Chapter

I

# *Installation*

The application MacTempas and its associated files are installed by double clicking on the installer package. After authorizing the installer with the administrator password, the installer will install MacTempas into a directory in your applications folder. The driver for the hardware key will also be installed.

## Installing the Hardware Protection Key

MacTempas uses a hardware copy protection key which must be installed on your computer. If you already have installed a key for use with CrystalKit, you do not need a second key to run MacTempas and you can proceed to the next paragraph describing how to activate the key for running MacTempas. Just plug the USB key into an open USB slot on your computer, keyboard or display.

## Activating the Hardware Key and Personalizing the Program

When MacTempas is run for the first time it will put up its installation screen. Enter your name and affiliation as appropriate together with the installation code for the hardware key. T

## Changing Hardware or Versions of the MacOS

If you have just changed your computer or installed a new clean version of the MacOS, you must ensure that the driver for the USB key is installed. Run the installation program for Mactempas once more to install the driver. Without the driver in place, the program will not recognize the hardware key and MacTempas will run in demonstration mode.

Chapter 1

# *Introduction to Image Simulation*

The best High Resolution Transmission Electron Microscopes (HRTEM) have a resolution approaching 1 Å which sometimes leads to the erroneous conclusion that using an electron microscope, all atoms in a structure can be resolved. However, it is not the inter-atomic distances that matter, but rather the projected distances between atoms seen from the direction of the incident electron. In order to obtain interpretable results, it is necessary to orient the specimen such that atomic columns are separated by distances that are of the order of the resolution of the microscope or larger. This is a condition that very often is difficult to satisfy and often limits the use of the HRTEM to studies of crystals only in low order zone-axis orientations. The HRTEM image is a complex function of the interaction between the high energy electrons (typically 200keV - 1MeV) with the electrostatic potential in the specimen and the magnetic fields of the image forming lenses in the microscope. Although images obtained from simple mono-atomic crystals often show white dots separated by spacings that correspond to spacings between atomic columns, these white dots fall on or between atomic columns depending on the thickness of the specimen and the focus setting of the objective lens (O'Keefe et al.,1989). Fortunately, in many cases it is only necessary to see the general pattern of image intensities to gain the desired knowledge. However, in general, the image can be best thought of as a complex interference pattern which has the symmetry of the projected atomic configuration, but otherwise has no one-to-one correspondence to atomic positions in the specimen. It is because of this lack of directly interpretable images that the need for image simulation arose. Image simulation grew out of an attempt to explain why electron microscope images of complex oxides sometimes showed black dots in patterns corre-

sponding to the patterns of heavy metal sites in complex oxides, and yet other images sometimes showed white dots in the same patterns (Allpress et al.,1972). This first application was therefore to characterize the experimental images, that is to relate the image character (the patterns of light and dark dots) to known features in the structure.

Most simulations today are carried out for similar reasons, or even as a means of structure determination. Given a number of possible models for the structure under investigation, images are simulated from these models and compared with experimental images obtained on a high-resolution electron microscope. In this way, some of the postulated models can be ruled out until only one remains. If all possible models have been examined, then the remaining model is the correct one for the structure. For this process to produce a correct result, the investigator must ensure that all possible models have been examined, and compared with experimental images over a wide range of crystal thickness and microscope defocus. It is also a good idea to match simulations and experimental images for more than one orientation.

The simulation programs can also be used to study the imaging process itself. By simulating images for imaginary electron microscopes, we can look for ways in which to improve the performance of present-day instruments, or even find that the performance of an existing electron microscope can be improved significantly by minor changes in some instrumental parameter. Alternatively, based on imaging requirements revealed by test simulations, we can adjust the electron microscope to produce suitable images of some particular specimen, or even of some particular feature in a particular specimen.

## Describing the Transmission Electron Microscope

In order to simulate an electron microscope image, we need firstly to be able to describe the electron microscope in such a way that we can model the manner in which it produces the image. As a first step, we can consider the usual geometrical optics depiction of the transmission electron microscope (TEM).
Figure 1 shows such a diagram of a TEM operated in two distinct modes, set up for microscopy (a), and for diffraction (b). In microscopy mode we see that the TEM consists of an electron source producing a beam of electrons that are focused by a condenser lens onto the specimen; electrons passing through the specimen are focused by the objective lens to form an image called the first intermediate image (I1); this first intermediate image forms the "object" for the next lens, the intermediate lens, which produces a magnified image of it called the second intermediate image (I2); in turn, this second intermediate image becomes the "object" for the projector lens; the projector lens forms the greatly-magnified final image on the viewing screen of the microscope. In microscopy mode, electrons that emerge from the same point on the specimen exit surface are brought together at the same point in the final image.

At the focal plane of the objective lens, we see that electrons are brought together that have left the specimen at different points but at the same angle. The diffraction pattern that is formed at the focal plane of the objective lens can be viewed on the viewing screen of the TEM by weakening the intermediate lens to place the microscope in diffraction mode (b).

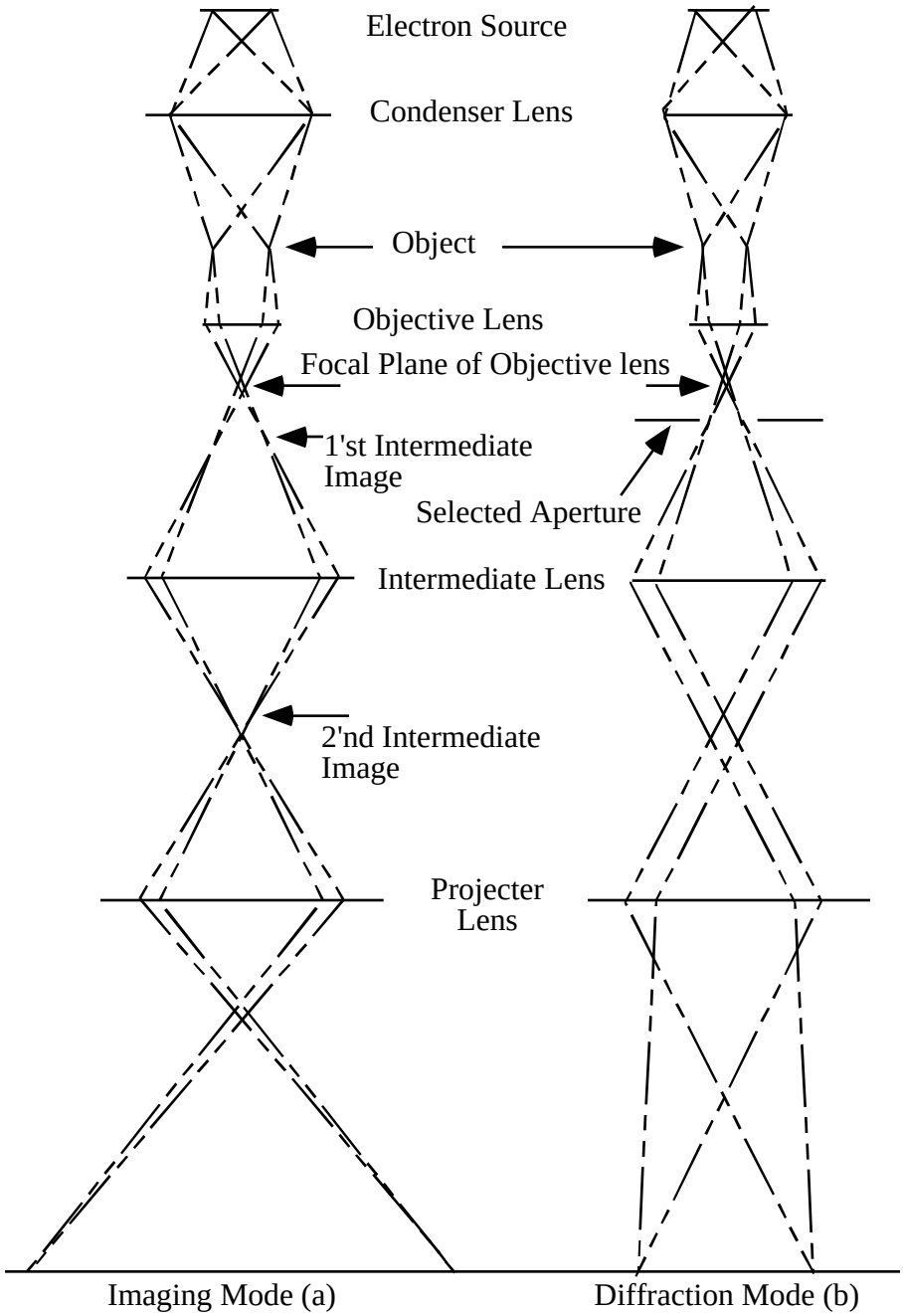


Figure 1. Geometrical optics representation of the TEM in imaging mode (a), and diffraction mode (b)

## Simplifying the Description of the Microscope

Consideration of the description of the electron microscope in figure 1 shows that the projector lens and the intermediate lens (or lenses) merely magnify the original image (I1) formed by the objective lens. For the purposes of image simulation we can reduce the TEM to three essential components; (1) an electron beam that passes through (2) a specimen, and then through (3) an objective lens (fig. 2).

Our next step in describing the electron microscope for image simulation is to move from the geometrical optics description of the TEM to a description based on wave optics. In this description of the microscope we examine the amplitude of the electron wavefield on various planes within the TEM, and attempt to determine how the wavefield at the viewing screen comes to contain an image of our specimen.
By treating the electrons as waves, and considering our simplified electron microscope (Figure 2), we see that there are three planes in the TEM at which we need to be able to compute the (complex) amplitude of the electron wavefield.

### (1)The image plane:

Working backwards, we start at our desired information, the electron wavefield at the image plane; this wavefield is derived from the wavefield at the focal plane of the objective lens by applying the effects of the objective aperture and the phase changes introduced by the objective lens.

### (2)The focal plane of the objective lens:

In turn, the electron wavefield at the focal plane of the lens is derived from the wavefield at the exit surface of the specimen by a simple Fourier transformation.

### (3)The specimen exit surface:

In order to know the exit-surface wavefield, we must know with which physical property of the specimen the wave interacts, and describe that physical property of our particular specimen.

## The Reduced Electron Microscope

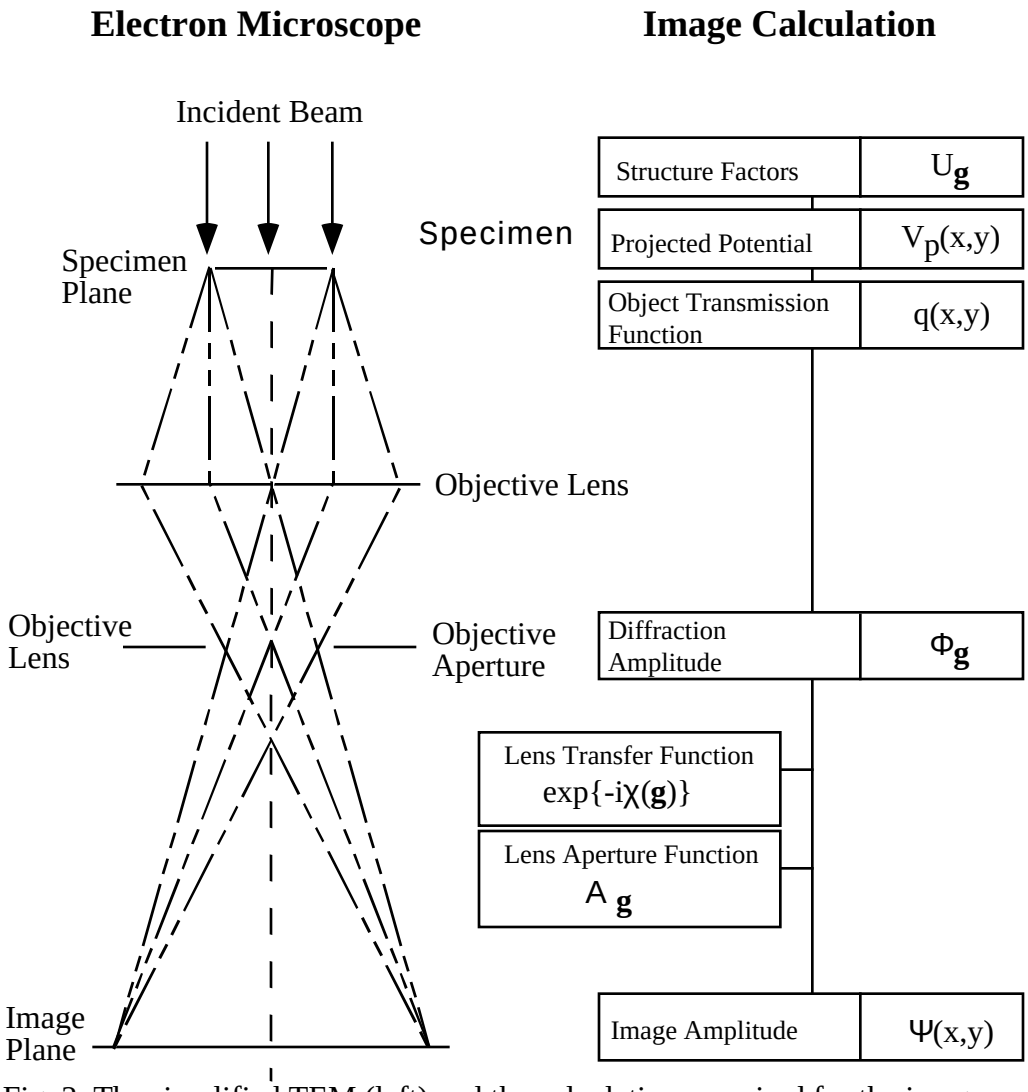


Fig. 2. The simplified TEM (left) and the calculations required for the image simulation (right). The three principal planes are marked.

Cowley and Moodie (1957) showed that the interaction of an electron beam with a specimen could be described by the so-called multislice approximation, in which electrons propagate through the specimen and scatter from the crystal potential, the electron scattering is described by the so-called phase-grating function, a complex function of the potential, and the electron propagation is computed with a propagation function dependent on the electron wavelength. Since then there have been numerous formulations of the multislice approximation derived from the Schrödinger equation.

## Simulating TEM Images

The problem of simulating images thus becomes a problem of computing the electron wavefields (wavefunction) at three microscope planes. Currently the best way to produce simulated images is to divide the overall calculation into three parts:

(1) Model the specimen structure to find its potential in the direction of the electron beam.

(2) Produce the exit-surface wavefield by considering the interaction of the incident electron wave on the specimen potential.

(3) Compute the image-plane wavefield by imposing the effects of the objective lens on the specimen exit surface wave.

Each of these steps will be covered in the next sections. However, because of space constraints, it is impossible to cover everything in great depth. For detailed derivation, the reader is encouraged to read the many excellent texts on the subject.

Chapter 2

# *Theory of Image Simulation*

## Modeling the Specimen

The specimen is a three dimensional objects consisting of a huge number of atoms. From a modeling point of view, it is necessary to reduce the number of parameters to a more manageable number. For crystalline materials described by a repeat of perfect unit cells this is easily accomplished. The unit cell in this case is defined by the lattice parameters **A**,**B** and **C** where **A** and **B** are in the plane the specimen perpendicular to the electron beam and **C** is in the main direction of the incoming electrons. **A**,**B** and **C** are related to the normal lattice vectors **a**,**b**, and **c** depending on the orientation of the specimen. The specimen is thus reduced to M number of unit cells, where M*__C__ is equal to the thickness of the sample, giving in the end a 2D image which covers the area given by **A** and **B**.
In the case of a defect structure which no longer can be modeled as a small repeating structure, it is necessary to limit the extent of the calculation by defining a supercell which contains the defect. The resulting image obtained from the calculation will contain artifacts which arise from limiting the structure at arbitrary boundaries and care must be taken to ensure that the image gives a faithful representation of the area of interest.
The entire electrostatic potential of the specimen is now defined by one unit cell with axes **a**,**b**, and **c**, angles *alpha*, *beta* and *gamma*, and N atoms with coordinates x,y,z. For simplicity, we use the nomenclature of the crystallographic unit cell even though we are referring to the transformed unit cell (**A**,**B**,**C**) as described above.
The electrostatic potential in the crystal can be written

$$\phi(\mathbf{r}) = \int d^3\mathbf{r}' \, \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad 1$$

where $\rho(\mathbf{r})$, the charge density is:

$$\rho(\mathbf{r}) = \sum_{\substack{all \\ atoms}} \rho_i(\mathbf{r} - \mathbf{r}_i) \qquad 2$$

with the sum extending over all atoms i at positions $\mathbf{r}_i$, each giving rise to a charge density

$$\rho_i(\mathbf{r}) = Z_i e\delta(\mathbf{r}) - e|\psi_i(\mathbf{r})|^2 \qquad 3$$

where $Z_i$ : atomic number, e: electronic charge, $\psi(\mathbf{r})$ : the quantum mechanical many electron wavefunction for the atom. The potential $\varphi(\mathbf{r})$ is described by its Fourier transform $\Phi(u)$ through the relationship

$$\varphi(\mathbf{r}) = \int \Phi(\mathbf{u}) e^{-2\pi i \mathbf{u}\,\mathbf{r}} d\mathbf{u} = \sum_{\mathbf{H}} \Phi(\mathbf{H}) e^{-2\pi i \mathbf{H}\,\mathbf{r}} \qquad 4$$

since because of the periodicity of the unit cell, $\Phi(\mathbf{u})$ is non-zero only when $\mathbf{u} = \mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ , $\mathbf{H}$ being a reciprocal lattice vector.
The potential $\Phi(\mathbf{H})$ is given as a sum over all atoms in the unit cell

$$\Phi(\mathbf{H}) = \sum_{\substack{all \\ atoms}} f_i^{el}(\mathbf{H}) e^{2\pi i \mathbf{u}\,\mathbf{r}_i} = \frac{e}{4\pi^2 \varepsilon_0} \sum_{\substack{all \\ atoms}} \frac{Z_i - f_i^x(|\mathbf{H}|/2)}{\mathbf{H}^2} e^{2\pi i \mathbf{u}\,\mathbf{r}_i}$$

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where the electron scattering factors $f_i^{el}$ and the x-ray scattering factors $f_i^x$ have been calculated from relativistic electron wavefunctions and parameterized. They can be found in various tables (Doyle and Turner, 1968) and are in use by most image simulation programs such as SHRLI (O'Keefe at al., 1978), NCEMSS (Kilaas, 1987) and EMS (Stadelman, ).
Taking into account any deviation from full occupancy at a particular site and the thermal vibration of the atom, the Fourier

coefficients of the crystal potential from one unit cell is calculated as:

$$\Phi(\mathbf{H}) = \sum_{\substack{unit\ cell \\ atoms\ i}} f_i^{el}(\mathbf{H}) Occ(\mathbf{r}_i) \exp[-B_i \mathbf{H}^2] e^{2\pi i \mathbf{H}\,\mathbf{r}_i} \qquad 6$$

B: Debye Waller factor; Occ($\mathbf{r}_i$) : The occupancy at position $\mathbf{r}_i$

## Simulating the Interaction Between the Electrons and the Specimen

The interaction between an electron of energy E and the crystal potential $\varphi(\mathbf{r})$ is given by the Schrödinger equation

$$[-\frac{h^2}{8\pi^2 m}\ ^2 - e\phi(\mathbf{r})]\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \qquad 7$$

where m is the relativistic electron mass and h is Planck's constant.

Before entering the specimen, the electron is treated as a plane wave with incident wavevector $\mathbf{k}_0$, $k_0 = 2\pi/\lambda$, so that the incident electron wave is written

$$\Psi_0(\mathbf{r}) = \exp\{i(\omega t - 2\pi \mathbf{k}_0\ \ \mathbf{r})\} \qquad 8$$

It is useful to define the quantity V(**r**) which will loosely be referred to as the potential as:

$$V(\mathbf{r}) = \frac{8\pi^2 me}{h^2}\phi(\mathbf{r}) \qquad 9$$

The Schrödinger equation above cannot be solved directly without making various approximations. Depending on how the problem is formulated, one can derive the most common solutions to the electron wavefield at a position T within the specimen.

## The Weak Phase Object Approximation

In the Phase Object Approximation (POA) (Cowley and Iijima, 1972), the phase of the electron wavefunction after traversing a specimen of thickness T is given as

$$\Psi(x, y, z = T) \approx \Psi(x, y, z = 0) \exp[-i\sigma V_p(x, y)T] \qquad 10$$

with

$$\sigma = 2\pi me\lambda \left[1 + \frac{eE}{mc}\right] / h^2 \qquad 11$$

where V(x,y) is the average potential per unit length. The specimen is considered thin enough so that electrons only scatter once and are subject only to an average projected potential. In the weak phase object approximation, the exponent is considered much less than one, so that the electron wavefunction emerging from the specimen is:

$$\psi(x, y, z = T) \approx \psi(x, y, z = 0)(1 - i\sigma V_p(x, y)T) \qquad 12$$

The WPOA only applies to very thin specimens of the order of a few tenths of Å, depending on the atomic number of the atoms in the structure (Gibson, 1994). The FT of the wavefunction gives the amplitude and phase of scattered electrons and in the WPOA one has:

$$\Psi(\mathbf{u}) = \delta(\mathbf{u}) - i\sigma V_p(\mathbf{u})T \qquad 13$$

where u is a spatial frequency.
Again, for periodic crystals, $V_p(\mathbf{u})$ are non-zero only for frequencies $\mathbf{u}=\mathbf{H}$ where **H** is a reciprocal lattice vector in the crystal.
We will now use V to mean $V_p$. Thus for single electron scattering and when the Fourier coefficients V(**H**) are real (true for all centro-symmetric zone axis), the WPOA illustrates clearly that:
i) Upon scattering, the electron undergoes a -90° phase shift.
ii) The amplitude of a scattered electron is proportional to the Fourier coefficient of the crystal potential.

