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System Design and Verification of the Precession Electron Diffraction Technique

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Christopher Su-Yan Own

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# ABSTRACT

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Christopher Su-Yan Own

Bulk structural crystallography is generally a two-part process wherein a rough starting structure model is first derived, then later refined to give an accurate model of the structure. The critical step is the determination of the initial model. As materials problems decrease in length scale, the electron microscope has proven to be a versatile and effective tool for studying many problems. However, study of complex bulk structures by electron diffraction has been hindered by the problem of dynamical diffraction. This phenomenon makes bulk electron diffraction very sensitive to specimen thickness, and expensive equipment such as aberration-corrected scanning transmission microscopes or elaborate methodology such as high resolution imaging combined with diffraction and simulation are often required to generate good starting structures.

The precession electron diffraction technique (PED), which has the ability to significantly reduce dynamical effects in diffraction patterns, has shown promise as being a "philosopher's stone" for bulk electron diffraction. However, a comprehensive understanding of its abilities and limitations is necessary before it can be put into widespread use as a standalone technique. This thesis aims to bridge the gaps in understanding and utilizing precession so that practical application might be realized.

Two new PED systems have been built, and optimal operating parameters have been elucidated. The role of lens aberrations is described in detail, and an alignment procedure is given that shows how to circumvent aberration in order to obtain high-quality patterns. Multislice simulation is used for investigating the errors inherent in precession, and is also used as a reference for comparison to simple models and to experimental PED data. General trends over a large sampling of parameter space are determined. In particular, we show that the primary reflection intensity errors occur near the transmitted beam and decay with increasing angle and decreasing specimen thickness. These errors, occurring at the lowest spatial frequencies, fortuitously coincide with reflections for which phases are easiest to determine via imaging methods. A general two-beam dynamical model based upon an existing approximate model is found to be fairly accurate across most experimental conditions, particularly where it is needed for providing a correction to distorted data. Finally, the practical structure solution procedure using PED is demonstrated for several model material systems.

Of the experiment parameters investigated, the cone semi-angle is found to be the most important (it should be as large as possible), followed closely by specimen thickness (thinner is better). Assuming

good structure projection characteristics in the specimen, the thickness tractable by PED is extended to 40-50 nm without correction, demonstrated for complex oxides. With a forward calculation based upon the two-beam dynamical model (using known structure factors), usable specimen thickness can be extended past 150 nm. For *a priori* correction, using the squared amplitudes approximates the two-beam model for most thicknesses if the scattering from the structure adheres to psuedo-kinematical behavior. Practically, crystals up to 60 nm in thickness can now be processed by the precession methods developed in this thesis.

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# References

Avilov, A.S., A.K. Kuligin, U. Pietsch, J.C.H. Spence, V.G. Tsirelson, and J.M. Zuo. 1999. Scanning system for high-energy electron diffractometry. *J. Appl. Cryst.* 32:1033–1038.

Bagdik'ianc, G.O., and A.G. Alexeev. 1959. *Izv. Akad. Nauk SSSR Ser. Fiz.* 23:773–779.

Batson, P.E., N. Dellby, and O.L. Krivanek. 2002. Sub-ångstroøm resolution using aberration corrected electron optics. *Nature* 418:617–620.

Berg, B.S., V. Hansen, P.A. Midgley, and J. Gjønnes. 1998. Measurement of three-dimensional intensity data in electron diffraction by the precession technique. *Ultramic.* 74:147–157.

Bethe, H.A. 1928. Theorie der beugung von elektronen an kristallen. *Ann. Phys. (Leipzig)* 87:55–129.

Blackman, M. 1939. On the intensities of electron diffraction rings. *Proc. Roy. Soc.* 173:68–82.

Cheng, Y.F., W. Nuchter, J. Mayer, A. Weickenmeier, and J. Gjønnes. 1996. Low-order structure-factor amplitude and sign determination of an unknown structure $al_m fe$ by quantitative convergent-beam electron diffraction. *Acta Cryst. A* 52:923–36.

