CHAPTER 6

Conclusions and Future Work

The precession technique was first introduced over ten years ago by Vincent and Midgley (1994). It was extremely promising, and over the past decade a small number of groups have attempted to solve difficult problems using the technique. The Al_mFe precipitate system was investigated by precession through the use of multiple 2D projections corrected for precession geometry merged into a 3D data set (Gjønnes et al. 1998a). A second study on the same system explored one zone axis using a very involved correction factor (Gjønnes 1997; Gjønnes et al. 1998b). Midgley et al. (1998) showed that the precession intensities can be used with Wilson plots to determine Debye-Waller factors fairly accurately in simple crystals, and Gemmi et al. (2003) have studied Ti_2P using a similar 3D merged projection method using geometry correction factors. Recently, the Marks research group has published an investigation on $La_4Cu_3MoO_{12}$ with the interest of understanding the scattering physics.

The results have been mixed. Precession electron diffraction technology has been deficient in two areas. Firstly, the early instrumentation was limited: there were few instruments available on which to conduct studies, and the poor probe localization crippled the technique as a true nanoprobe method. The instrumentation limitation caused considerable confusion in the results by confounding the effects of thickness averaging with the other linearizing (toward kinematical) effects of precession, such as the resistance to systematic diffraction paths. The second problem was that experimental parameters were not well-understood. The latter was badly needed to understand in more detail what the ideal conditions for the experiment were. With a better understanding of the experimental parameters, one can start to build robustness into the method. For example, the mediocre R-factors obtained in Gjønnes et al. (1998b) and Gjønnes et al. (1998a) — 32% (unrefined) and 42% (refined), respectively — were due to too large thickness and variability in the first study, and too low precession angle combined with thickness in the second study. These could be avoided relatively easily by the researcher at the microscope; in the first, a thinner specimen would have been preferred, and in the second, the 3D merge might have been better if no corrections were applied and larger angles were used.

There is frequently a large gap between the introduction of a technique and its successful widespread application. This thesis endeavors to take a large step toward the realization of precession electron diffraction as a useful and reliable crystallography technique. The two issues mentioned above have been treated here, first through a development phase where new precession instrumentation based upon the early concept was designed and refined from an applications engineering standpoint. The design stressed versatility and user-friendliness, so

it is easily re-configurable for functionality, yet always ensures usability by the end user. The versatile instrument design aided the successful acquisition of high quality PED patterns for comparison with theoretical models. The second phase involved development of the technique from a standpoint of basic scattering theory. Multislice simulation allowed control of variables and a thorough investigation of experiment space. The correction factors in the literature were investigated in detail through comparison with the multislice and exact two-beam models, and from these a new set of guidelines for PED experiments have been formulated.

Through thorough investigation of experimental parameter space, it has been found that the variables cone angle ϕ and specimen thickness determine the majority of the data set behavior. Their interaction, along with the specimen's extinction characteristics, causes modification of the intensities to a pseudo-kinematical model for specimens of small-to-moderate thickness, given that large ϕ is used. In the limit of large thickness, the intensities converge to a two-beam model. This is because the only major dynamical effect occurs when the systematic row condition is satisfied, which behaves superficially like the two-beam condition so it does not cause large deviation. This happens twice during the precession, and with large cone angle the duration is short. Very little n-beam interaction occurs otherwise in the PED experiment.

In more specific practical terms, a large cone angle of $\phi = 50$-75 mrad is best used under all conditions. The probe localization is linked to the precession angle, so it may be compromised if very high angle is desired. Provided that large ϕ is used, the amplitudes can be interpreted as pseudo-kinematical amplitudes up to thicknesses about 35-50 nm, depending upon the distribution of strong reflections with g and projection characteristics of the material. The correction factor that acts only on geometry (C_{kin}) is useful for very thin specimens (under 20 nm) but is ill-advised for thick specimens. The geometry correction C_{Gj} proposed by Gjønnes (1997) is invalid except for large thickness, where it must be used in conjunction with the dynamical correction factor (the full correction factor $C_{Blackman}$ or C_{2beam}). This is because the geometry term is independent of dynamical effects, hence applying only C_{Gj} will result in incomplete scaling and force weak beams above beams that have been damped by dynamical exchange.

