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The Nature of Precession Electron Diffraction Data

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The Vincent & Midgley precession electron diffraction technique is a unique approach to data collection for structure solution. The technique, less than ten years old, has been used to aid structure refinement of a quasicrystal [1] and a rare earth oxide [2], and more recently has been found to be an accurate tool for measuring Debye-Waller factors [3]. While originally developed for *ab initio* structure determination of unknown phases, no structure to date has been solved solely using precession. This is likely due in part to the difficulty in predicting precession data behavior, since it is neither dynamical nor kinematical.

The commonly used approximation for diffraction due to conical illumination is an integration using two-beam dynamical theory [4]. Gjønnes has provided geometrical correction factors to this approximation, which for selected area diffraction gives the equation:

$$\frac{I_{prec}}{I_{kin}} \propto g\sqrt{1-\left(\frac{g}{2R_0}\right)^2}\cdot\frac{1}{A_{hkl}}\int_0^{A_{hkl}} J_0(2x)dx \qquad (1)$$

where A_{hkl} is a normalization factor proportional to thickness and to the structure factor of the *hkl* reflection, and R_0 is the radius of the zeroth order Laue circle [5]. Precession and conventional diffraction data gathered from the complex cell oxide $La_4Cu_3MoO_{12}$ using a precession-capable instrument [6] have been compared to the Blackman approximation [7], and precession was shown to approximate Blackman theory rather well. However, coincidence with the Blackman curve alone is insufficient for straightforward structure solution, especially for large unit cell crystals that exhibit complicated intensity ordering in their diffraction patterns.

A subtle consequence of Blackman theory is that specimen thickness affects the distribution of structure factors, forming separate quasi-linear regimes in the dynamical v. kinematical intensity plot (fig. 1). Linearity indicates that the ratio between measured and kinematical intensities is nearly constant; when strong reflections follow a linear trend (fig. 2b), the data is ideal for kinematical structure solution techniques. Increasing specimen thickness decreases the y-offset of the trendline, which strengthens the data set by incorporating medium intensity reflections into the linear regime of the stronger reflections. Additionally, cautious removal of weak (high order and/or low structure factor) reflections narrows the data set into a more linear band of reflections, further aiding interpretation of intensities by direct methods algorithms. In summary, Blackman theory surprisingly indicates that in the case of precession, thicker specimens will improve tractability of the structure problem, both by improving linearity of strong reflections and by assimilating medium intensity reflections into the strong reflection trendline.

The precession data set in fig. 2b, which exhibits approximately linear precession intensities, produced the preliminary structure solution of $La_4Cu_3MoO_{12}$ shown in fig. 3 using the fs98 direct methods software package. Electron diffraction of powder specimens of the complex cell oxide provided evidence of two phases with similar base structures. The precession-derived structure

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shows strong similarities to that previously determined by Vander Griend, et al. [8], demonstrating metal atoms surrounded by clearly defined oxygen atoms (trigonal bipyramids). This second phase shares major structural reflections with Vander Griend's phase, which has twice the unit cell spacing along ***a***, hence X-Ray data from that study would not distinguish between the two phases if both were present in a polycrystal.

An alternative to the Blackman approximation is a model of precession by integration of a channeling approximation, which is considerably more exact than the integration over excitation error in previous analyses. This approximation and a comparison of its accuracy in relation to the Blackman model will be presented. [9]

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[9] This work possible with support from the Hertz Foundation (also sponsor of primary author's graduate study). Acknowledgement goes to the Marks research group for feedback and discussion.

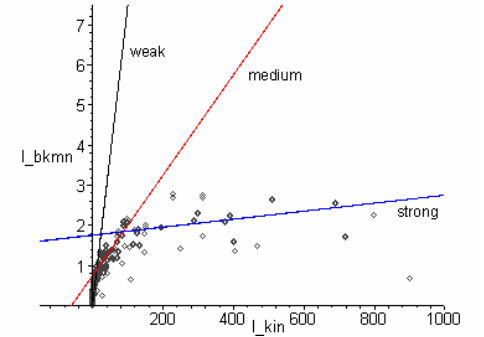

Fig. 1. Calculated v. kinematical intensity for t = 25nm. Weak, medium, and strong reflections can be divided into separate quasi-linear regions.

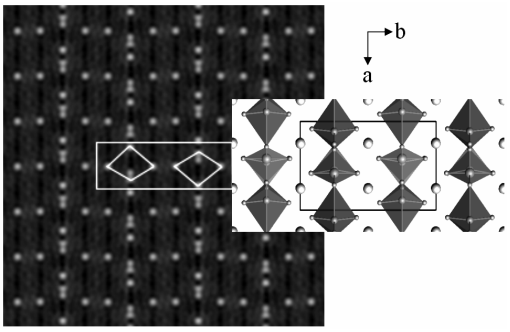

Fig. 3. (Left) Structure of $La_4Cu_3MoO_{12}$ solved using precession intensities. a=3.43Å,b=10.97Å. Vector a is half that of the suggested structure (right) [8], indicating a relaxation of the magnetically frustrated bi-pyramid substructure that generates the larger cell.

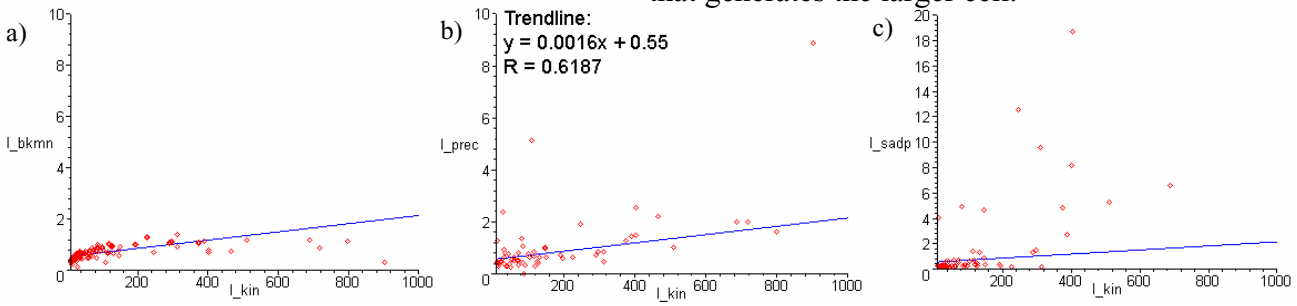

Fig. 2. a) Calculated v. kinematical intensity for t = 50nm. b) Precession data and c) SADP data from $La_4Cu_3MoO_{12}$ crystal. All data is symmetry-averaged; trendline generated from data in b) is shown in a) and c) for comparison.

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