg's Law.
- Experimental methods for single & polycrystalline samples, effect of crystallite size (thickness) per Scherrer's equation.
- Scattering of x-rays by electrons, atoms and unit cells.
- Structure factor for various crystals. Other factors which determine intensity of diffracted beams. Application to powder diffraction.
- Use of PowderCell software. Use of intensity ratios to determine fractions of phases in a mixture.
- Indexing diffraction patterns, determination of crystal structure. Precise determination of lattice parameters
- Determination of phase diagrams.
- Ordered and disordered alloys.
- Measurement of micro-strain and residual macro-stress. Separation of line broadening due to micro-strain and crystallite size.
- Comparison of x-ray, electron & neutron diffraction methods. Scattering factors for electrons and neutrons.
- Selected area diffraction (SAD) on the transmission electron microscope (TEM), indexing of SAD patterns.
- Small angle x-ray scattering (SAXS)
- Quasicrystals, discovered in 1984

Goals for this course:

To address ABET Student Outcomes and Program Criteria, students will have

1. an ability to identify, formulate, and solve complex engineering problems by applying principles of engineering, science, and mathematics
6. an ability to develop and conduct appropriate experimentation, analyze and interpret data, and use engineering judgment to draw conclusions.

and the course will

- prepare graduates to apply advanced science … and engineering principles to materials systems …
- prepare graduates to utilize experimental, statistical, & computational methods …

More specifically:

(1) Students will become familiar with the crystal structures of most metals and ceramics, how those structures are determined experimentally, and how they are described in the literature.
(2) Students will become familiar with how such structure information is used to determine strains, stresses, composition, orientation, density, and size of features in the crystalline solid.
(3) Students will be able to assess the technical literature on this subject.

Optional Supplemental Reading

X-Ray Diffraction by B.E. Warren, Dover 1990 $17 (Addison-Wesley, 1969) A rigorous graduate-level text, detailed mathematical theory, includes thermal vibration effects, order-disorder phenomena, crystal imperfections, structure of amorphous materials, and diffraction of x-rays in perfect crystals.

Fundamentals of Crystallography by Giacovazzo, Monaco, Viterbo, Giacovazzo & Scordari, Oxford U. Press, 1992 about $30 used ...advanced graduate level text from IUCr, includes crystal symmetry, computational methods, physics of diffraction, instrumentation & methods, ionic and molecular crystals, protein crystallography, etc.

Introduction to Diffraction in Materials Science and Engineering by Aaron Krawitz. A well-written book, intended as a one-semester introduction, on a level comparable to our text, but with more emphasis on neutron diffraction and little concerning electron diffraction. Krawitz taught 435/535 class at Rice for several years.

Solid State Physics by Ashcroft & Mermin (Holt Rinehart, 1976). See chapters 4,5,6,7,19,20 and Appendices F & N.

ASM Handbook by ASM Handbook Committee sometimes available via http://libguides.rice.edu/go.php?c=27371619. See especially ***Volume 9, Metallography and Microstructures*** (2004)**:** "Crystal Structure", "Ordered Structures", and "Textured Structures". ***Volume 10, Materials Characterization*** (1986): "X-Ray Powder Diffraction", "Single Crystal X-Ray Diffraction", "Neutron Diffraction", and "Analytical Transmission Electron Microscopy". ***Volume 3: Alloy Phase Diagrams*** (2016). ASM Handbooks are a great resource for all practicing materials scientists and engineers.

Phase Equilibria Diagram Books*, *Volumes I through XIV from American Ceramic Society and National Institute for Standards and Technology. Also offered in digital formats.

The Basics of Crystallography and Diffraction by C. Hammond, Oxford. Univ. Press and Int. Union of Crystallography, 1997 $72 (paperback) ...a good introductory undergraduate-level text which avoids much of the mathematical theory.

Introduction to Crystallography by Donald E. Sands. Another good, inexpensive paperback from Dover. Includes two chapters on the theory and methods of x-ray diffraction.