Chukhovskii, F.N., J.J. Hu, and L.D. Marks. 2001. Statistical dynamical direct methods ii: The three-phase structure invariant. *Acta Cryst. A* 57:231–239.

Cochran, W. 1955. Relations between the phases of structure factors. *Acta Cryst.* 8:473–478.

Combettes, P.L. 1996. Method of successive projections for finding a common point of sets in metric spaces. *Adv. Imag. Elec. Phys.* 95:155–261.

Cowley, J.M., and A.F. Moodie. 1957. The scattering of electrons by atoms and crystals. i. a new theoretical approach. *Acta Cryst.* 10:609–619.

Deng, B., and L.D. Marks. 2005 in preparation.

Dorset, D.L. 1995. *Structural electron crystallography*. New York:Plenum Publishing Co.

Dorset, D.L., S. Hovmoller, and X. Zou, eds. 1997. *Electron crystallography*. Dordrecht:Kluwer Academic.

Edwards, D.D., T.O. Mason, W. Sinkler, L.D. Marks, K.R. Poeppelmeier, Z. Hu, and J.D. Jorgensen. 2000. Tunneled intergrowth structures in the $ga_2o_3$-$in_2o_3$-$sno_2$ system. *Journal of Solid State Chemistry* 150:294–304.

Egerton, R.F. 1989. *Electron*. New York:Plenum Press.

Franco, S. 2002. *Design with operational amplifiers and analog integrated circuits*. New York:McGraw-Hill.

Gemmi, M. 2001. Precession technique. In *Electron crystallography and cryo-electron microscopy on inorganic materials and organic and biological molecules*, ed. J. Puiggali, A. Rodriquez-Galan, L. Franco, and M.T. Casas, L91–L97. Barcelona:Universitat Politecnica De Catalunya.

Gemmi, M., X.D. Zou, S. Hovmoller, A. Migliori, M. Vennstrom, and Y. Andersson. 2003. Structure of ti$_2$p solved by three-dimensional electron diffraction data collected with the precession technique and high-resolution electron microscopy. *Acta Cryst. A* 59:117–126.

Gjønnes, J., V. Hansen, B.S. Berg, P. Runde, Y.F. Cheng, K. Gjnnes, D.L. Dorset, and C.J. Gilmore. 1998a. Structure model for the phase al$_m$fe derived from three-dimensional electron diffraction intensity data collected by a precession technique. comparison with convergent-beam diffraction. *Acta Cryst. A* 54:306–319.

Gjønnes, J., and A.F. Moodie. 1965. Extinction conditions in dynamic theory of electron diffraction. *Acta Cryst.* 19:65–&.

Gjønnes, K. 1997. On the integration of electron diffraction intensities in the vincent-midgley precession technique. *Ultramicroscopy* 69:1–11.

Gjønnes, K., Y.F. Cheng, B.S. Berg, and V. Hansen. 1998b. Corrections for multiple scattering in integrated electron diffraction intensities. application to determination of structure factors in the 001 projection of al$_m$fe. *Acta Cryst. A* 54:102–119.

Griend, D.A. Vander, S. Boudin, V. Caignaert, K.R. Poeppelmeier, Y.G. Wang, V.P. Dravid, M. Azuma, M. Takano, Z.B. Hu, and J.D. Jorgensen. 1999. La$_4$cu$_3$moo$_{12}$: A novel cuprate with unusual magnetism. *J. Am. Chem. Soc.* 121:4787.

Haider, M., S. Uhlemann, and B. Kabius. 1999. Towards sub-ångstrøm resolution by correction of spherical aberration. *Scanning* 21:89–90.

Haider, M., S. Uhlemann, E. Schwan, H. Rose, B. Kabius, and K. Urban. 1998. Electron microscopy image enhanced. *Nature* 392:768–769.

Harker, D., and J.S. Kasper. 1948. Phases of fourier coefficients directly from cyrstal diffraction data. *Acta Cryst.* 1:70–75.

Hauptman, H.A. 1991. The phase problem of x-ray crystallography. *Rep. Prog. Phys.* 54:1427–1454.