## The Bloch Wave Approximation

In the BWA the electron wavefunction of an electron with wavevector **k** is written as a linear combination of Bloch waves b(**k**,**r**) with coefficients ε (Howie, 1963). Each Bloch wave is itself expanded into a linear combinations of plane waves which reflect the periodicity of the crystal potential.

$$\psi(\mathbf{r}) = \sum_j \varepsilon^{(j)} b^{(j)}(\mathbf{k},\mathbf{r}) = \sum_j \varepsilon^{(j)} \sum_{\mathbf{g}} c_{\mathbf{g}}^{(j)} \exp[-2\pi i(\mathbf{k}_0^{(j)} + \mathbf{g})\ \mathbf{r}] \qquad 14$$

The formulation above gives rise to a set of linear equations expressed as

$$[k_0^2 - (\mathbf{k}^{(j)} + \mathbf{H})^2] c_{\mathbf{H}}^{(j)} + \sum_{\mathbf{H}'} V(\mathbf{H}') c_{\mathbf{H}-\mathbf{H}'}^{(j)} = 0 \qquad 15$$

which needs to be solved. Detailed derivation of the Bloch wave approximation can be found elsewhere.
Characteristics of the Bloch wave formulation are:

- Requires explicit specification of which reflections g are included in the calculation.
- Easy to include reflections outside the zero order Laue zone.
- Very good for perfect crystals, not suited for calculating images from defects.
- The solution is valid for a particular thickness of the specimen.

- Allows rapid calculation of convergent beam electron diffraction patterns.
- Includes dynamical scattering.

## The Multislice Approximation

The multislice formulation (Goodman and Moodie, 1974 & Self et al., 1983) i s by far, the most commonly used method of calculating the electron wavefield emerging from the specimen. Although it does not as easily include scattering outside the zero order Laue zone as the BWA, the multislice formulation is more versatile for use with structures containing any kind of defects, either they be point-defects, stacking faults, interfacial structures, etc. The multislice solution gives the approximate solution to the electron wavefunction at a depth z+dz in the crystal from the wavefunction at z. In the multislice approximation one has:

$$\psi(x, y, z + dz) \approx \exp[-i\sigma dz \ {}^{2}_{x,y}] \ \exp[-i\sigma \int_{z}^{z+dz} V(x, y, z')dz']\psi(x, y, z)$$

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Thus starting with the wavefunction at z=0, one can iteratively calculate the wavefunction at a thickness n*dz, by applying the multislice solution slice by slice, taking the output of one calculation as the input for the next. Equation 16 is solved in a two step process.

The potential due to the atoms in a slice dz is projected onto the plane t=z, giving rise to a scattered wavefield

$$\psi_1(x, y, z + dz) = \exp[-i\sigma \int_{z}^{z+dz} V(x, y, z')dz']\psi(x, y, z) \equiv q(x, y)\psi(x, y, z)$$

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The function q(x,y) is referred to as the phasegrating.

Subsequently, the wavefield is propagated in vacuum to the plane t=z+dz, according to

$$\psi(x, y, z + dz) = \exp[-i\sigma dz \; {}^{2}_{x,y}] \; \psi_1(x, y, z) \qquad 18$$

The last equation represents a convolution in real space and is solved more efficiently in Fourier space (Ishizuka and Uyeda, 1977), where the equation transforms to

$$\Psi(\mathbf{H}, z + dz) = \exp[-i\pi\lambda dz\mathbf{H}^2] \quad \Psi(\mathbf{H}, z) \equiv p(\mathbf{H}, dz) \; \Psi_1(\mathbf{H}, z) \quad 19$$

where $\Psi(\mathbf{H},\mathbf{z})$ are the Fourier coefficients of $\psi$(x,y,z). p(**H**,dz) is called the propagator.
The multislice formulation is a repeated use of the last two equations and will give the wavefield at any arbitrary thickness T of the specimen. If the slice-thickness is chosen as the repeat distance of the crystal in the direction of the electron beam, only the zero order Laue reflections are included in the calculation as the unit cell content is projected along the direction of the electron beam. Three dimensional information which involves including higher order Laue reflections can be included by reducing the slice thickness (Kilaas et al, 1987).

## Sampling Criteria

Any numeric calculation must be performed for a limited set of data points (x,y) or reciprocal spatial frequencies u. Working with periodically repeated structures; if the lateral dimensions of the unit cell is a and b, which we for simplicity make orthogonal so that the axes are associated with an orthogonal x,y coordinate system, then for a given sampling interval dx=dy, we have

$$N = \frac{a}{dx} \; ; \qquad M = \frac{b}{dy} \qquad 20$$

defining the calculation to a grid of N*M points. The sampling interval automatically restricts the calculation in reciprocal space as well. The maximum reciprocal lattice vector for orthogonal axes is given as

$$\mathbf{H}_{\max}^2 = \left| h_{\max}\mathbf{a}^* + k_{\max}\mathbf{b}^* \right|^2 = \left(\frac{N}{2a}\right)^2 + \left(\frac{M}{2b}\right)^2 \qquad 21$$

Because most implementations of the multislice formulation makes use of Fourier transforms, the calculation grid N and M is adjusted so that both are powers of 2. This is because Fourier transform algorithms can be performed much faster for powers of 2 rather than arbitrary dimensions. This results in uneven sampling intervals dx,dy when a ≠ b. In order to not impose an arbitrary symmetry on the calculation, a circular aperture is imposed on the propagator. In practice, this aperture is set to 1/2 of the minimum of ($h_{max}$, $k_{max}$) as defined above in order to avoid possible aliasing effects associated with digital Fourier transforms. The sampling must be chosen such that the calculation includes all (or sufficiently enough) scattering that takes place in the specimen.

## The Image Formation

After the electron wavefield emerge from the specimen, it is subjected to the varies magnetic field of the lenses that form the imaging and magnification part of the microscope. Of these lenses, only the first lens, the objective lens, is considered in the image formation calculation. Since the angle with which the electron forms with the optic axis of the lens varies inversely with the magnification, only the aberrations of the objective lens are important. The remaining lenses serve to just magnify the image formed by the objective lens. The effects of the lens which normally are included in the calculation are spherical aberration, chromatic aberration and lens defocus. Two-fold and three-fold astigmatism, including axial coma, are considered correctable by the operator although they can be included in the equations.
Without any aberrations, no instabilities and with the specimen

in the focal plane of the objective lens, the image observed in the electron microscope would be am magnified version of

$$I(x,y) = \left|\psi(x,y,z = exitplane\ \ of\ \ specimen)\right|^2 = \psi_e(x,y)\psi_e(x,y)$$

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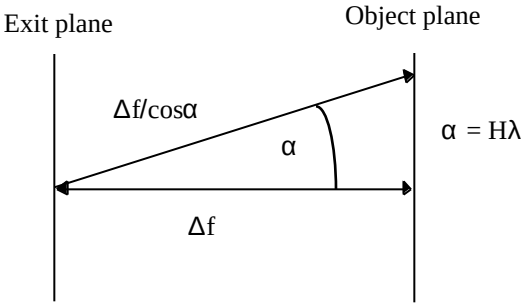
## Objective Lens Defocus

Consider an electron traveling from the plane defined by the exit surface of the specimen to the plane given as the plane of focus for the objective lens. This distance is referred to as the objective lens defocus Δf.



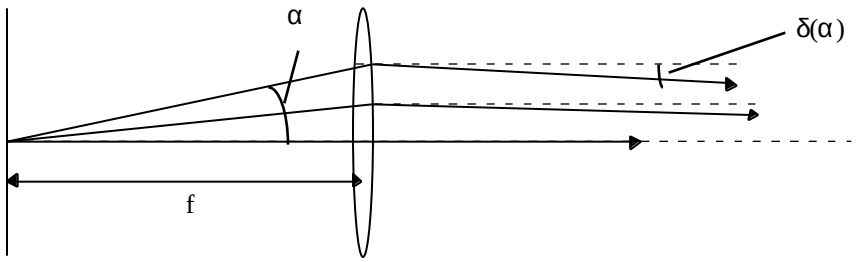

The electron traveling along the optic axis will have a path length of Δf while an electron that has been scattered an angle α=Hλ, will travel a distance Δf /cosα. This can be expressed as a phase difference

$$\frac{2\pi}{\lambda}\left(\Delta f \Big/ \cos\alpha - \Delta f\right) \approx \pi\lambda\Delta f\mathbf{H}^2 \qquad 23$$

## Spherical Aberration

Electrons crossing the optic axis with an angle a at the focal

plane of the objective lens should form parallel paths emerging from the lens.




However, the spherical aberration of the lens causes a phase shift relative to the path of the unscattered electron ($\alpha$=0) which is written as (Scherzer, 1949):

$$2\pi/\lambda \quad 1/4\, C_x \alpha^4 = 1/2\, \pi C_s \lambda^3 \mathbf{H}^4 \qquad 24$$

If there were no other effects to consider, the image would be obtained as follows:

- Calculate the wavefield emerging from the specimen according to one of the approximations.
- Fourier transform the wavefield which gives the amplitude and phase of scattered electrons.
- Add the phase shift introduced by the lens defocus and the spherical aberration to the Fourier coefficients.
- Inverse Fourier transform to find the modified wavefunction.
- Calculate the image as the modulus square of the wavefield.

However, there are two more effects that are usually considered. Variations in electron energy and direction.

## Chromatic Aberration / Temporal Incoherence

Electrons do not all have exactly the same energy for various

reasons. They emerge from the filament with a spread in energy and the electron microscope accelerating voltage varies over the time of exposure. The chromatic aberration in the objective lens will cause electrons of different energies to focus at different planes. Effectively this can be thought if as rather than having a given defocus $f_0$, one has a spread in defocus values centered around $f_0$. The value $f_0$ is what is normally referred to as $\Delta$f as indicating defocus. The images associated with different defocus values add to make the final image. Assuming a Gaussian spread in defocus of the form

$$D(f - f_0) \quad \exp[-\frac{(f - f_0)^2}{\Delta^2}] \qquad 25$$

gives:

$$I = \int |\Psi(f - f_0)|^2 D(f - f_0) df \qquad \Psi(\mathbf{H}) \rightarrow \Psi(\mathbf{H}) \exp[-1/2(\pi\lambda\Delta\mathbf{H}^2)^2]$$

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This states that each Fourier term (diffracted beam) is damped according to the equation above].

## Beam Divergence / Spatial Incoherence

The electron beam is not an entirely parallel beam of electrons, but form rather a cone of an angle $\alpha$. This implies that electrons instead of forming a point in the diffraction pattern form a disk with a radius related to the spread in directions. As for a variation in energy, the images formed for different incoming angles are summed up by integrating over the probability function for the incoming direction. It turns out that this also leads to another damping of the diffracted beam (Frank, 1973) so that:

$$I(\mathbf{r}) = \int |\psi(\mathbf{r},\alpha)|^2 D(\alpha) d\alpha \qquad \Psi(\mathbf{H}) \rightarrow \Psi(\mathbf{H}) \exp[\pi\alpha\lambda(C_s\mathbf{H}^2\lambda^2 + \Delta f)]^2 \qquad 27$$

## The Final Image

Equation 26 and equation 27 are only valid when the intensities of the scattered beams are much smaller than the intensity of the central beam. Thus the image results from scattered beams interfering with the central beam, but not with each other. This is referred to as linear imaging. Although the formulation is slightly more complicated in the general case, the expressions above give sufficient insight into the image formation. Image simulation programs do however include the more general formulation which include non-linear imaging terms (O'Keefe, 1979). Each Fourier component is damped by the spread in energy and direction and the image is formed by adding this to the recipe in section 4.2

## The Contrast Transfer Function CTF

When reading about HRTEM, it is impossible not to encounter the expression "Contrast Transfer Function". Loosely speaking, the CTF of the microscope refers to the degree with which Fourier components of the electron wavefunction (spatial frequencies) are transferred by the microscope and contribute to the Fourier transform of the image. Although the CTF only holds for thin specimen and linear imaging, it is often generalized and wrongly applied to all conditions. However, the CTF does provide insight into the nature of HRTEM images. In order to derive the expression for the CTF, we start by calculating the image intensity as given by the Weak Phase Object approximation. In the WPOA:

$$\Psi(x,y,z=T) \approx 1 - i\sigma V_p(x,y)T \qquad 28$$

and

$$\Psi(\mathbf{H}) = \delta(\mathbf{H}) - i\sigma V_p(\mathbf{H})T \qquad 29$$

Applying the phase shift due to the spherical aberration and the

objective lens defocus which we will call $\chi(\mathbf{H})$, we get that the FT of the wavefunction is (for simplicity $V = V_p$):

$$\Phi(\mathbf{H}) = \delta(\mathbf{H}) - i\sigma V(\mathbf{H}) e^{i\chi(\mathbf{H})} A(\mathbf{H}) \qquad 30$$

where A(**H**) is the damping terms arising from partial coherence.

The FT of the intensity is now given as

$$I(\mathbf{H}) = FT(\psi\ \psi) = \sum_{\mathbf{H}'} \Psi(\mathbf{H}')\Psi^*(\mathbf{H}-\mathbf{H}') \approx$$

$$\sum_{\mathbf{H}'} \left(\delta(\mathbf{H}') - i\sigma A(\mathbf{H}')V(\mathbf{H}')e^{i\chi(\mathbf{H}')}\right)\left(\delta(\mathbf{H}-\mathbf{H}') - i\sigma A(\mathbf{H}-\mathbf{H}')V(\mathbf{H}-\mathbf{H}')e^{i\chi(\mathbf{H}-\mathbf{H}')}\right) \approx$$

$$\delta(\mathbf{H}) + 2\sigma A(\mathbf{H})V(\mathbf{H})\sin\chi(\mathbf{H})$$

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The last result is very useful and it leads to the frequently used concept of the Contrast Transfer Function (CTF). The CTF is defined as $A(\mathbf{H})\sin\chi(\mathbf{H})$ The equation above states that each reflection **H** contributes to the image intensity spectrum with a weight that is proportional to the CTF. Figure 3. shows a plot of a CTF including sinχ and the damping curves. When $\sin\chi(\mathbf{H}) = -1$ for a large range of frequencies **H**, which is the condition referred to as Scherzer defocus[11], the image can be thought of as:

$$I(x,y) \approx 1 - 2\sigma U(x,y) \qquad 32$$

where U(x,y) is a potential related to the original crystal potential, but keeping only the Fourier coefficients related to frequencies transferred by the microscope. The equation above shows the often used rule of thumb. For thin specimens, under Scherzer imaging conditions, atoms are black.

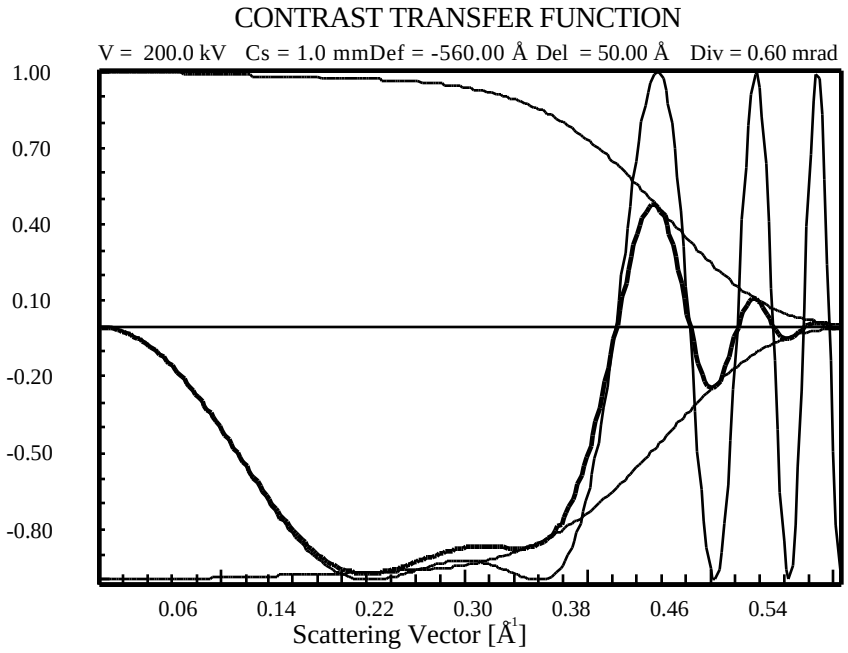


Figure 3. Plot of the Contrast Transfer Function for a 200kV microscope with the parameters indicated.

## References

**References**

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Chapter 3

# *Introduction to MacTempas*

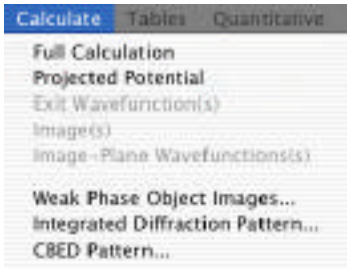
Since the simulation process can be subdivided into independent calculations involving the structure, the scattering process and the imaging process, MacTempas allows one to invoke these independent calculations separately through the “Calculate” menu.

## The Three Simulation Steps

**Full Calculation**
This command will start the calculation from the required starting point and proceed to calculate finale images.

**Projected Potential**
generates the crystal potential that produces electron scattering from the structural data, unit cell dimensions, symmetries, and atom positions, occupancies, and temperature factors.

**Exit Wavefunctions(s)**
generates the electron wavefield at the specimen exit surface; it uses projected potential combined with information about the accelerating voltage of the electron microscope, and the specimen thickness and tilt. The computation algorithm is the multislice approximation.




**Image(s)**
generates the image intensity at the microscope image plane; the effects of the objective lens phase changes and resolution-limiting aberrations are included via parameters like defocus, spherical aberration, incident beam convergence, spread of defocus, and the position and size of the objective aperture.

**Image Plane Wavefunctions(s)**- generates the electron wavefunction at the imaging plane in the microscope. This is equiva-

lent to the application of the Contrast Transfer Function to the Fourier transform of the electron wavefunction at the exit surface of the specimen followed by an inverse Fourier transform. The calculation of the image plane wavefunction is used for comparing with the electron wavefunction found by the use of electron holography.

Thus "***Projected Potential***" calculation considers only the specimen structure, "***Exit Wavefunctions(s)***" calculation treats the interaction of the specimen with the electron wave, and the "***Image(s)***" calculation simulates how the wave leaving the specimen interacts with the lens system of the electron microscope. Once a simulation has been made, any additional simulation will usually not require a full re-calculation; any change in microscope parameters will not affect the results of the "***Projected Potential***" and "***ExitWavefunctions(s)***" calculations, and only **Image(s)** will need to be re-run; any change in microscope voltage or in specimen thickness and tilt will not affect the output of "***Projected Potential***", but "***Exit Wavefunctions(s)***" and "***Image(s)***" will need to be re-run. Of course, any change in the specimen structure will require the re-running of all three subprograms.

## Generated Files

MacTempas generates and stores various files in the course of a simulation. The 6 possible data files are:

(1) <**structurename**>**.at** stores all the structure and microscope information needed to run the simulation. This information is derived from user input and the supplied data files. In particular, the string "**structurename**" is a unique name for the structure, input by the user when creating the structure file. This is an editable file of type 'TEXT'.

(2) <**structurename**>.**pout** is the result of running the **projected potential** routine from the information stored in <**structurename**>.**at**; it contains the specimen potential

in the direction of the electron beam. This is a BINARY file of type Real 4. The first 80 bytes consists of record information and the data starts at byte 80. The first line of data contains the data for the bottom line of the "image" since the coordinate system for MacTempas is at the lower left corner of the image/unit cell. Thus if the data is imported into a program for viewing, the image will appear flipped.

(3) <**structurename**>.**mout** is the result of running the **multislice** routine using the data in <**structurename**>.**pout** with those in <**structurename**>.**at**; it contains the exit-surface wavefunction at one or more selected specimen thicknesses. This is also a BINARY file with the same structure as <**structurename**>.**pout,** except for the fact that the data is complex, pairs of numbers (real and imaginary). The data starts at byte 80 and the file can contain more than one exit wavefunction.

(4) <**structurename**>.**iout** is the result of running the **image formation** routine to apply the effects of the microscope parameters in the <**structurename**>.**at** file to the exit-surface wave; it contains one or more images ready to be displayed. This again is a BINARY file with data starting at byte 80 and the file can contain more than one image. Data is Real 4

(5) <**structurename**>.**hout** is the result of calculating the image plane electron wavefunction(s) instead of calculating the simulated images. The data is complex, pairs of numbers (real and imaginary). The data starts at byte 80 and the file can contain more than one image plane exit wavefunction.