For thicker specimen ranges, correction factors are necessary to correct for two-beam dynamical effects that cause the data to deviate from psuedo-kinematical. For *a priori* investigations where structure factors are not known, thicker specimens may be linearized by squaring the structure factors in the limit of large thickness; if the structure is known to be thick, it will likely fall under the limit of the Blackman equation. This will not, however work for exceptionally large thicknesses (> 60 nm, to be conservative) because it only works to correct strong intensities that have deviated from their values due to two-beam dynamical exchange. At such large thickness, multi-beam mixing is so strong that many weak reflections may become as intense as the strong reflections, so phase relationships are not preserved.

Not all types of structures will be amenable to precession. PED will work best on structures that better obey the statistics that preserve phase relationships between scattered intensities. In the best case, the intensities will behave within a completely pseudo-kinematical interpretation. In the worst case where the structures do not project well or become extremely

dynamical at small thickness, statistical dynamical direct methods will hopefully still apply. With pseudo-kinematical data, the intensity relationships will largely be preserved, hence the phase relationships will more likely match the true phase relationships rather than approximate them. Therefore, structures that project well are most suitable. Structures with poor projection (such as Mordenite) have intensity ordering at high spatial frequency, representing an ill-conditioned problem for DM (e.g., small changes in intensity easily corrupt the recovered phase relationships). Fortunately, the imaging capabilities of the electron microscope can be used in tandem to acquire phases in these cases: specimens that are suitable for high-resolution imaging are usually thin, so if HREM is employed the precession pattern is simultaneously available. Additionally, the phases of low-index reflections — for which intensities may unavailable in precession due to large error — are the easiest to acquire in HREM.

The major problem we set out to solve was whether precession electron diffraction could be the universal bulk electron crystallography tool. It is difficult to definitively state that PED will or will not work in a general sense because its operation is inherently statistical in nature; it depends strongly on specimen type and morphology. The results here show that thus far it is not the final solution for bulk electron diffraction ultimately because of thickness limitation, but it does provide the crystallographer with a new tool for solving many structure problems that would ordinarily be very difficult, very time-consuming, or simply impossible. Elucidation of a standard procedure with which to employ PED represents a significant step toward routine bulk structural crystallography via electron direct methods.

6.1. Future Work

While the results in this thesis show that the technique is ready to be used in the field, this work can be extended in a number of areas. The foremost extension is application to more structures to build a repertoire of structures solved by PED. We have looked at known structures in order to build and confirm an accurate model of the physics of precession. Unknown structures need to be solved to garner more attention for the technique.

In the discussion on instrumentation (chapter 2), the topic of aberration correction was introduced as a way to extend cone semi-angle. Originally developed for direct imaging, it has now found use in diffraction as well. It would be interesting to see the limits of the technique in terms of ultra-high-angle precession instrumentation. Methods for data collection from individual Laue zones would need to be developed to avoid Laue zone overlap, but an inherent advantage of large cone angle is that reliable 3-D precession may be possible. Advanced instrumentation will enable fancy scanning configurations allowing, for example, circumvention of multi-beam excitation conditions that cause deviation from two-beam excitation.

Ab initio recovery of the structure from very thick specimens is still out of reach. One suggestion that may allow thick specimen investigation by PED is to develop an iterative dynamical Lorentz correction that could start from a set of rough structure factors and refine them to the true structure factor (suggested at the end of chapter 4). This will require a detailed analysis of how the conditioning of the two-beam model behaves. A more complex analytical

model would be ideal for developing this correction. Work in the Marks group on developing a reduced analytical form is already underway.

A final idea that has garnered great interest lately is using diffraction to probe the charge density of structures. The atom positions are useful as a starting point for describing the materials, but it is the electronic structure that determines the properties of the material. Beam electrons scatter from the electron charge, therefore they are inherently more sensitive to the charge in the structure than X-rays. It would be advantageous if, instead of locating atoms, the charge density can be determined directly from the diffraction experiment. It has been seen that the reflections most sensitive to charge density are the low-index reflections (Deng and Marks 2005), but unfortunately the reflections with the most error in PED are the same ones. A robust correction factor applied to these reflections may restore their usefulness in revealing the charge density within the structure.