Hirsch, P.B., A. Howie, R.B. Nicholson, and D.W. Pashley, eds. 1965. *Electron microscopy of thin crystals*. London:Spottiswoode, Ballantyne, & Co. Ltd.

Horowitz, P., and W. Hill. 1989. *The art of electronics*. New York:Cambridge University Press.

Hu, J.J., F.N. Chukhovskii, and L.D. Marks. 2000. Statistical dynamical direct methods. i. the effective kinematical approximation. *Acta Cryst. A* 56:458–469.

Hwang, J.H., D.D. Edwards, D.R. Kammler, and T.O. Mason. 2000. Point defects and electrical properties of sn-doped in-based transparent conducting oxides. *Solid State Ionics* 129:135–144.

Jansen, J., D. Tang, H.W. Zandbergen, and H. Schenk. 1998. Msls and a least-squares procedure for accurate crystal structure refinement from dynamical electron diffraction patterns. *Acta Cryst. A* 54: 91–101.

Khattak, C.P., D.E. Cox, and F.F.Y. Wang. 1975. Magnetic ordering in ba$_2$mnreo$_6$. *J. Solid State Chem.* 13:77–83.

Kilaas, R., L.D. Marks, and C.S. Own. 2005. Edm 1.0: Electron direct methods. *Ultramic.* 102:233–237.

Krivanek, O.L., N. Dellby, and A.R. Lupini. 1999. Towards sub-å electron beams. *Ultramic.* 78:1–11.

Krivanek, O.L., and P.A. Stadelmann. 1995. Effect of three-fold astigmatism on high resolution electron micrographs. *Ultramic.* 60:103.

Landree, E., C. Callazo-Davila, and L.D. Marks. 1997. Multi-solution genetic algorithm approach to surface structure determination using direct methods. *Acta Cryst. B* 53:916–922.

Levi, A., and H. Stark. 1984. Image restoration by the method of generalized projections with application to restoration form magnitude. *J. Opt. Soc. Am. A* 1:932–943.

Mancini, R. 2002. *Op amps for everyone*. Dallas:Texas Instruments, Inc.

Marks, L.D., E. Bengu, C. Callazo-Davila, D. Grozea, E. Landree, C. Leslie, and W. Sinkler. 1998. Direct methods for surfaces. *Surf. Rev. Let.* 5:1087–1106.

Marks, L.D., and W. Sinkler. 2003. Sufficient conditions for direct methods with swift electrons. *Micros. and Microanal.* 9:399–410.

Midgley, P.A., M.E. Sleight, M. Saunders, and R. Vincent. 1998. Measurement of debye-waller factors by electron precession. *Ultramic.* 75:61–67.

Nellist, P.D., M.F. Chisholm, N. Dellby, O.L. Krivanek, M.F. Murfitt, Z.S. Szilagyi, A.R. Lupini, A. Borisevich, W.H. Sides, and S.J. Pennycook. 2004. Direct sub-ångstroøm imaging of a crystal lattice. *Science* 205:1741–1741.

Newsam, J.M. 1988. Synthesis and structural characterization of a lithium gallosilicate with the zeolite abw framework. *J. Phys. Chem* 92:445–452.

Nicolopoulos, S., J.M. Gonzalezcalbet, M. Valletregi, A. Corma, C. Corell, J.M. Guil, and J. Perezpariente. 1995. Direct phasing in electron crystallography — *ab-initio* determination of a new mcm-22 zeolite structure. *J. Am. Chem. Soc.* 117:8947–8956.

O'Keefe, M.A., and R. Kilaas. 1988. Advances in high-resolution image simulation in image and signal processing in electron microscopy. In *Scanning microscopy supplement 2*, ed. P.W. Hawkes, F.P. Ottensmeyer, W.O. Saxton, and A. Rosenfeld, 225. AMF O'Hare, IL:SEM, Inc.

Own, C.S., and L.D. Marks. 2004. Hollow-cone electron diffraction system. US Patent application no: 60/531,641.

———. 2005a. Prospects for aberration-corrected precession. *Micros. and Microanal.* submitted.