(6) <**structurename**>.**aout** contains the complex amplitudes of several diffracted beams at one-slice increments in specimen thickness. The beams are specified by the

user, and can be plotted as a function of specimen thickness.

In addition, two "print" files are produced (but rarely printed) just in case additional information about a computation is required by the user. These files are:

(7) <**structurename**>.**p_prnt** contains information about the way in which the "***Projected Potential***" subprogram processed the <**structurename**>.**at** data to produce the specimen potential.

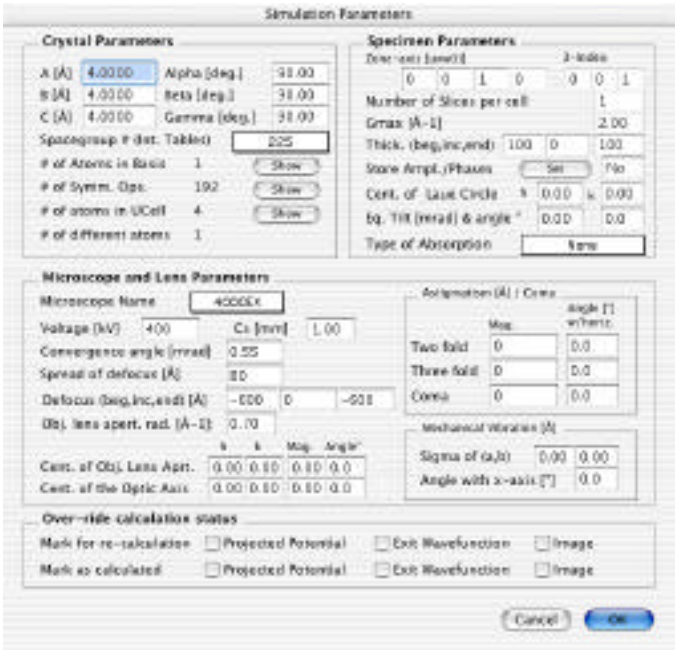
(8) <**structurename**>.**m_prnt** contains information about the way in which the "***Exit Wavefunctions(s)***" subprogram processed the <**structurename**>.**pout** data with the <**structurename**>.**at** to produce the exit-surface wave; that is, it contains information from the multislice computation.

Chapter 4

# *Running MacTempas*

## Generating an Input Structure

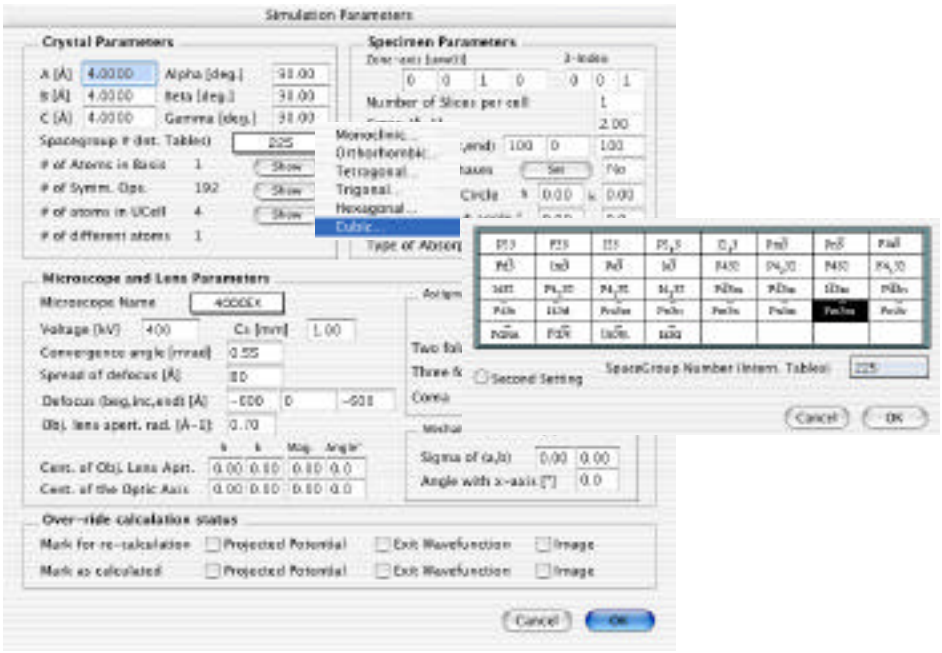
The first step in running a simulation is generating the structure input file. This is done through **New Structure File...** in the FILE menu. This generates the input dialog window with values for a default cubic structure. Use this template to modify the date to fit your structure..




**a, b, c,**
**alpha, beta, gamma**
These are the unit cell dimensions in Ångstrøm units, and the unit cell angles in degrees. MacTempas will automatically set the angles depending on the spacegroup, if possible. The program will also automatically set lattice parameters depending on the spacegroup. Thus if the user chooses a cubic system, **b** and **c** are set equal to **a**

**Space group#**

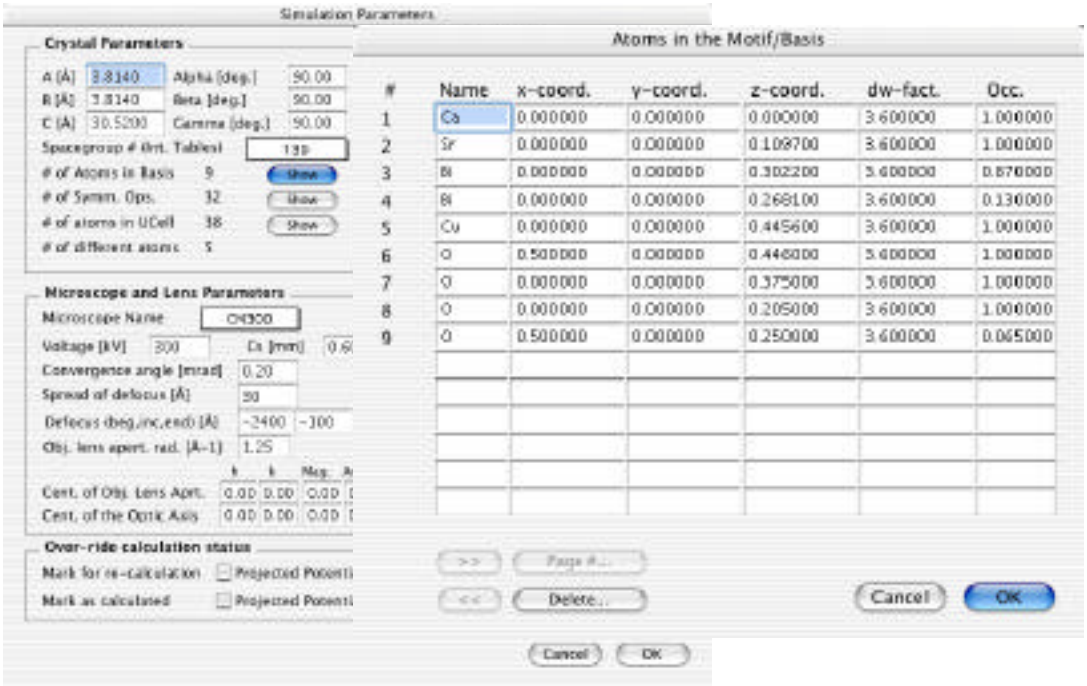
MacTempas generates symmetry operators for the any one of the 230 space groups when selecting the number or the symbol of the space group (as listed in the International Tables for Crystallography). By clicking on the pop up menu “Space Group” one can choose one of the 230 spacegroups by first selecting the type of crystal-structure, i.e. hexagonal or cubic. The user can choose one of the spacegroups by clicking on the symbol for the spacegroup or by entering the number for the spacegroup.




The input also allows for choosing the second setting for a specific spacegroup if one exists. If no space group is required, one should use the space group P1 (1), in which case the only symmetry operator is x,y,z. Additional symmetry operators can be entered by opening the dialog displaying the symmetry operators.

**Show (Basis atoms)**

Use this button to bring up the dialog window that enables the input of the atoms in the basis.



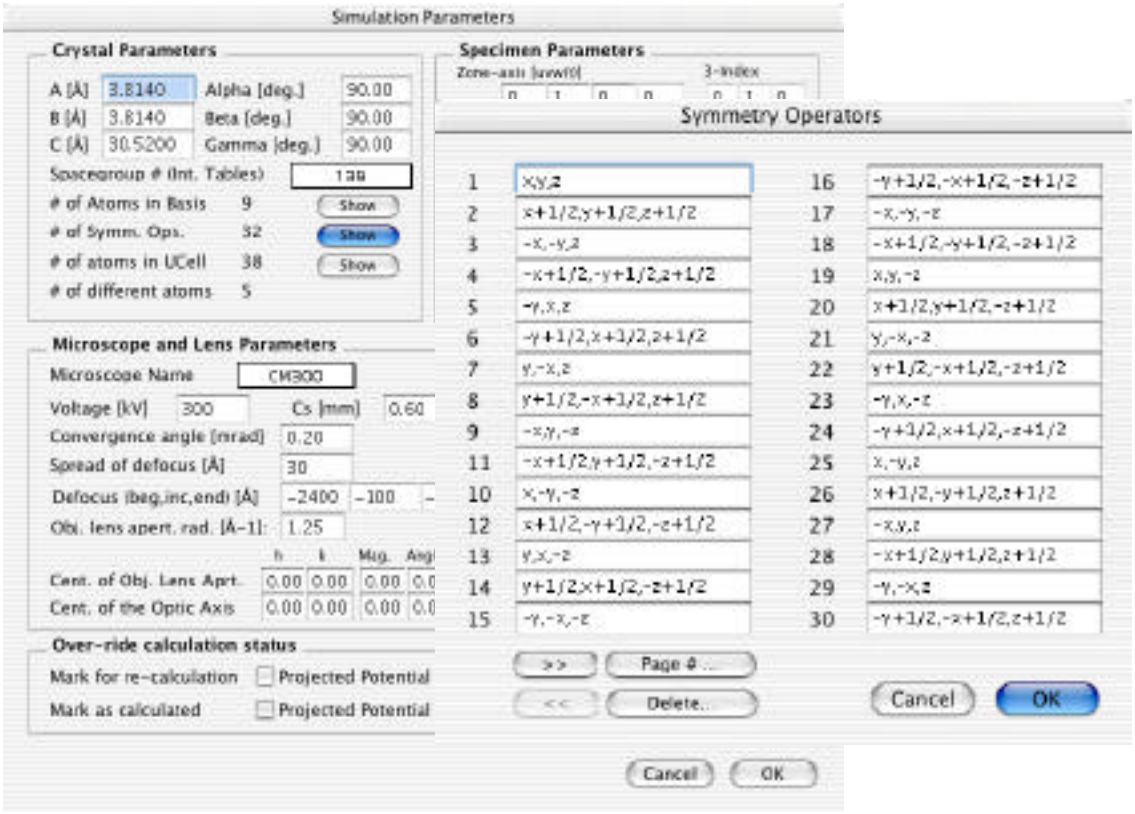

**Number of Atoms in the Basis**

This value is the number of independent atom positions in the basis or asymmetric unit of the cell. When operated on by the symmetry operators, the basis generates all the atom positions within the cell. This value is never modified by the user since the program always recalculates this number depending on the data entered.

**Show (Symmetry Operators)**

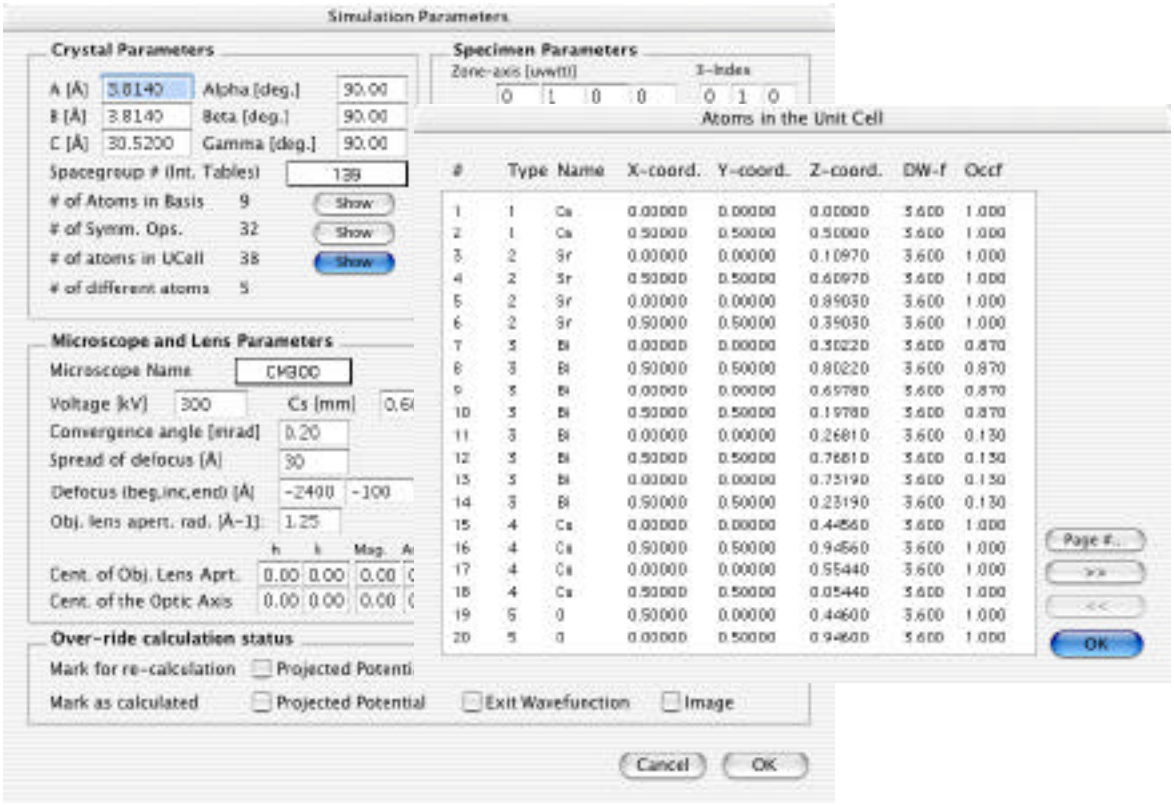
The symmetry operators are automatically created by specifying the spacegroup. By clicking on this button, a window dis-

playing the symmetry operators are shown.




**Show (Atoms in Unit Cell)**
The atoms in the unit cell are automatically created by the operation of the symmetry operators on the atoms in the basis. The number of atoms is given and by clicking on the button “Show”,

a window displaying the atoms in the unit cell appears.




**Number of different atoms**
This value is the number of different types of atoms in the specimen structure; difference is due to a different atomic number or a different Debye-Waller factor. The correct value is calculated by MacTempas and displayed.

**Zone Axis**
Specimen orientation in relative real space axes units.

**Number of slices per unit cell**
For unit cells with large repeat distances in the beam direction, moderate values of $\mathbf{G}_{max}$ may allow the Ewald sphere to approach the so-called pseudo upper-layer line that the multi-

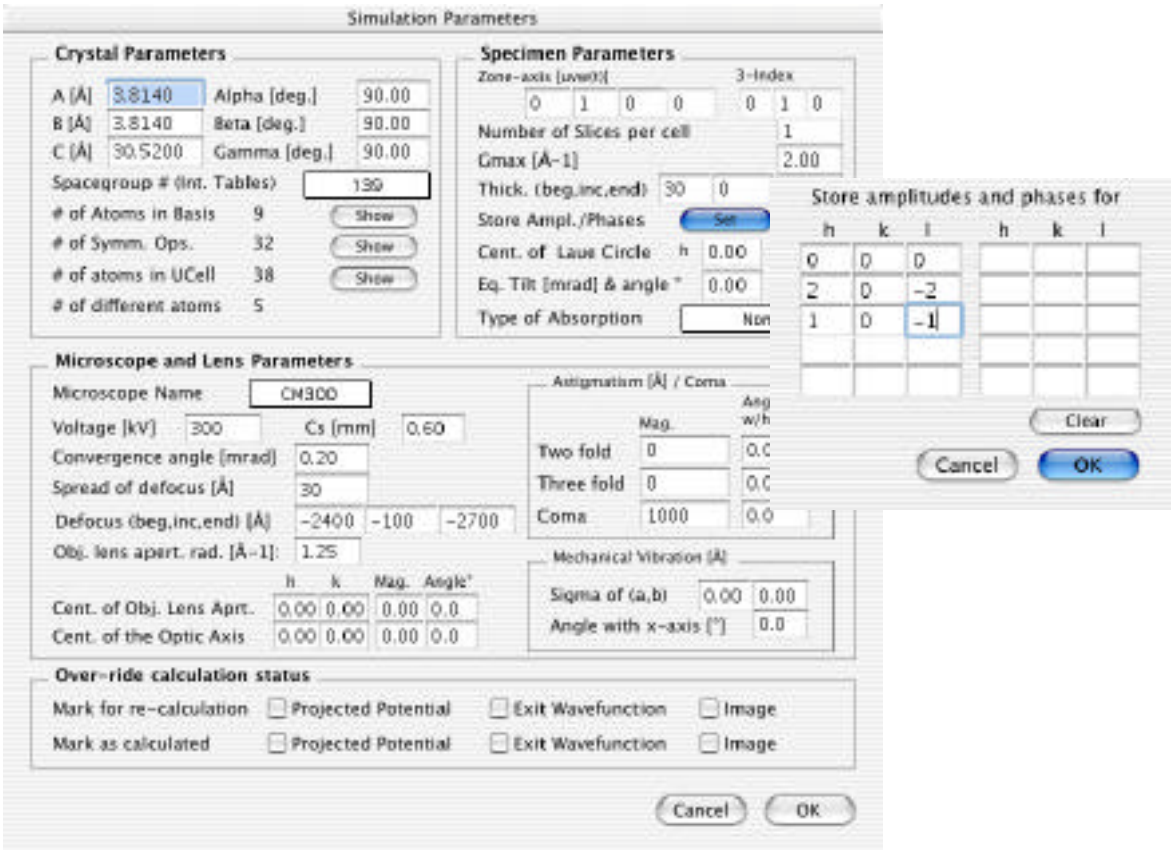
slice allows at the reciprocal of the chosen slice thickness. In this case MacTempas will sub-divide the slice into two or more subslices. How this is done depends upon the potential setting chosen in the Option menu.

**Gmax**
The maximum value (in reciprocal Ångstrøm units) of any scattering vector to be included in the multislice diffraction calculation. This value imposes an “aperture” on the diffracted beams included in the dynamic scattering process. It should be large enough to ensure that all significant beam interactions are included. The default value is 2.0. MacTempas will compute phase-grating coefficients out to twice $\mathbf{G}_{max}$ in order to avoid aliasing in the multislice calculations.

**Specimen Thickness**
The thickness of the specimen foil is entered as a beginning thickness, an ending thickness and an incremental thickness. All numbers are in Ångstrøm units. A series of thicknesses represented by the upper and lower bounds and a thickness step; e.g. 100 50 250 will cause MacTempas to store the exit wavefield at specimen thicknesses of 100Å to 250Å in steps of 50Å (a total of four thicknesses).

**Store Ampl./Phases - Set...**
Clicking this button allows a number of diffracted beams to be selected for plotting of their intensity and phase variation as a

function of specimen thickness. The reflections to be tracked




are determined by entering the hkl values for the reflection. Only 10 reflections can be tracked this way.