Quasicrystals: A Primer 2nd Ed. by C. Janot, Oxford Univ. Press, about $55

The Annual Book of ASTM Standards. 77 volumes containing about 12,000 "standards" documents relating to the production, testing, and performance of countless materials of commercial importance. For details see www.astm.org or Annual Book of Standards or Standards Search. Our library has the entire set on microfilm and your instructor has several volumes too. About 20 or so ASTM standards involve XRD, everything from instrument alignment to measurement of stress, particle size, composition and orientation. See list at H&M Analytical using the Wayback Machine: https://web.archive.org/web/20080517105205/http://www.h-and-m-analytical.com/pdfs/standards.pdf

Crystallography Resources On the Web

- **Discovery of the Electron**, historical developments from the AIP: www.aip.org/history/electron/
- **Int. Union of Crystallography**: Links to everything crystallographic. www.iucr.org. See especially Educational Resources at www.iucr.org/cww-top/edu.index.html for example, www.iucr.org/iucr-top/comm/cteach/pamphlets/16/index.html, The Study of Metals and Alloys by X-ray Powder Diffraction Methods.
- **XRD on Mars**: Curiosity's CheMin instrument using a Co source tube, 28 kV power supply, and 360 K pixel CCD detector: www.iucr.org/news/research-news/the-first-x-ray-diffraction-measurements-on-mars and http://journals.iucr.org/m/issues/2014/06/00/yu5005/index.html and https://www.youtube.com/watch?v=20zeFVQ87ro starting at 41:10.
- **American Crystallographic Association** – see www.amercrystalassn.org
- **Crystal lattice structures** from the Naval Research Lab. These were taken offline a few years ago and have to be accessed through the Wayback Machine at archive.org/web/: See http://cst-www.nrl.navy.mil/lattice/ also many useful links at: http://cst-www.nrl.navy.mil/lattice/others.html. An alternative is AFLOWlib.org .
- **Crystallographic Space Group Diagrams & Tables** http://img.chem.ucl.ac.uk/sgp/mainmenu.htm Univ. College London
- **XRayView**, a virtual X-Ray crystallography laboratory from George Phillips: www.bioc.rice.edu/Bioch/Phillips/Papers/XRayView/
- LawrenceBerkeley: **X-ray interactions with matter**, data & calculations henke.lbl.gov/optical_constants/ and xdb.lbl.gov including x-ray reflectivity modeling software, mass absorption coefficients, atomic scattering factors, etc.
- **Neutron scattering coefficients** from Brookhaven National Lab www.nndc.bnl.gov/exfor/endf00.jsp
- "***neutron scattering, A PRIMER***" by Roger Pynn www.ncnr.nist.gov/summerschool/ss16/pdf/NeutronScatteringPrimer.pdf or as lecture slides at https://neutrons.ornl.gov/sites/default/files/intro_to_neutron_scattering.pdf
- Tutorial on **protein crystallography** www.ruppweb.org/Xray/101index.html from B. Rupp at QED Life Sciences
- **PowderCell** software from the German Fed. Inst. for Materials Research & Testing (BAM). https://web.archive.org/web/20150226175100/http://www.bam.de:80/de/service/publikationen/powder_cell.htm. Download version 2.4 for 64-bit Windows from https://web.archive.org/web/20070309190802/http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/powdcell/Powder_Cell/pcw23.exe Although the filename indicates ver 2.3 (32 bit) it's really ver. 2.4 (64 bit). See also site CCP14 search https://www.google.com/search?domains=ccp14.ac.uk&num=50&ie=UTF-8&oe=UTF-8&q=powdercell&sitesearch=ccp14.ac.uk&btnG=Go%21
- **Collaborative Computational Project Number 14**: www.ccp14.ac.uk . Lots of helpful tutorials and free software for single crystal and powder diffraction. Plenty of information about Powdercell.
- **International Centre for Diffraction Data** - purveyors of the Powder Diffraction File (PDF) www.icdd.com
- **Crystallography Open Database**: www.crystallography.net searchable and free. Results are given in the CIF (crystallographic information file) ASCII text format. See www.iucr.org/resources/cif for details.
- **Mineral structural information:** MINCRYST, searchable by name, composition & other parameters: database.iem.ac.ru/mincryst/ and webmineral.com which is full of useful mineralogy & crystallography information and also the American Mineralogist Crystal Structure Database http://rruff.geo.arizona.edu/AMS/amcsd.php
- **Quasicrystals:** Introduction by S. Weber: jcrystal.com/steffenweber/qc.html and also by Ron Lifshitz at TAU: www.tau.ac.il/~ronlif/quasicrystals.html .
- **Commercial XRD labs:** Lambda Research, founded by Cullity www.lambdatechs.com. See especially publications www.lambdatechs.com/publications/publications.html. Rigaku, who sell XRD instruments and also provide XRD measurement services www.rigaku.com/en/applications. H&M Analytical Services www.h-and-m-analytical.com. All three labs provide plenty of application notes, papers and other technical literature for free download.