———. 2005b. Rapid structure determination of a metal oxide from pseudo-kinematical electron diffraction data. *Ulramic.* in press.

Own, C.S., L.D. Marks, and W. Sinkler. 2005a. Electron precession: A guide for implementation. *Rev. Sci. Instr.* 76:Art. no. 033703.

Own, C.S., W. Sinkler, and L.D. Marks. 2005b in preparation.

Own, C.S., A.K. Subramanian, and L.D. Marks. 2004. Quantitative analyses of precession diffraction data for large cell oxides. *Micros. and Microanal.* 10:96–104.

Sayre, D. 1952. The squaring method: a new method for phase determination. *Acta Cryst.* 5:60–65.

Scherzer, O. 1936. Uber einige fehler von elektronenlinsen. *Zeit. Phys.* 101:593.

Sinkler, W., W. Bengu, and L.D. Marks. 1998a. Application of direct methods to dynamical electron diffraction data solving bulk crystal structures. *Acta Cryst. A* 54:591–605.

Sinkler, W., and L.D. Marks. 1999a. Dynamical direct methods for everyone. *Ultramic.* 75:251–268.

———. 1999b. A simple channelling model for hrem contrast transfer under dynamical conditions. *J. Microscopy* 194:112–123.

Sinkler, W., L.D. Marks, D.D. Edwards, T.O. Mason, K.R. Poeppelmeier, Z. Hu, and J.D. Jorgensen. 1998b. Determination of oxygen atomic positions in a ga-in-sn-o ceramic using direct methods and electron diffraction. *Journal of Solid State Chemistry* 136:145–149.

Spence, J.C.H. 2003. *High-resolution electron microscopy*. Oxford:Oxford Univ. Press.

Spence, J.C.H, and J.M. Zuo. 1992. *Electron microdiffraction*. New York:Plenum Press.

Suzuki, Y., A. Takeuchi, H. Takano, and H. Takenaka. 2005. Performance test of fresnel zone plate with 50 nm outermost zone width in hard x-ray region. *Jap. J. Appl. Phys. 1* 44:1996–2000.

Vainshtein, B.K. 1964. New York:Pergamon Press.

Vainshtein, B.K., B.B. Zvyagin, and A.S. Avilov. 1992. Electron diffraction structure analysis. In *Electron diffraction techniques, vol.2*, ed. J.M. Cowley, 216–312. Oxford:Oxford University Press.

Vincent, R., and D.M. Bird. 1986. Measurement of kinematic intensities from large-angle electron-diffraction patterns. *Phil. Mag. A* 53:L35–L40.

Vincent, R., D.M. Bird, and J.W. Steeds. 1984. Structure of augeas determined by convergent-beam electron diffraction: 1. derivation of basic structure. *Phil. Mag. A* 50:745–763.

Vincent, R., and P. Midgley. 1994. Double conical beam-rocking system for measurement of integrated electron-diffraction intensities. *Ultramic.* 53:271–282.

Weirich, T.E. 2004. The crystal structure of $zr_2se$ reinvestigated by electron crystallography and x-ray powder diffraction. *Cryst. Rep.* 49:379–389.

Xu, P., G. Jayaram, and L.D. Marks. 1994. Cross-correlation method for intensity measurement of transmission electron diffraction patterns. *Ultramic.* 53:15–18.

Youla, D.C. 1987. Mathematical theory of image restoration by the method of convex projections. In *Image recovery: theory and applications*, ed. H. Stark, L91–L97. Orlando:Academic press, Inc.

Yu, B.Y., A. Abramov, V.G. Tsirelson, V.E. Zavodnik, S.A. Ivanov, and I.D. Brown. 1995. The chemical bond and atomic displacements in $srtio_3$ from x-ray diffraction analysis. *Acta Cryst. B* 51:942–951.

Zukhlistov, A.P., M.S. Nickolsk, B.B. Zvyagin, A.S. Avilov, A.K. Kulygin, S. Nicolopoulos, and R. Ochs. 2004. Imaging plates - a new life for electron diffraction structure analysis. *Zeit. Krist.* 219:2004.