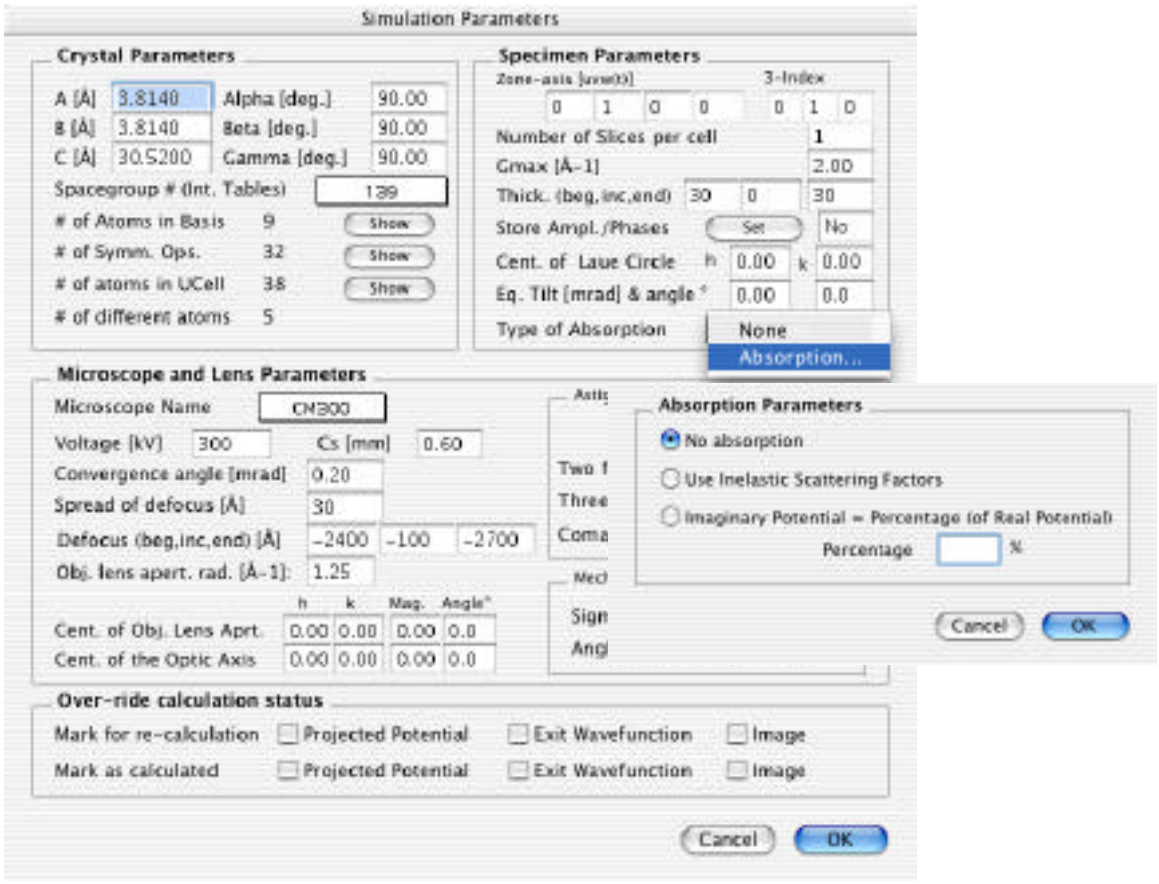
**Center of the Laue Circle**

Specimen tilt is specified by entering the center of the Laue circle in units of the h and k indices of the projected two-dimensional reciprocal-space unit cell. The new indices and their relationship to the original reciprocal cell is found in the data file <**structurename**>.**p_prnt**

**Type of Absorption**

Absorption can be included in the program by introducing an

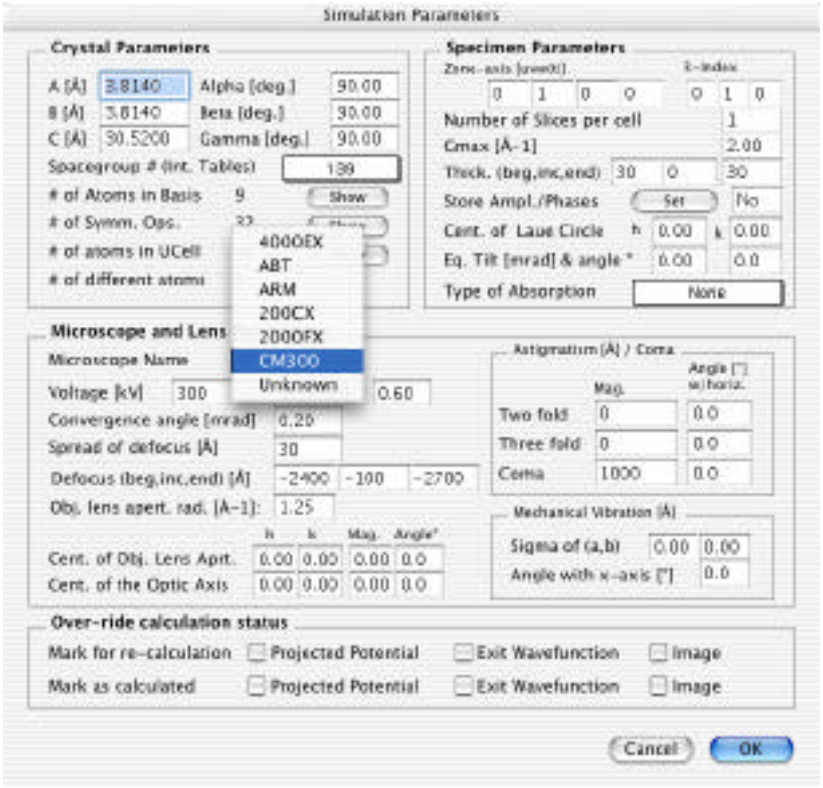
imaginary projected potential.




**Microscope**

The type of electron microscope used to generate the imaging parameters. Predefined microscopes are shown in the popup menu together with one undefined microscope. If a predefined microscope is used, MacTempas provides values for Cs, the spherical aberration coefficient of the objective lens (in mm.); DEL, the halfwidth of a Gaussian spread of focus due to chromatic aberration (in Ångstrøm units); TH., the semi-angle of incident beam convergence (in milliradian). If the type of microscope is unknown to MacTempas, the above values must be entered separately (We will see later how a new microscope

may be made known to MacTempas).




**Voltage**
The electron microscope accelerating voltage in kilovolts.

**Objective Lens Defocus**
The defocus of the objective lens is entered in Ångstrøm units with a negative value representing underfocus (weakening of the lens current). As for the speciment thickness parameter, the input is a range specified by the upper and lower bounds and an increment.

**Cs, Spherical Aberration**
The spherical aberration of the objective lens in mm.

**Convergence Angle**

This is the spread in angle for the cone of incoming electrons depending on the condenser lens aperture. The angle is given in mrad.

**Spread of Defocus**
This is the effective spread in defocus which results from the distribution of energies of the imaging electrons and the chromatic aberration of the objective lens. The unit is Å.

**Aperture Radius**
The radius of the objective aperture is specified in $Å^{-1}$

**Center of objective Aperture**
The center of the objective lens aperture is defined in units of h and k of the two dimensional reciprocal space unit cell, as for the Laue circle center.

**Center of the Optic Axis**
The center of the optic axis of the electron microscope is specified in terms of the h and k indices of the two-dimensional reciprocal-space unit cell, just as for the Laue circle center and the aperture center.

**Two-fold astigmatism**
The two fold astigmatism of the objective lens and the angle with the x-axis. The magnitude is given in Å.

**Three-fold astigmatism**
The two fold astigmatism of the objective lens and the angle with the x-axis. The magnitude is given in Å.

**Coma**
The coma of the objective lens and the angle with the x-axis. The magnitude is given in Å.

**Mechanical Vibration**
This simulates the effect of a slight vibration of the microscope. One finds that often the simulated images show details that are

not present in the experimental data regardless of other imaging conditions. This may be due to image degradation caused by microscope vibration or other effects not included and thus one can introduce a slight mechanical vibration in an attempt to create more realistic simulated images. It is possible to specify an anisotropic vibration by introducing the amplitude in two perpendicular directions with the diagonal of the ellipse at an angle with the a axis (as in the unit cell viewed in the zone axis orientation).

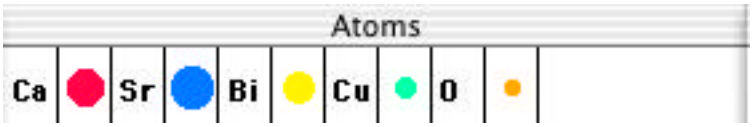
Chapter 5

# *Windows*

This chapter explains the windows of Mactempas, the information presented in each and how one interacts with the contents of the windows.


## Status Window

This window shows the current status of the program indicating the number of phasegrating coefficients calculated, the current slice number being calculated, the current image being calculated etc.




## Atom Window

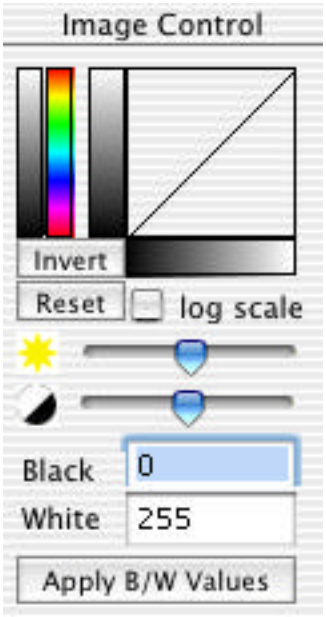
This window shows which atoms are present in the structure, the color the atom will be drawn in (if colored atoms are set) and the relative sizes of the atoms to be drawn. To change the color of an atom, choose the Color Picker tool from the Tools Window, click on a color in the Color Window and deposit that color on an atom by clicking on the colored circle representing the atom. The color of the atom will be set to the new color.

To change the atomic radius, double-click on the chemical sym-


bol. A dialog window will pop up and a new value for the atomic radius can be entered (units in Å).

## Image Control-Window

This window is used primarily to control the appearance of images. The black and white values of the current selected image is shown and can be changed by typing in new values. The contrast and brightness can be changed by using the appropriate sliders. An image can be shown on a logarithmic scale which is the default for images in frquency space (reciprocal space). The line in the graph represents how input image values are mapped to output display values. Thus an image can be pseudo colored by choosing a color from the color bar with the color picker tool selected and “depositing” this color in the vertical gray scale bar showing the display vlaues. The histogram of the current image is shown and black and white values can be chosen by clicking and dragging to select a region of the histogram. To invert the display, click in the “Invert” button. Similarily the image is reset to the original values through the “Reset” button. This window is also used to set the color of a particular atom species and the color of lines and text. To choose a color, the Color Picker Tool must have been chosen.



## Tools Window


The following tools are currently defined:

**Pointer**
Used for general moving around objects in the display window. If an object is selected and the “Option” key is held down while dragging an object, a copy is made of the object.

**Text Tool**
Clicking on this tool turns the cursor into an i-beam cursor which can be used to select an insertion point for text. To set the insertion point for text to be typed in the image window click the mouse at the desired point. The Font, Size and style of the text is determined from the menu bar. The text will be drawn in the current foreground color and can be left, canter or right justified.

**Magnifying Glass**
When selected the cursor turns into a magnifying glass which can be used to zoom in on a selected part of the display. Each time the mouse is clicked in the image window, the image is zoomed by a factor of two. By holding down the Option key while clicking, the image will be zoomed out by a factor of 1/2 for every click. Double-clicking the magnifying glass returns the image to normal. Currently no other tools work in zoomed mode.

**Line Tool**
This tool is used to draw lines on the display. If the Shift key is down, only vertical or horizontal lines will be drawn.

**Selection Tool**
This tool is used to select a portion of the screen for several possible operations such as copying, cutting, histogram computation etc. To select an area, click at a point in the display and

drag the cursor while the mouse button is pressed.

**Trace Tool**
This tool is used to get a line trace for the line drawn with the Trace Tool being the current tool.

**Color Picker Tool**
This tool when selected, allows the user to pick a color from the Color Window and color atoms, selecting fore-/back-ground colors and pseudo-color atoms. The selection of color is described under Color Window above

**Hand Tool**
Use this tool to move images around in the image window.

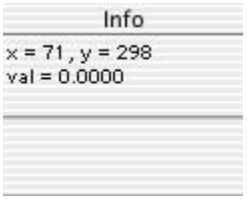
**Ruler Tool**
Use this tool to measure distances in an image. An image can be calibrated from the menu command under Process after a line is drawn using the ruler tool..

**Rotate Tool**
This tool is used to rotate drawings of crystal structures. In order for it to be active, a structure must have been selected first.

**Masking Tools**
The last 5 tools are masking tool normally used in reciprocal space, but they can be used in real space as well. The masks are
a) **Spot mask**. A reflection and its conjugate is selected.
b) **Lattice mask**. A mask defined by two lattice vectors.
c) **Band Pass mask**. This mask is defined by an inner and an outer circle.
d) **Wedge mask**. Defined by two lines.
e) **Line mask**. Defined by a line and a single lattice vector.
All these masks can be transparent or opaque, meaning they work on the region within or outside of the mask. The mask parameters can be edited by double clicking on the mask or selecting the mask and choosing “Edit Mask” from the “Pro-

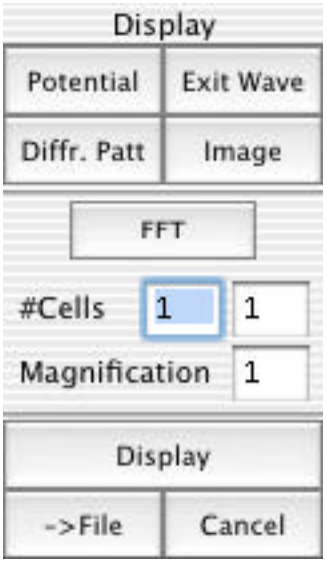
cess" menu. The number of lattice spacings for the vector(s) for the lattice mask and line mask can also be changed by clicking in the end point of the vector with the "Option" key down. Each click increments the number of lattice spacings to the endpoint by one. Holding down the "Shift" key and the "Option" key decreases the number of lattice spacings by one.

## Info Window




This window shows the current position of the cursor within the image window and the intensity of the underlying pixel. When dragging a rectangle, the dimensions of the rectangle are shown. Line lengths and angles are also displayed. Image statistics is displayed in this window when invoked through the "Statistics" in the "Process" menu.

## Display Window

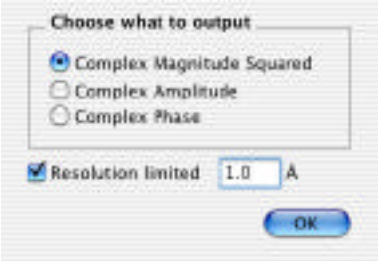



Use this window to define which part of the calculation to display. The choices are:

**Projected Potential** - Essentially the output of the projected potential routine. There is a one to one correspondence between the points in the projected potential and those in the image if displayed under equivalent conditions.

**Exit Wavefunction** - This is the output of the multislice component of the programand shows the distribution of electrons as they emerge from the bottom of the specimen, or at a predefined depth in the specimen. By holding down the **Option** key when selecting the button, one can select to display either the magni-

tude squared (default), the complex amplitude or the complex




phase of the electron wavefunction at the exit surface of the specimen.

**Diffraction Pattern** - Select this option to display the diffraction pattern for one of the selected specimen thicknesses. This is a dynamical diffraction pattern including multiple scattering in the specimen.

**Image** - When selected, one of the calculated images becomes the source of the operations defined by clicking in the Operand Window. By holding down the **Option** key when selecting the button, one can select to display either the image intensity


(magnitude squared, default), or if the image plane wavefunction(s) has been calculated, the complex amplitude or the complex phase of the electron wavefunction at the image.

**FFT**
Use this to perform a Fourier Transform on the selected source. Operating on the Projected Potential will yield the structure fac-

tors, operating on the Exit Wavefield will yield the diffraction pattern and operating on the image will give the Power spectrum of the image.

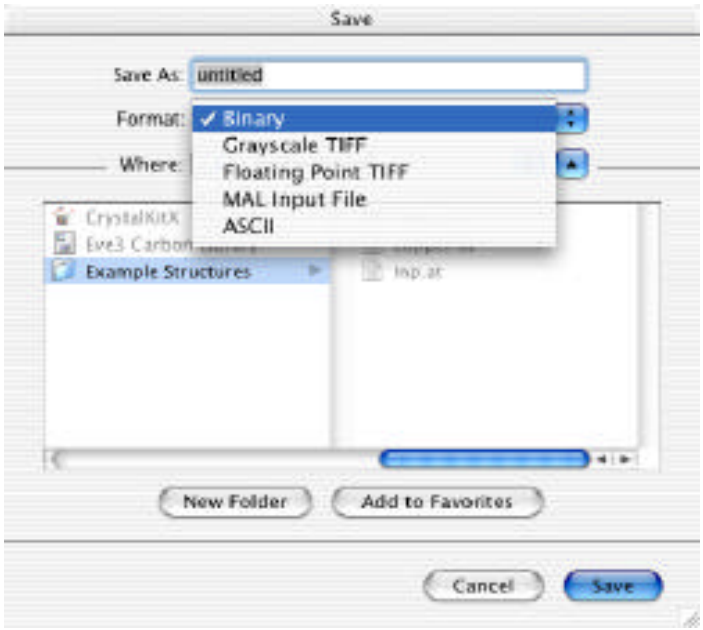
**#Unit cells**
Use this to specify the number of unit cells that should be displayed. The input determines the number of cells in the a-direction and b-direction.

**Zoom**
Use this selection to Zoom the object to either magnify the object or to reduce the object. A zoom factor greater than 1. magnifies and a zoom factor less than 1. reduces the object.

**Display**
Before the result of operating on a selected source is displayed in the image window, **Display** must have been clicked. Choosing the source and operations only selects the functions to be performed. When **Display** gets activated, the functions get executed.

**->File**
This will allow for output of the numeric values of images, amplitudes and phases to a file. Options allow for writing the data in ascii format or binary format. Images can also be written

as TIFF files in this fashion.



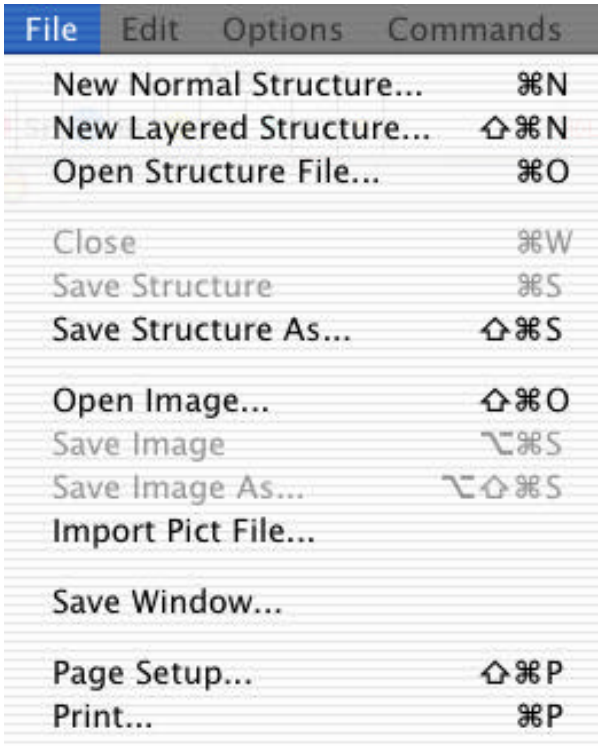

**Cancel:**
Use this button in case the wrong sequence of commands was chosen or anything else was entered wrong. This cancels the set functions.

Chapter 6

# *Menus*

Many of the functions in MacTempas are run from one of the MacTempas menus, including the multislice calculation. In addition, most options are set from one of the menus. This is a list of the currently available menus and a description of their function.

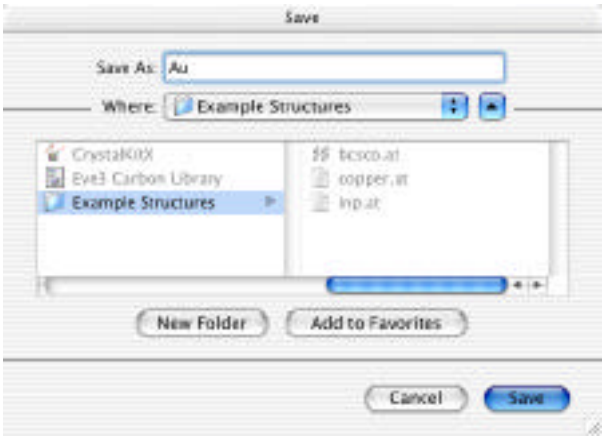
## File Menu



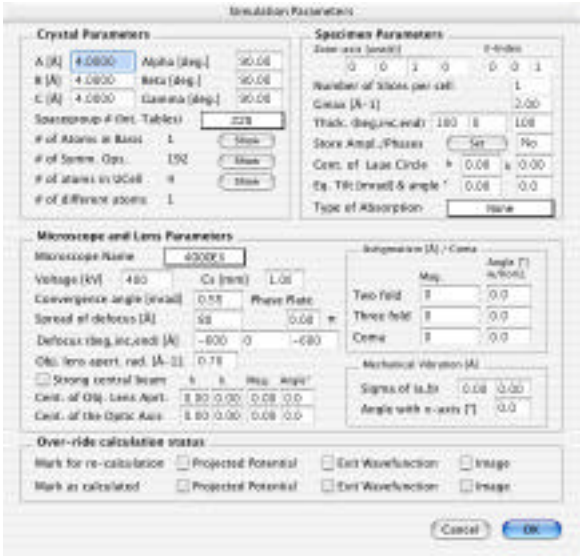

This menu contains the following commands:

**New Normal Structure...**

Create a new structure file. A name is prompted for before input is made. Enter a unique structure name, the program will append the extension .at. Make sure that you do not add an extension of the type .at in which case MacTempas will not properly deal with the file later on. Also make sure the filename does not have a period in it. This opens a new structure with

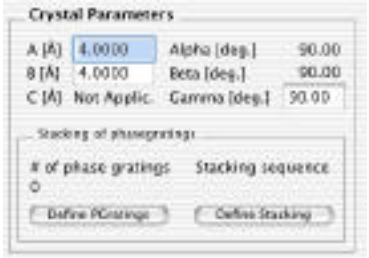



default values for all the parameters. Change the input to reflect



the structure that you want to create

**New Layered Structure...**
Create a new layered simulation file. A name is prompted for before input is made. Enter a unique structure name, the program will append the extension .lay. A layered structure is characterized by being made up of a sequence of pre-calculated projected potantials. Thus a layered simulation file does not contain atomic positions. The structure information in the input dialog is replaced by .




Only A and B and Gamma have meaning for a layered “structure”. The buttons “Define PGratings” and “Define Stacking” are used to choose the different projected potentials and to define their sequence to make up the entire specimen.

**Open Structure File...**
Open an existing structure or a leyered file. The standard Macintosh file open dialog is presented and only files of the type ‘TEXT” with the extension “.at” or “lay” are displayed as selectable. The name of the display window will change to reflect the name of the current structure.

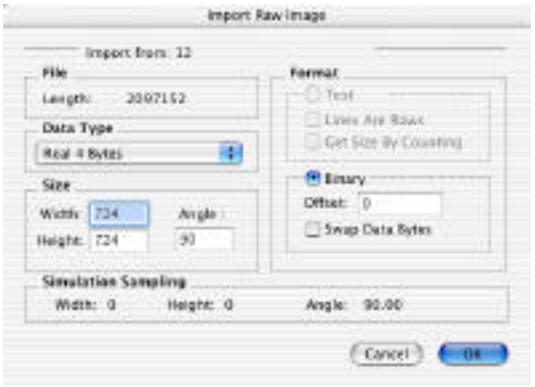
**Close**
Close the file, image or window currently selected

**Save Structure**
Save the current data for the structure file in use. The current data will be written to the file, overwriting any old data.

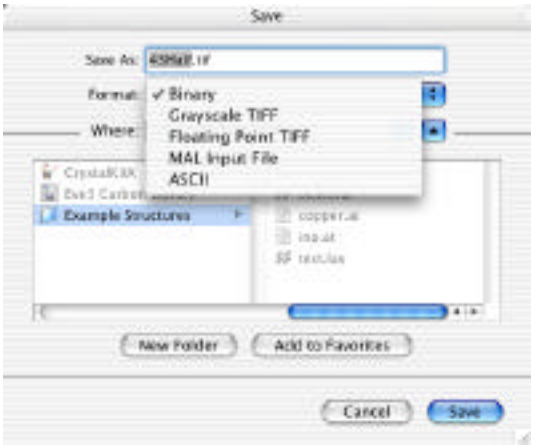
**Save Structure As...**
Save the current structural information. Do not use a name with

an extension if the file being saved is a structure file for later use by MacTempas.

**Open Image...**
Open an image. Supported images are currently tiff files and binary files. RGB tiff files and compressed tiff files are not supported. Binary files can be of integer or float types with different length and byte order.




**Save Image...**
Saves the content of the image window into a file. MAL input




files are binary files used by the mal or TrueImage program for exit wave reconstruction from a through focal series.


**Save Image As...**
Similar to “Save Image”.

**Import PICT File...**
Import a PICT file and display it in the MacTempas image window.

**Save Window...**
Saves the content of the image window as a PICT file..

**Page Setup...**
Set the options for the page to be printed.

**Print...**
Print the front window..

## Edit Menu

**Undo**

**Undo / Redo** the last operation. These operations do not cur-


rently work in MacTempas.

**Cut**
Cut the selected Object or the Selection made by the selection tool.

**Copy**
Copy the selection or the selected object.

**Paste**
Paste the content of the paste buffer into the display window. The source for the paste can be an image cut out from another application or through the cut/copy commands of MacTempas. If the object is an image, the image will be pasted into the display window if it is currently selected or into a separate image window if not.

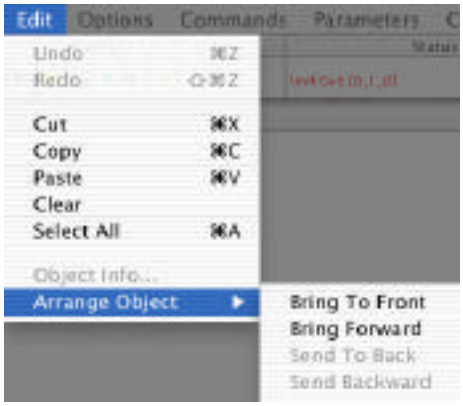
**Clear**
Clears the selection made by the selection tool

**Select All**
Select all objects in the display window or an entire image.

**Object Info**
Shows the clipboard and the content of the clipboard.

### Arrange Object

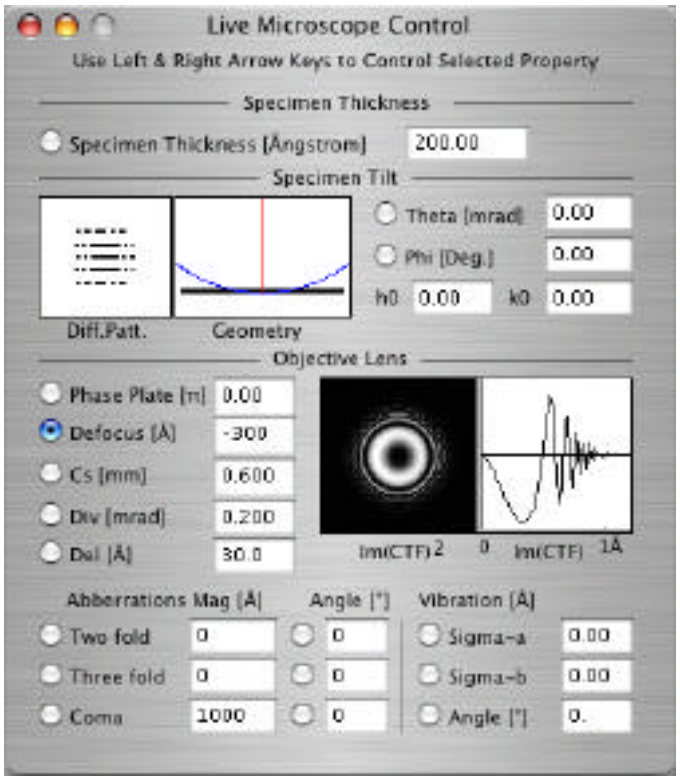
Shows the clipboard and the content of the clipboard.



## Options Menu


**Live Microscope Control...**
When a calculated image is selected, this command can be invoked to bring up an interactive window for changing the calculation parameters for this image. Changes in the parameters

are reflected live aslong as the calculation time is reasonable..

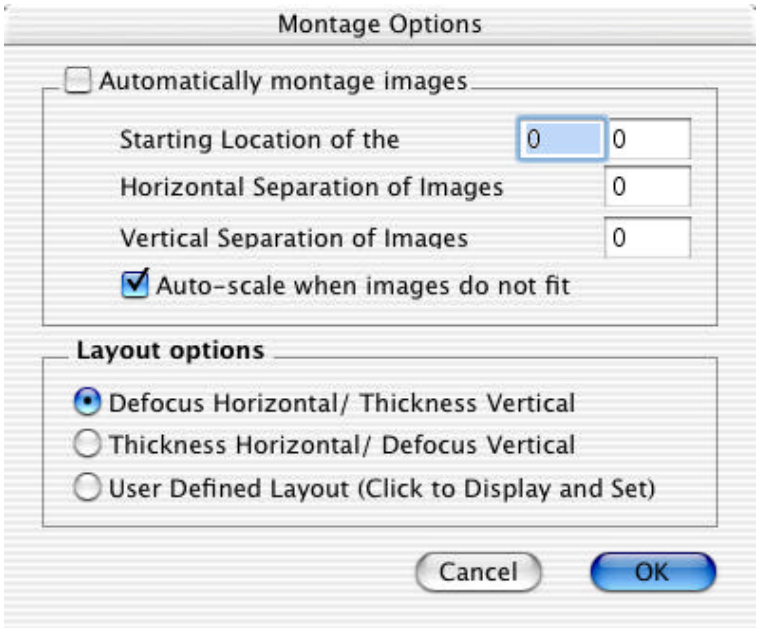



**Automatic Erase**
Toggles whether you are prompted for the position of the upper left corner of the image to be displayed.

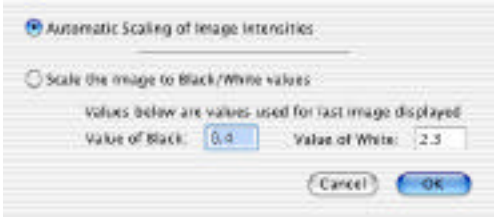
**Atom Overlay**
If set, the atom positions will be drawn in as circles on top of images. The circles are scaled to the atomic radius and the color is the color set for that atom species. If the Option key is held down while the image is "drawn", only the circles are drawn (no image).

**Montage...**
Brings up a dialog box, allowing the user to select automatic montage of a series of images, the position of the series of

images and the number of pixels to leave between images.

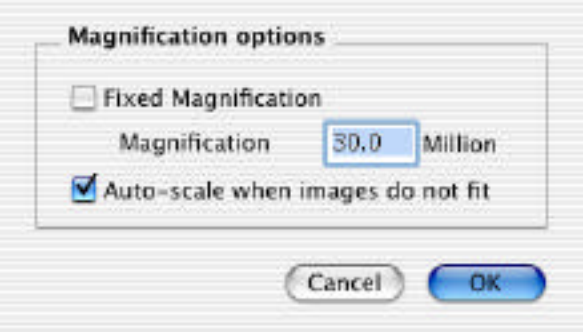



**Intensity Scaling...**
Brings up a dialog box, allowing the user to manually set the intensity values to be mapped to black and white. The values shown correspond to the last image displayed with automatic scaling.

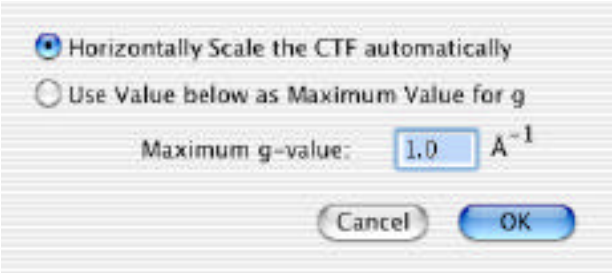



**Magnification**
Allows the user to set the magnification to a set value. The magnification depends on a screen with a resolution of 72 dots/

inch. If Auto-scaling is set, images will scale to fit the window.

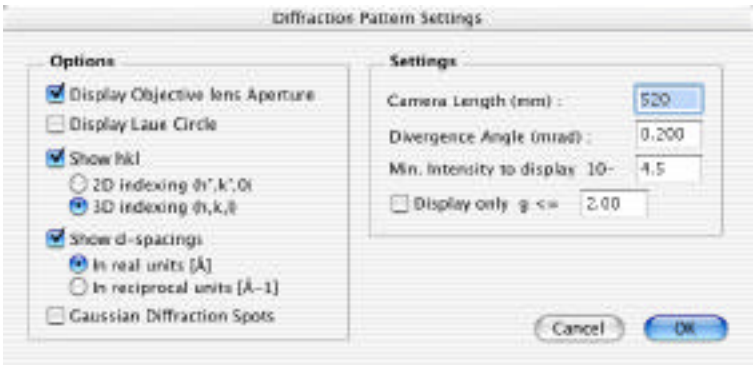



**CTF Scaling...**
Brings up a dialog box, allowing the user to set the maximum scale of the reciprocal axis during plotting of the Contrast Transfer Function.

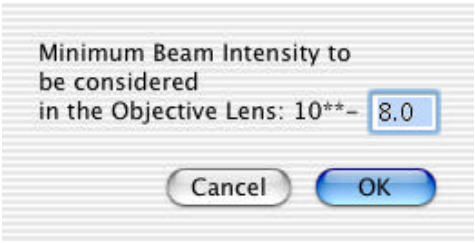



**Diffraction Pattern...**
Displays a dialog box, allowing the user to select the position of the diffraction pattern, the camera length and the minimum diffracted intensity that can be displayed. The user can also choose whether the objective lens aperture should be superimposed on the diffraction pattern. The indices of the diffracted beams can be superimposed on the diffraction pattern as well as the corresponding real space distances. Selecting Circular Diffraction spots instead of Gaussian Diffraction Spots results in solid circles. One can also set a cut-off such that diffracted beams with

g-vectors larger than the cut-off will not be displayed.

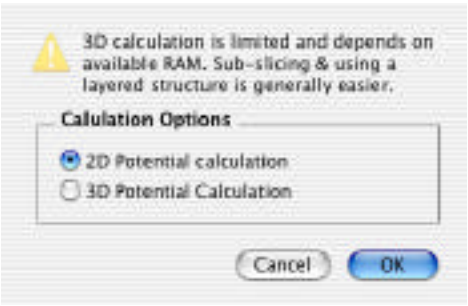



**Min Lens Intensity...**
Displays a dialog box, allowing the user to manually set the minimum intensity required of a diffracted beam for inclusion in the formation of the image.

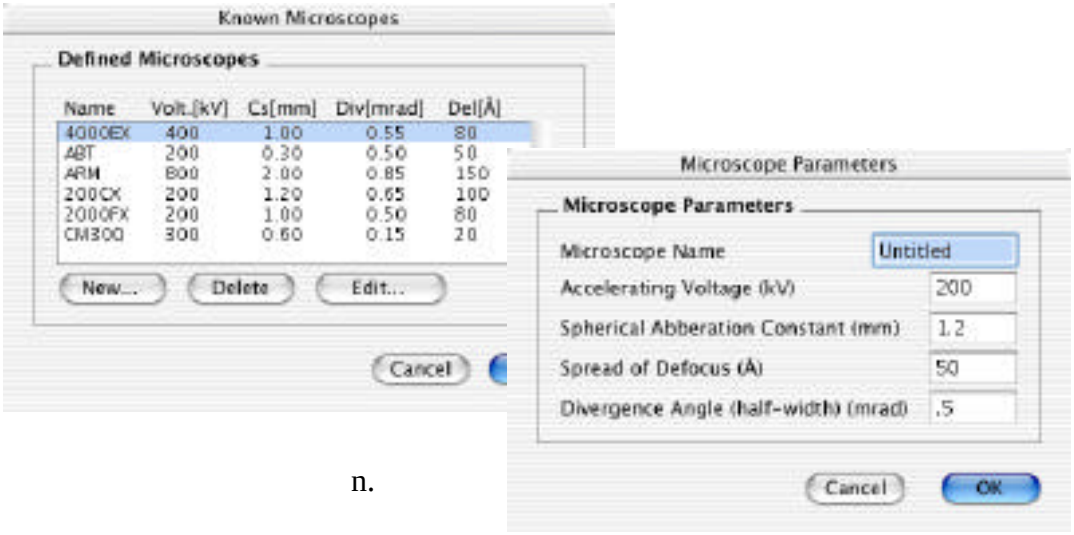



**Slice Method...**
Allows the user to select the option to perform a three dimensional calculation of the projected potential by summing over

the third dimension (l) in reciprocal space.




**Show Microscopes...**
Displays a dialog, showing the user which microscopes are known to MacTempas. The default parameters associated with a known microscope can be changed by the user and a new microscope may be made known to MacTempas. MacTempas currently only allows a maximum of 10 microscopes to be made known



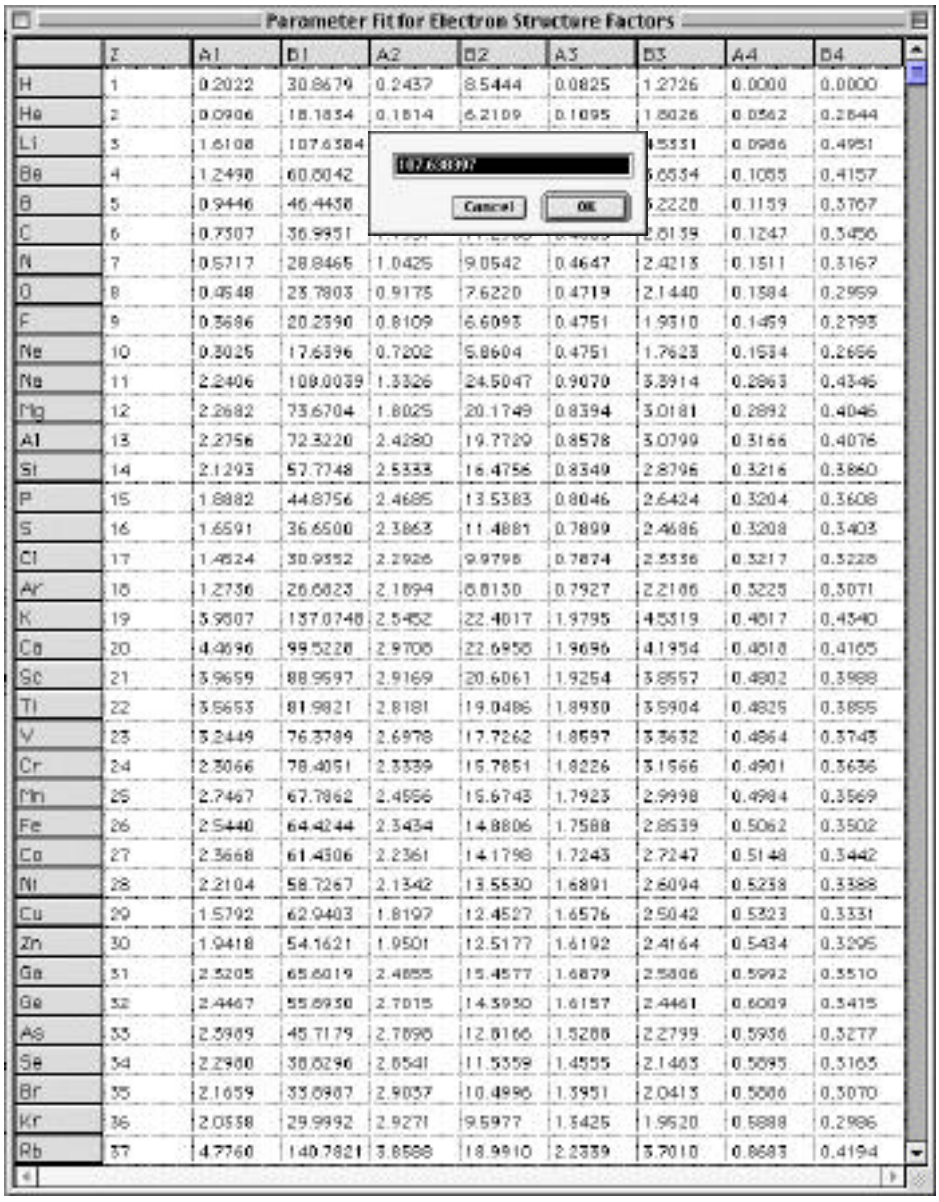

n.

**Use Fit For Electron Scattering Factors / Use Fit For X-Ray Scattering Factors**
MacTempas can use either the 8 parameter fit for the Electron Scattering Factors or the 9 parameter fit for the X-Ray Scatter-

ing factors. The menu item text will reflect the current setting.

**Edit Scattering Factor Parameters...**
Brings up a table of the fitting parameters. Double clicking in the value -field brings up a dialog box prompting for a new value. See next page.

**Treat as Monolayer**
When this option is set, the calculation treats the unit cell as a non-repeating structure such that the entire specimen is represented by a single unit cell with the thickness of the specimen as the thickness of the unit cell.

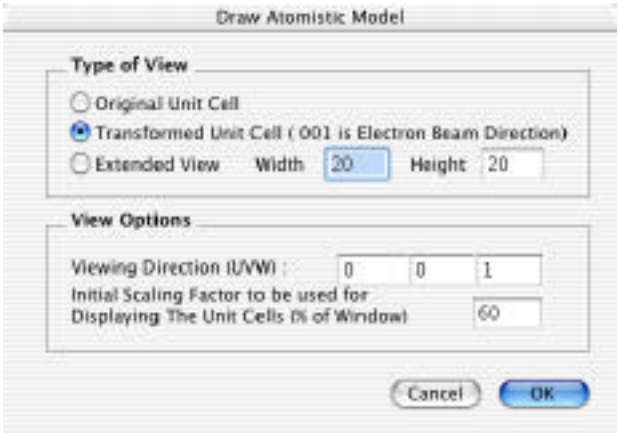



| | Z | A1 | B1 | A2 | B2 | A3 | B3 | A4 | B4 |
|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0.2022 | 30.8679 | 0.2437 | 8.5444 | 0.0825 | 1.2726 | 0.0000 | 0.0000 |
| He | 2 | 0.0906 | 18.1854 | 0.1814 | 6.2109 | 0.1095 | 1.8026 | 0.0562 | 0.2644 |
| Li | 3 | 1.6108 | 107.6384 | | | | 5551 | 0.0986 | 0.4951 |
| Be | 4 | 1.2498 | 60.8042 | | | | 6554 | 0.1055 | 0.4157 |
| B | 5 | 0.9446 | 46.4438 | | | | 2220 | 0.1159 | 0.3767 |
| C | 6 | 0.7307 | 36.9951 | | | | 0139 | 0.1247 | 0.3456 |
| N | 7 | 0.5717 | 28.8465 | 1.0425 | 9.0542 | 0.4647 | 2.4218 | 0.1511 | 0.3167 |
| O | 8 | 0.4548 | 23.7803 | 0.9175 | 7.6220 | 0.4719 | 2.1440 | 0.1584 | 0.2959 |
| F | 9 | 0.3686 | 20.2390 | 0.8109 | 6.6093 | 0.4751 | 1.9510 | 0.1469 | 0.2795 |
| Ne | 10 | 0.3025 | 17.6396 | 0.7202 | 5.8604 | 0.4751 | 1.7623 | 0.1534 | 0.2656 |
| Na | 11 | 2.2406 | 109.0039 | 1.3326 | 24.5047 | 0.9070 | 3.3914 | 0.2863 | 0.4346 |
| Mg | 12 | 2.2682 | 73.6704 | 1.8025 | 20.1749 | 0.8394 | 3.0181 | 0.2892 | 0.4046 |
| Al | 13 | 2.2756 | 72.3220 | 2.4280 | 19.7729 | 0.8578 | 3.0799 | 0.3166 | 0.4076 |
| Si | 14 | 2.1293 | 57.7748 | 2.5333 | 16.4756 | 0.8349 | 2.8796 | 0.3216 | 0.3860 |
| P | 15 | 1.8882 | 44.8756 | 2.4685 | 13.5383 | 0.8046 | 2.6424 | 0.3204 | 0.3608 |
| S | 16 | 1.6591 | 36.6500 | 2.3863 | 11.4881 | 0.7899 | 2.4686 | 0.3208 | 0.3403 |
| Cl | 17 | 1.4824 | 30.9552 | 2.2926 | 9.9798 | 0.7874 | 2.3536 | 0.3217 | 0.3228 |
| Ar | 18 | 1.2736 | 26.6823 | 2.1694 | 8.8130 | 0.7927 | 2.2186 | 0.3225 | 0.3071 |
| K | 19 | 3.9507 | 137.0746 | 2.5452 | 22.4017 | 1.9795 | 4.5319 | 0.4817 | 0.4340 |
| Ca | 20 | 4.0696 | 99.5228 | 2.9708 | 22.6950 | 1.9696 | 4.1954 | 0.4810 | 0.4165 |
| Sc | 21 | 3.9659 | 88.9597 | 2.9169 | 20.6061 | 1.9254 | 3.8557 | 0.4802 | 0.3988 |
| Ti | 22 | 3.9653 | 81.9821 | 2.8181 | 19.0486 | 1.8930 | 3.5904 | 0.4825 | 0.3855 |
| V | 23 | 3.2449 | 76.3789 | 2.6978 | 17.7262 | 1.8697 | 3.3632 | 0.4864 | 0.3743 |
| Cr | 24 | 2.3066 | 78.4051 | 2.3339 | 15.7851 | 1.8226 | 3.1566 | 0.4901 | 0.3636 |
| Mn | 25 | 2.7467 | 67.7862 | 2.4556 | 15.6743 | 1.7923 | 2.9998 | 0.4984 | 0.3569 |
| Fe | 26 | 2.5440 | 64.4244 | 2.3434 | 14.8806 | 1.7588 | 2.8539 | 0.5062 | 0.3502 |
| Co | 27 | 2.3668 | 61.4306 | 2.2361 | 14.1798 | 1.7243 | 2.7247 | 0.5148 | 0.3442 |
| Ni | 28 | 2.2104 | 58.7267 | 2.1342 | 13.5530 | 1.6891 | 2.6094 | 0.5238 | 0.3388 |
| Cu | 29 | 1.5792 | 62.9403 | 1.8197 | 12.4527 | 1.6576 | 2.5042 | 0.5323 | 0.3331 |
| Zn | 30 | 1.9418 | 54.1621 | 1.9501 | 12.5177 | 1.6192 | 2.4164 | 0.5434 | 0.3295 |
| Ga | 31 | 2.5205 | 65.6019 | 2.4855 | 15.4577 | 1.6879 | 2.5806 | 0.5992 | 0.3510 |
| Ge | 32 | 2.4467 | 55.8930 | 2.7015 | 14.5950 | 1.6157 | 2.4461 | 0.6009 | 0.3415 |
| As | 33 | 2.3969 | 45.7179 | 2.7896 | 12.8166 | 1.5208 | 2.2799 | 0.5936 | 0.3277 |
| Se | 34 | 2.2900 | 38.6296 | 2.6541 | 11.5359 | 1.4555 | 2.1463 | 0.5895 | 0.3165 |
| Br | 35 | 2.1659 | 33.0987 | 2.5037 | 10.4996 | 1.3951 | 2.0413 | 0.5886 | 0.3070 |
| Kr | 36 | 2.0558 | 29.9992 | 2.9271 | 9.5977 | 1.5425 | 1.9520 | 0.5888 | 0.2986 |
| Rb | 37 | 4.7760 | 140.7821 | 3.6598 | 18.9910 | 2.2339 | 3.7010 | 0.8683 | 0.4194 |

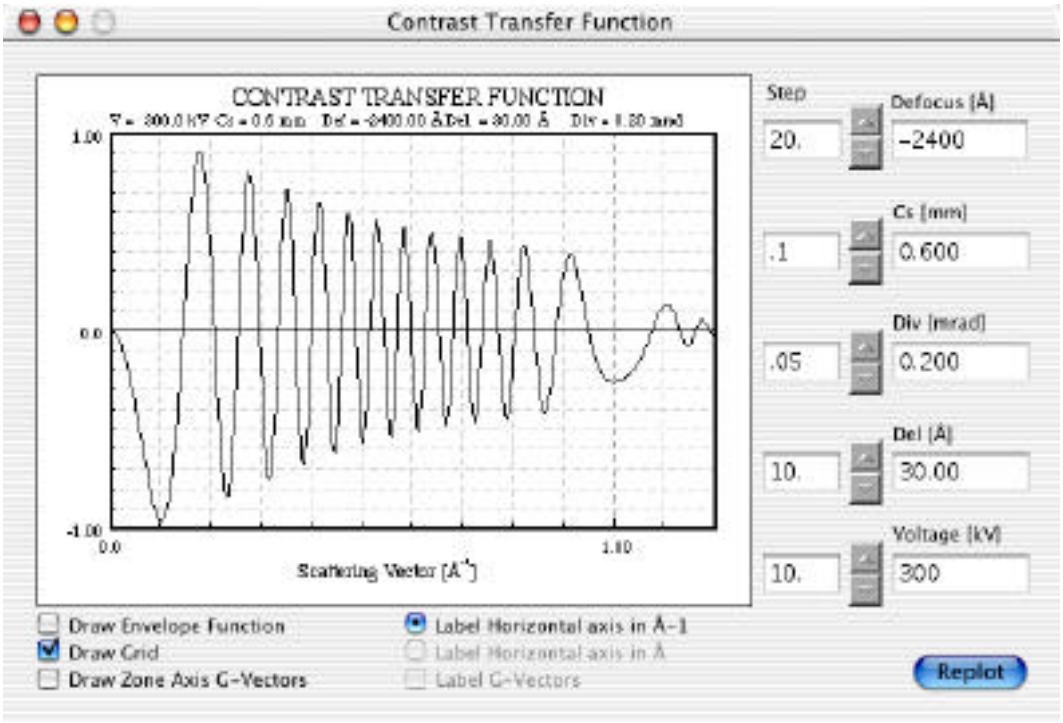

## Commands Menu

**Erase**
Erases the selection made by the selection tool.

**Draw Atomic Model...**
Displays a dialog box, from which the user can select to display the original or transformed unit cell from any direction, including perspective view. The transformed cell corresponds to the unit cell that MacTempas uses in the multislice calculation. To view the cell as "seen" by the electrons, the transformed (new) unit cell should be viewed in the 001 orientation. It should be noted that the viewing direction is in units of the real space unit cell axes. One can also view a cross-section of the material in a given direction. A dialog box allows the user to specify the field of view in Å for the two directions.



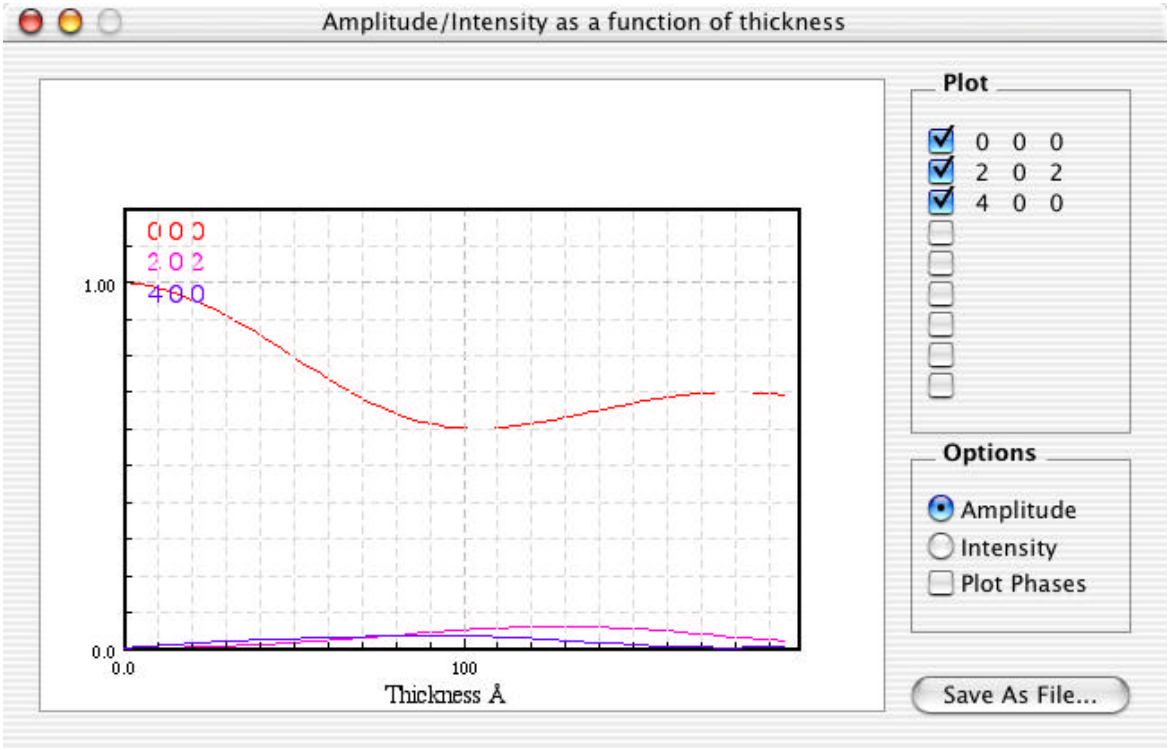
**Draw the CTF**
Draws the Contrast Transfer Function for the current microscope values. The original microscope values are taken from the structure data, but the user is free to change the values associated with the CTF independent of the values used in calculating the image. Clicking in the CTF will show a bar with the values




of the CTF and the resolution. The bar moves with the mouse.

**Draw Pendelløssung Plots...**
In case the user has selected to store a set of diffracted beams for plotting of amplitudes and phases as a function of specimen thickness, this brings up a dialog box allowing the user to set the plotting conditions. One can choose to have the amplitudes

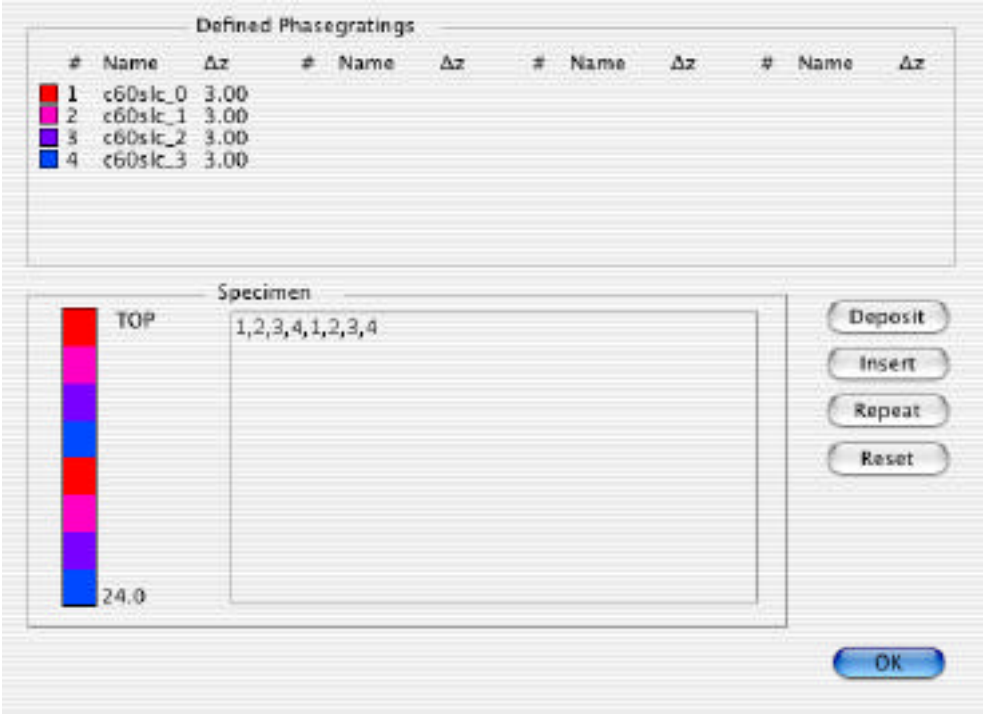
or the intensities plotted as well as the phases of the diffracted beams. Each reflection can be plotted by itself, or several reflections can be superimposed on the same plot. Instead of plotting the values, the values can also be written to a file for further manipulation or inspection.



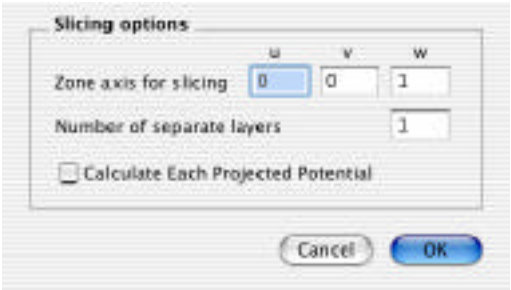

**Define Projected Potentials...**
This allows the user to specify which potentials to be used in the layered structure.

**Stack Potentials...**
This allows the user to specify the sequence of potentials that should be used in the multislice calculation. This applies only to layered structures. See Chapter 9 for a more detailed instruc-

tion on how to create a layered structure.

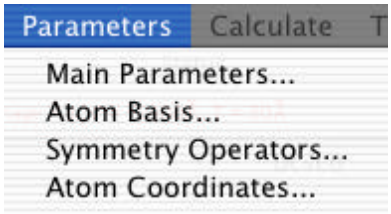



**Slice Unit Cell...**
Use this option to subdivide a structure into separate layers for use in a layered structure calculation. The direction perpendicular to the slices and the number of slices must be specified.

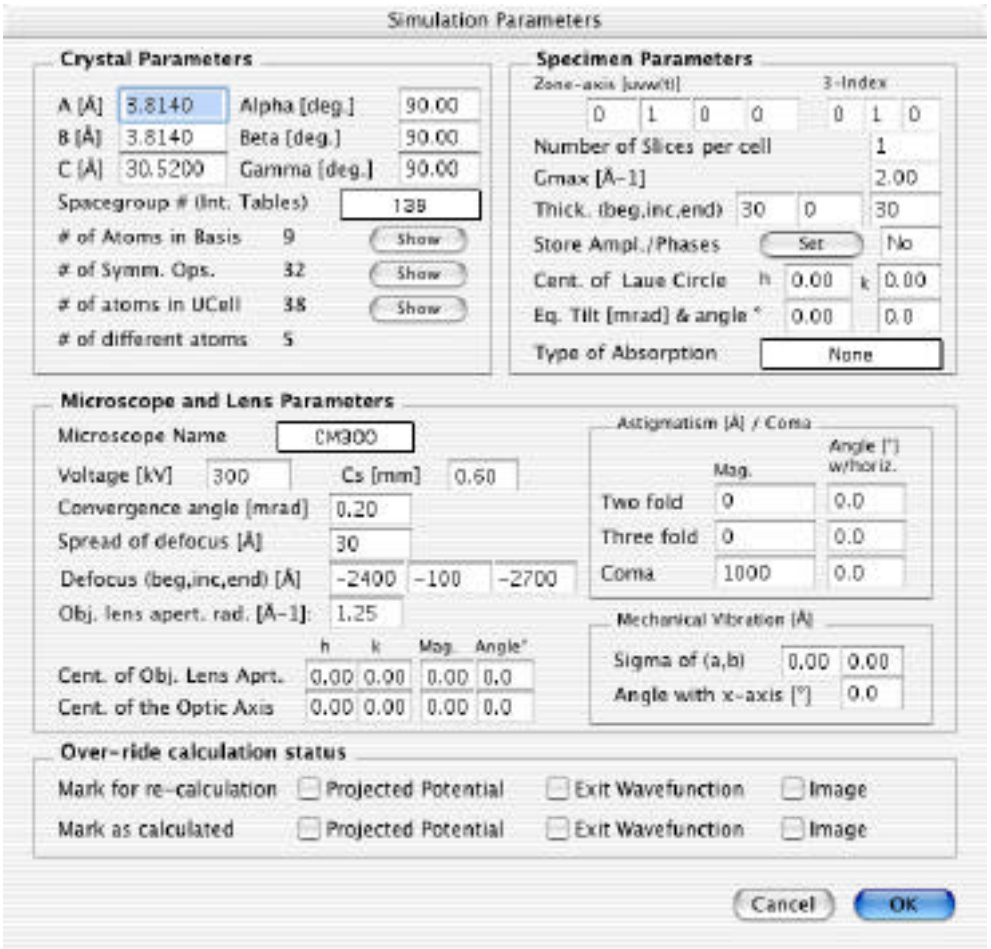

Slicing options
u
v
w
Zone axis for slicing
0
0
1
Number of separate layers
1
Calculate Each Projected Potential
Cancel
OK

## Parameters Menu

### Main Parameters...

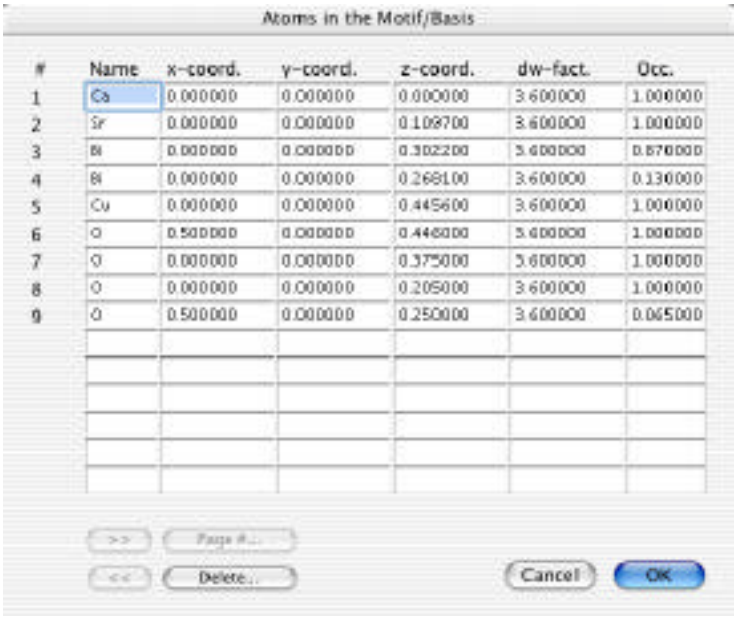



This brings up a dialog box showing the current conditions for the simulation. The values are taken from the input given to the



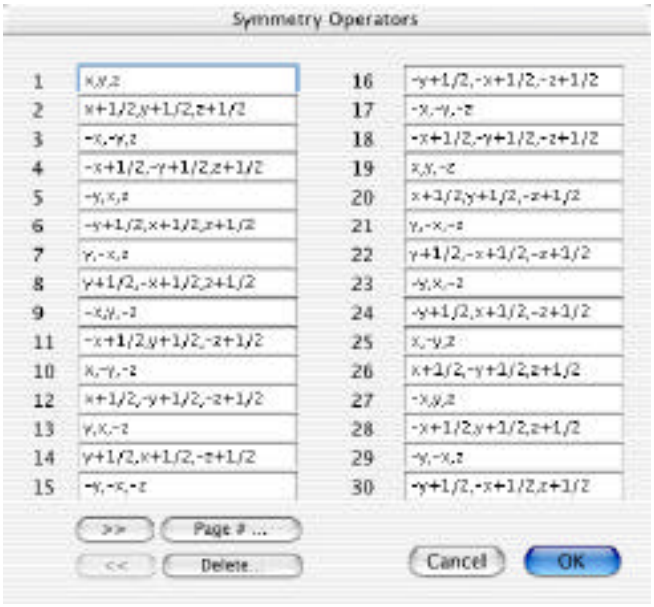

New... command in the FILE menu. The parameters can be changed as to bring about a new simulation.

**Atomic Basis...**
Brings up the list of all the atoms forming the set of basis atoms for the current structure. The atomic coordinates etc. can be edited and atoms can be added to or deleted from the list.



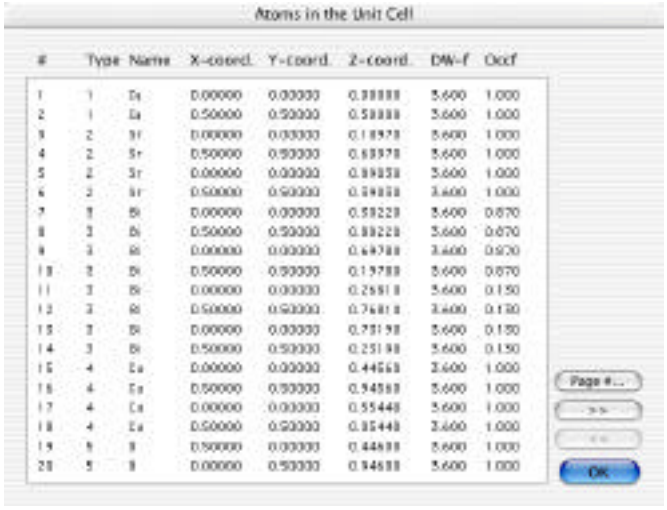

**Symmetry Operators...**
This brings up the list of symmetry operators either associated by the space group or entered manually by the user. The symmetry operators can be edited, and new ones may be added to

the list or existing ones deleted.



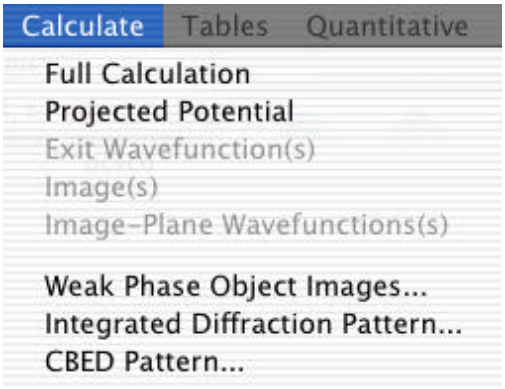

**Atomic Coordinates...**

This shows all the atoms within the unit cell. This list of atoms are generated by applying the symmetry operators on to the set of basis atoms above. This list can not be changed, the changes must take place in the atomic basis or the symmetry operators.



## Calculate Menu

The active commands in this menu depends on the current sta-




tus of the calculation. If the simulation has already been carried out for the current set of parameters, then no commands will be active. If a change has been made or the file is a newly created structure file, the commands showing which subprograms needs to be run are shown active.

**Full Calculation**
Use this command if you would like the program to run the multislice calculation to its end starting from the point required by the last change made to the simulation parameters.

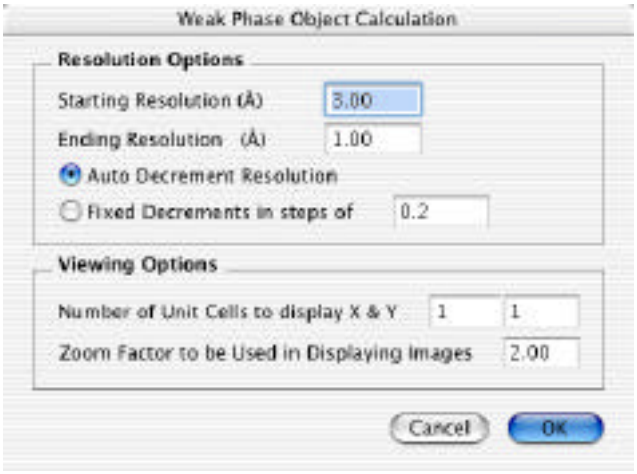
**Projected Potential**
Execute this command if you only want to run the PHSGRT program at this time. After the phasegrating is run, the multislice option is highlighted.

**Exit Wavefunctions(s)**
Execute this command if you only want to run the MSLICE program at this time.

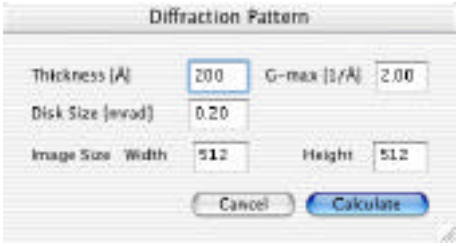
**Image(s)**
Execute this command if you only want to run the IMAGE program at this time.

“

**Weak Phase Object Images**
is a separate module that allows the calculation of images that would be produced in the case of an ideal Scherzer lens and validity of the weak phase object approximation. The “wpo” calculation is discussed more in detail elsewhere.

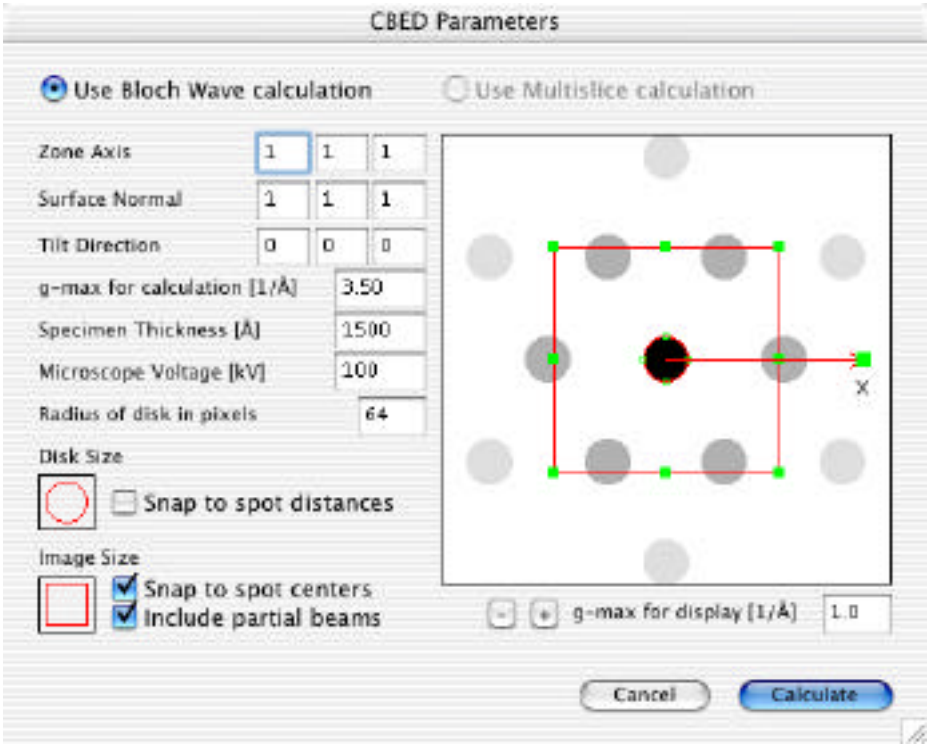



**Integrated Diffraction Pattern**- calculates the diffraction pattern by adding up the intensities for each tilt angle within the cone of incident electron directions.




**CBED Pattern**
Will calculate the CBED pattern for the given input parameters

using the Bloch-Wave approximation.

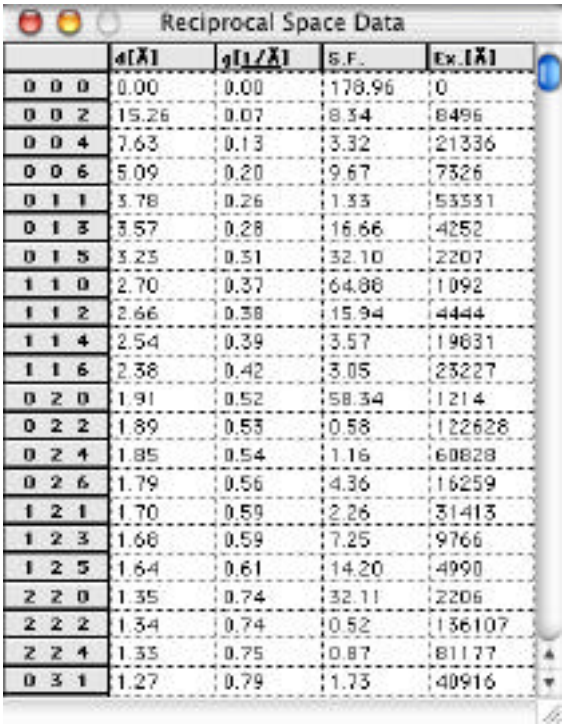



## Tables


The current operations in this menu are:

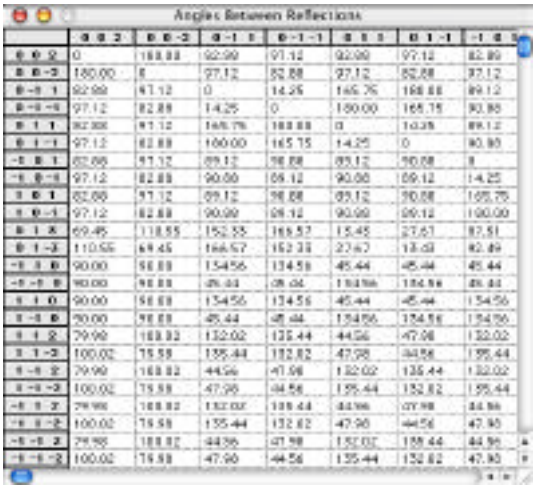
**Reciprocal Space Info...**
Displays information about reciprocal space data for the current structure. The data can be sorted on the reciprocal vector or the

structure factor/extinction distance.

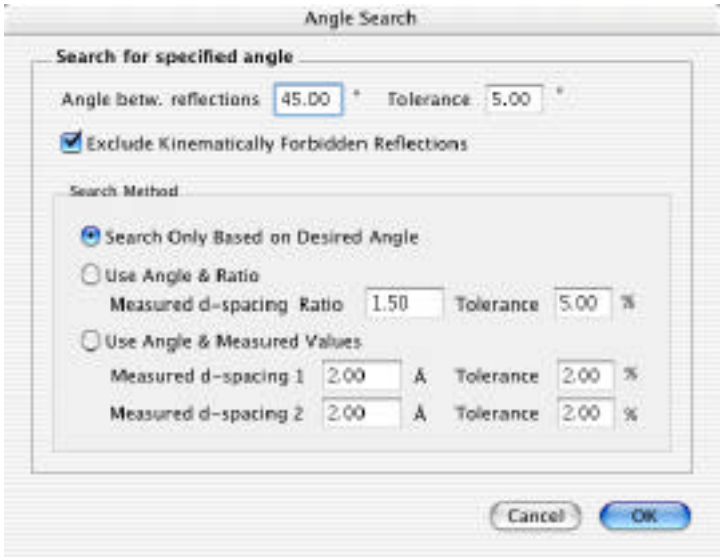



| | d[Å] | g[1/Å] | S.F. | Ex.[Å] |
|---|---|---|---|---|
| 0 0 0 | 0.00 | 0.00 | 178.96 | 0 |
| 0 0 2 | 15.26 | 0.07 | 8.34 | 8496 |
| 0 0 4 | 7.63 | 0.13 | 3.32 | 21336 |
| 0 0 6 | 5.09 | 0.20 | 9.67 | 7326 |
| 0 1 1 | 3.78 | 0.26 | 1.33 | 53331 |
| 0 1 3 | 3.57 | 0.28 | 16.66 | 4252 |
| 0 1 5 | 3.25 | 0.31 | 32.10 | 2207 |
| 1 1 0 | 2.70 | 0.37 | 64.88 | 1092 |
| 1 1 2 | 2.66 | 0.38 | 15.94 | 4444 |
| 1 1 4 | 2.54 | 0.39 | 3.57 | 19831 |
| 1 1 6 | 2.38 | 0.42 | 3.05 | 23227 |
| 0 2 0 | 1.91 | 0.52 | 58.34 | 1214 |
| 0 2 2 | 1.89 | 0.53 | 0.58 | 122628 |
| 0 2 4 | 1.85 | 0.54 | 1.16 | 60828 |
| 0 2 6 | 1.79 | 0.56 | 4.36 | 16259 |
| 1 2 1 | 1.70 | 0.59 | 2.26 | 31413 |
| 1 2 3 | 1.68 | 0.59 | 7.25 | 9766 |
| 1 2 5 | 1.64 | 0.61 | 14.20 | 4990 |
| 2 2 0 | 1.35 | 0.74 | 32.11 | 2206 |
| 2 2 2 | 1.34 | 0.74 | 0.52 | 136107 |
| 2 2 4 | 1.33 | 0.75 | 0.87 | 81177 |
| 0 3 1 | 1.27 | 0.79 | 1.73 | 40916 |

**Angles Between Reflections...**
Shows the angles between a set of the reflections in the structure.



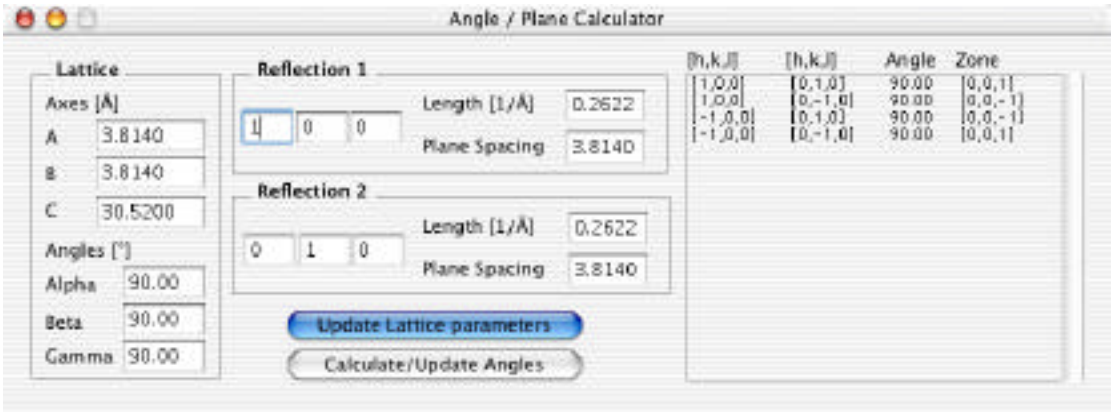
**Seaech for Angle...**
One cacn search for reflections which satisfy a search criteria based on the ratio of the length of the vectors and/or the angle between the measured reflections. This can be used when trying to index diffraction patterns. One can give aan accepted toler-




anse for the ratio, the measured spacings and the measured angle.

**Spacing and Angle Calculator...**
Shows the lengths and d-spacing for a type/family of reflections. Two reflections can be displayed and the zone in which a set of reflection exist and the angle between them is shown in

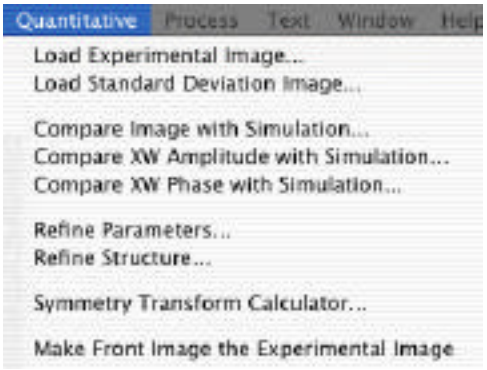
the right part of the window.The reflections can be typed in and




when the “Calculate?Update Angles” button is clicked, the angls between the family of reflections and the zone in which they occur will show to the right. The length of the vectors and the corresponging plane spacing is updated live when typing in a new reflection. The lattice parameters can be changed and invoked through the “Update Lattice Parameter” such that the calculator can be used for structures different from the one that is loaded.

## Quantitative Menu

This is the menu for quantitative comparison between experimental images and exit wavefunctions with calculated data. Structure refinement and imaging parameter refinement is also




invoked from this menu.

**Operating The Routines**

All the routines except for the “Symmetry Transform Calculator” requires the presence of an image that is considered the experimental image. The purpose of this package is to provide the user with tools that permit the following attempts:

•Q

Quantitative comparison of experimental images with those simulated from a structure model

•A

Automatic refinement of parameters such as the thickness of the specimen, the defocus of the objective lens, crystal tilt, aberrations, etc..

•A

Automatic refinement of structural parameters such as atomic positions, debye- waller factors and occupancy factors for selected atoms in the structure.

The experimental image can be compared with the computed images using a number of goodness of fit criteria. A sub-area of the experimental image can also be compared to a sub-area of the simulated image. For more information on quantitative comparison methods and structure refinement see the chapter on “Introduction to Quantitative Comparison of simulated HRTEM images with experiment”.

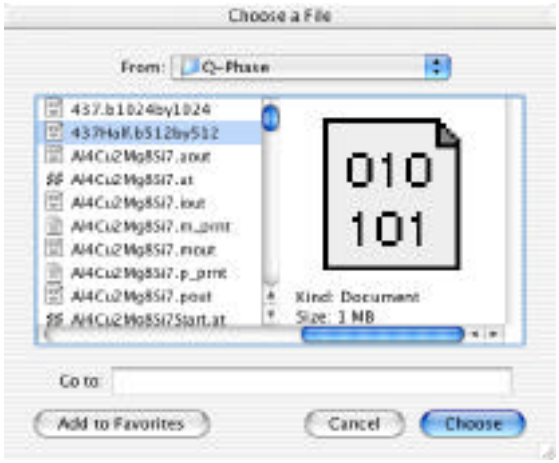
*Note*: All the procedures expect that the experimental image covers the exact area of that of the unit cell used in the calculation. Thus it is up to the user to make sure that the unit cell motif is extracted from the experimental data prior to usage. The term Unit Cell is loosely used since it only refers to the size of the model used in the simulation. The experimental image does not need to be sampled equal to the simulation, since the routines will resample the experimental data to fit that of the simulation.

For parameter refinement and structure refinement, there are a number of algorithms that attempt to look for the “one” solution of parameters that maximize the fit between the experiment and

the simulation. This plug-in uses an algorithm based on simulated thermal annealing which is described further in the chapter at the end of this manual. No claims are made as to the effectiveness of this method and there is no guarantee that the final solution represents the global maximum/minimum in the goodness-of-fit parameter. The effectiveness of optimization routines depend on the starting parameters. There is no recipe for setting the initial starting condition and it is necessary to develop some experience using the optimizing routine in this program. Some trial and error is a definitive part of the parameter/structure refinement. Suffice it to say, “good hunting”.

**Load Experimental Image**

Load Experimental Image is the starting point for loading in the image to be used in the comparison. The command will bring up a standard File Open dialog with a look that depend on the version of the MacOS you are using and what else of Finder utilities you have loaded.

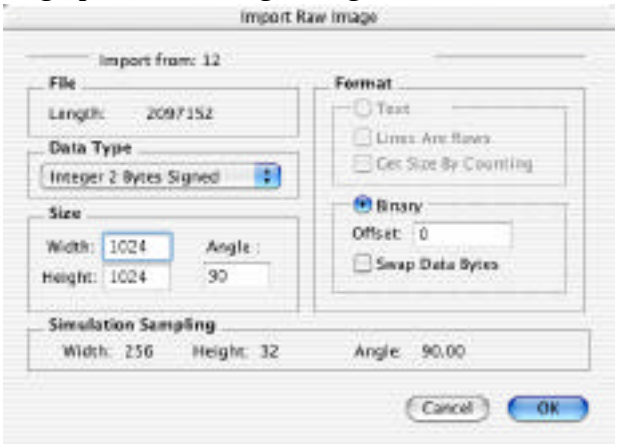



The dialog will show you all files and it is up to you to select an appropriate file to read in. Currently, two distinct types of files are supported. These are

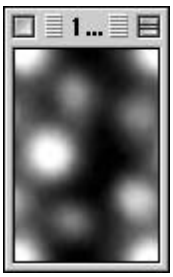
1) **Binary Files**

The data can be Real 4 or Integer 1,2,4 byte
2) **TIFF**
Real 4, Integer 1,2,4 byte

If the routine recognizes the file as a TIFF file, it will just open the file and display the image.
For Binary files, you will need to specify the data type, the width and the height of the image. Byte swapping is also supported. If the program does not recognize the file as type TIFF it will bring up the following dialog




Although the dialog box indicates that the program supports input of text files, this is currently unsupported.
The dimensions of the simulated image are shown at the bottom of the dialog box for binary files.
Once the routine has read in the file, it will display the image in



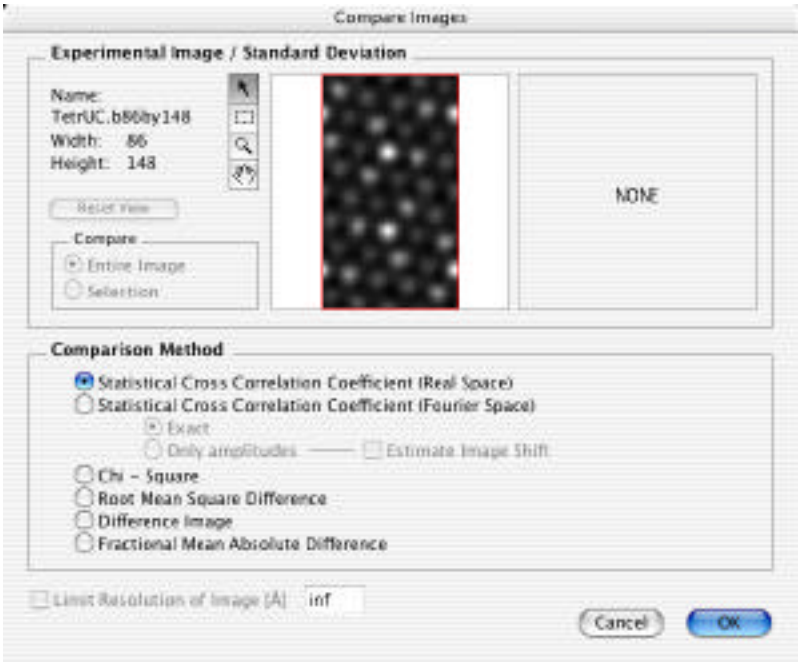

a separate window.
**Load Standard Deviation Image**

This command allows you to read in a standard deviation image to be used together with the average experimental image for comparison with simulated images. The standard deviation image will be used in conjunction with the average image for computing c-square deviations between the experimental data and the computed data. Otherwise the input works exactly as for the loading of the average experimental image. Again, the image will show up in its own window after it has been loaded.


Note: If the windows are covered by other windows, it may be necessary to move these to bring the “experimental” image and the “standard deviation” image to the foreground since there is no command to bring these automatically to the front.

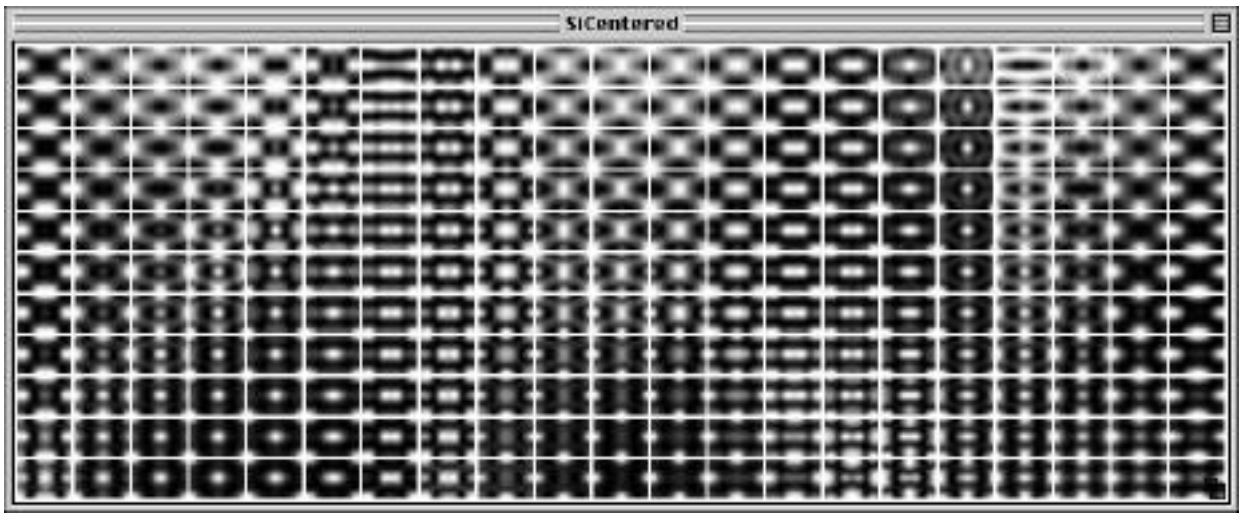
**Compare Experiment With Simulation**

This brings up a dialog window which shows the loaded experimental image and the standard deviation image (if loaded). The name of the experimental image together with the dimensions are shown to the left of the image.




When comparing images, the experimental image will be resampled such that the sampling corresponds to the sampling of the calculated image.

The example used here will be that of a set of simulated images of Silicon in the [110] zone axis orientation
The simulated images for a range of thickness and defocus are shown below.




**Tools**

Pointer Tool

Used essentially to ensure that no other tool is active

Selection Tool

Use this to mark an area in the image which will be used for comparison. It is okay to go outside the image, since the selection will be cropped to the actual image.

Hand Tool

Use this tool to move the image within the display area.

Magnification Tool

Use this tool to magnify the image. Holding down the Option key when clicking within the image will reduce the magnification. Holding down the shift key when clicking will increase/ decrease the magnification by a factor of 2.

**Reset View**

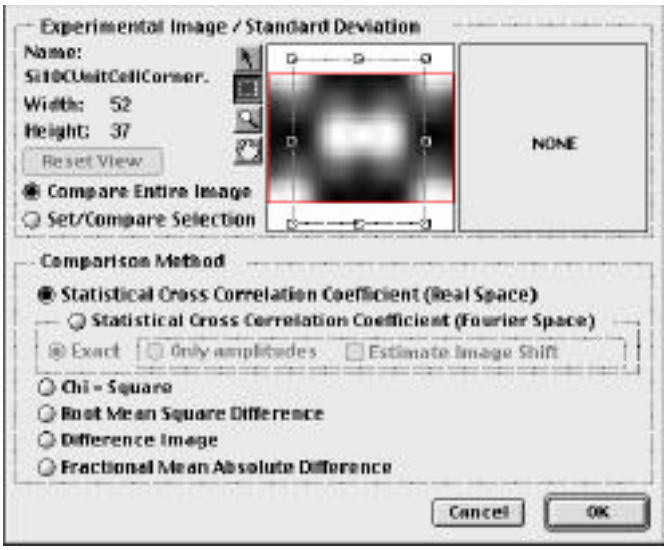
Click here to reset the view/pan/zoom of the image.

**Selecting an area for comparison**

The user choose to compare the entire image region or only a

selection of the image.

Two radio buttons are provided:
*Compare Entire Image*
By clicking on this radio button, the selection area will automatically be set to be that of the entire image. The comparison area is shown as a red rectangle.
*Set/Compare Selection*
The user must first use the selection tool to mark a region of the image. Upon clicking on the radio button, the selection will be marked in red and this area will be used for comparing images. For changing an already defined regions, mark a new one and click again in the radio button.



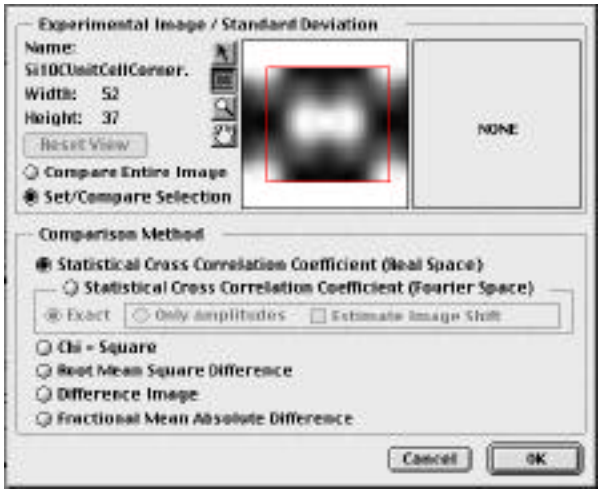

Note: The selection does not work for the Difference Image which automatically compares the entire image.

**Selecting a method of comparison**
The method of comparison or goodness of fit criteria is chosen by a set of radio buttons and the choices and the corresponding description and output is given below. The goodness of fit criteria is computed for each image that is compared and displayed in a table. This table can be saved in a text file for further use.

**Statistical cross correlation coefficient (CCC):**

A note about the cross correlation coefficient:
The cross correlation coefficient measures similarity in the pattern between the experimental image and the computed image. Since the images to be compared are set to a mean level of 0 and normalized, any scaling of the type I(exp) = a * I(calc) + b would give a cross correlation coefficient of 1. Exact fit is given as CCC = 1 and a reverse contrast gives CCC = -1.

*Real Space*

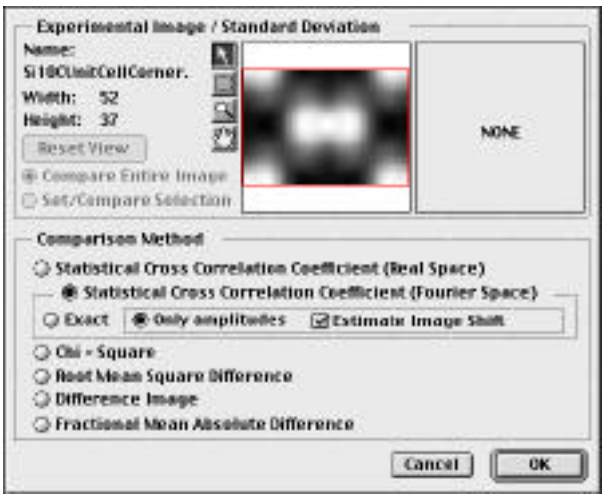



This is a straight calculation of the normalized cross correlation coefficient between the experiment and the calculated image(s). For it to give meaningful results, the origin of the experimental image neeeds to coincide with the calculated image.

*Reciprocal Space*

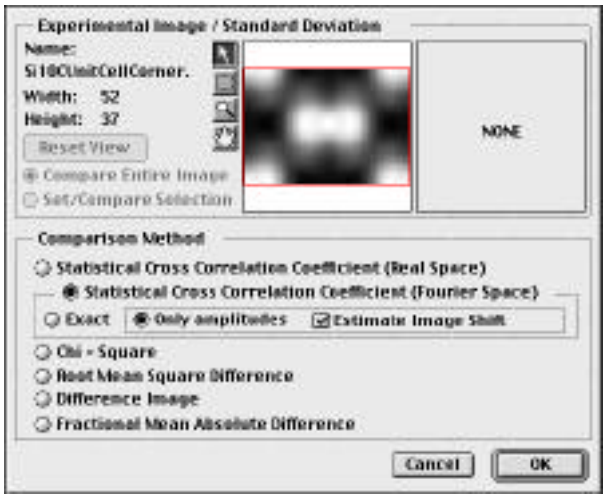
There are two options for calculating the cross correlation in reciprocal space.
The first is an exact calculation which is equivalent to the real space CCC. The entire Fourier transform of the experimental image is compared with the Fourier transform of the simulated image and the CCC is just the reciprocal space equivalent of the calculation in real space. Thus the reciprocal space CCC is equal to the real space CCC.

Exact



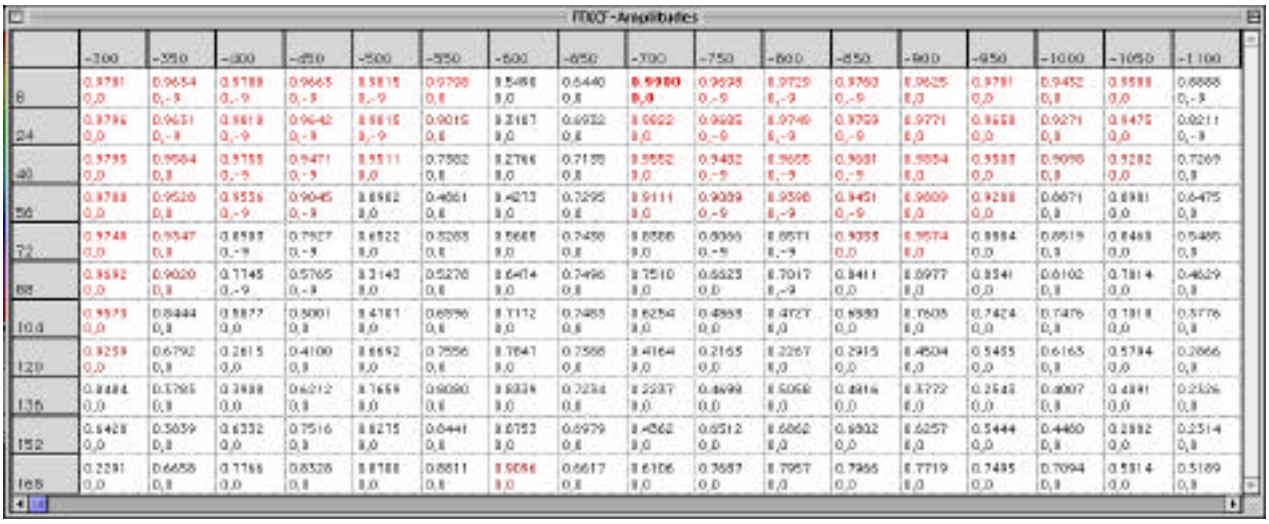
.

Only Amplitudes



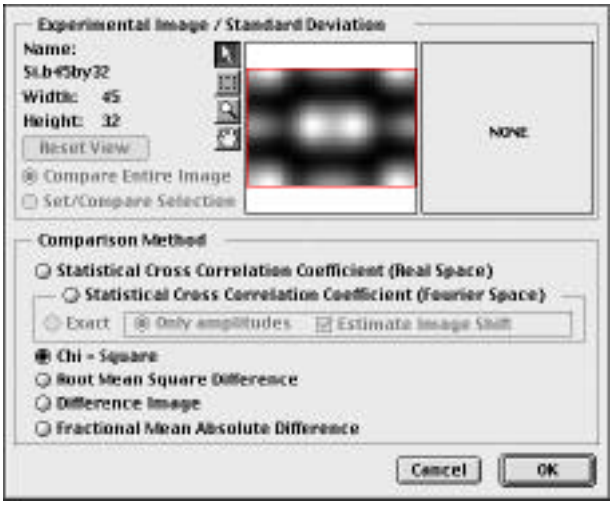

This calculates the CCC based only on the Fourier amplitudes and (optionally) the program will try to estimate the shift between the experimental and the calculated image. This can be very useful for aligning images and to compare images when the origin of the experimental image is not known. The numbers given are the shift of the origin that should be attempted to be made on the experimental image before the experimental data is

compared to the simulation using the exact formulation.




## Chi-Square

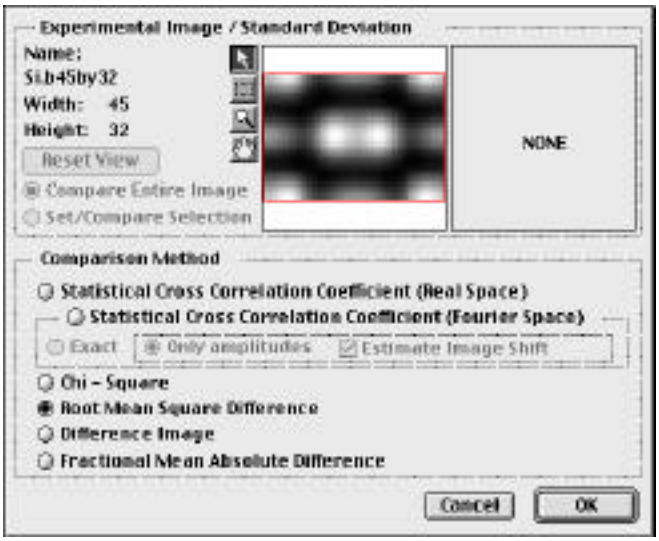
This computes the chi-square deviation between the calculated image(s) and the experimental images, optionally using the standard deviation image for obtaining the uncertainty associated with the average pixel value.



If no standard deviation image is given, the uncertainty in the pixel value is set to 10% of the intensity in the pixel. The Chi-square goodness of fit criteria is sensitive to the mean level of the images and the scales the calculated images so that they have the same mean as the experiment before computing chi-square. Lower values indicate better fit, with a value of 1 meaning that the experiment and simulation agree within the uncertainty of the experimental values.


**Root Mean Square Difference**

This calculates the root mean square difference between the experiment and the simulation. Lower values indicate better fit with 0 being exact fit between experiment and simulation. Since the values depend on the mean level of the images that are compared, the simulation is scaled to have the same mean as the experiment.

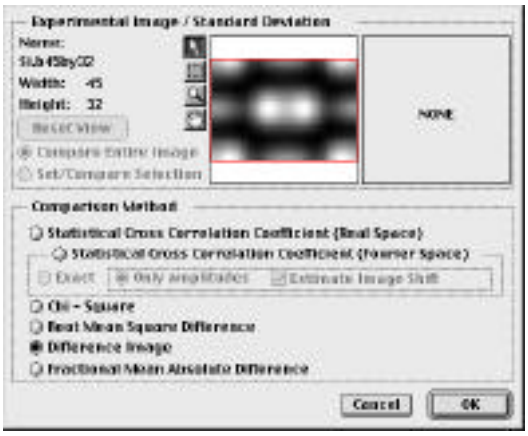



The table below shows the result from the RMSD comparison.

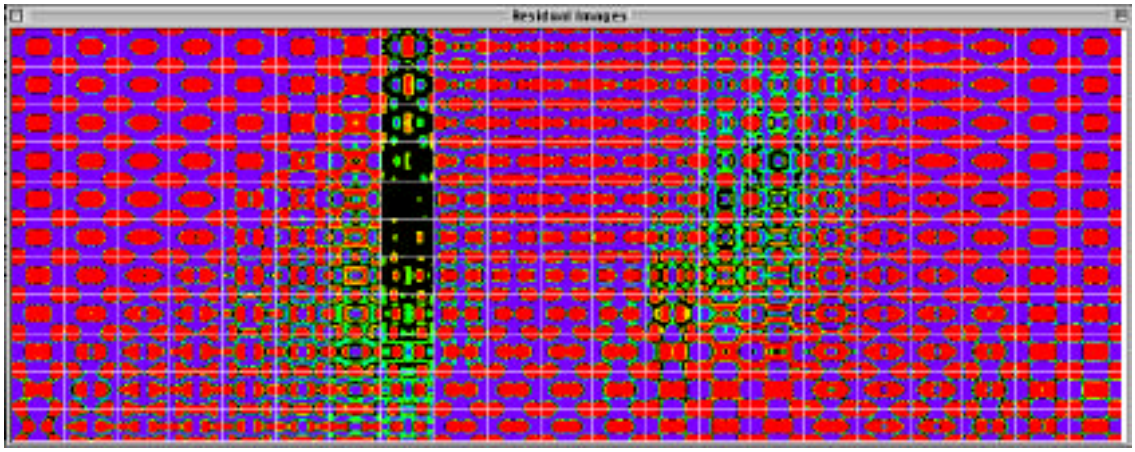
RMSD

| | -300 | -350 | -400 | -450 | -500 | -550 | -600 | -650 | -700 | -750 | -800 | -850 | -900 | -950 | -1000 | -1050 | -1100 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 0.6512 | 0.6889 | 0.7110 | 0.7239 | 0.7195 | 0.6468 | 0.4129 | 0.1257 | 0.2806 | 0.4421 | 0.4808 | 0.4461 | 0.3627 | 0.2737 | 0.2292 | 0.2885 | 0.5240 |
| 24 | 0.6452 | 0.6812 | 0.7035 | 0.7162 | 0.7018 | 0.5786 | 0.3091 | 0.0771 | 0.2536 | 0.4256 | 0.4670 | 0.4249 | 0.3309 | 0.2427 | 0.2064 | 0.2674 | 0.4945 |
| 40 | 0.6391 | 0.6723 | 0.6939 | 0.7054 | 0.6768 | 0.4976 | 0.2382 | 0.0488 | 0.2312 | 0.4085 | 0.4527 | 0.4040 | 0.3002 | 0.2146 | 0.1859 | 0.2467 | 0.4672 |
| 56 | 0.6326 | 0.6610 | 0.6792 | 0.6864 | 0.6327 | 0.4025 | 0.1815 | 0.0264 | 0.2137 | 0.3895 | 0.4346 | 0.3779 | 0.2645 | 0.1852 | 0.1656 | 0.2253 | 0.4430 |
| 72 | 0.6244 | 0.6435 | 0.6516 | 0.6436 | 0.5414 | 0.2988 | 0.1319 | **0.0114** | 0.2026 | 0.3691 | 0.4082 | 0.3373 | 0.2114 | 0.1473 | 0.1429 | 0.2016 | 0.4182 |
| 88 | 0.6157 | 0.6223 | 0.6128 | 0.5782 | 0.4411 | 0.2344 | 0.1039 | 0.0220 | 0.2047 | 0.3608 | 0.3874 | 0.2972 | 0.1535 | 0.1106 | 0.1255 | 0.1870 | 0.3997 |
| 104 | 0.6036 | 0.5900 | 0.5525 | 0.4897 | 0.3578 | 0.1967 | 0.0901 | 0.0409 | 0.2245 | 0.3714 | 0.3845 | 0.2800 | 0.1090 | 0.0803 | 0.1159 | 0.1860 | 0.3848 |
| 120 | 0.5808 | 0.5253 | 0.4540 | 0.3916 | 0.2981 | 0.1797 | 0.0935 | 0.0687 | 0.2764 | 0.4107 | 0.4164 | 0.3324 | 0.1867 | 0.1236 | 0.1389 | 0.2154 | 0.3743 |
| 136 | 0.5455 | 0.4353 | 0.3680 | 0.3327 | 0.2702 | 0.1801 | 0.1110 | 0.0997 | 0.3420 | 0.4545 | 0.4566 | 0.4027 | 0.3076 | 0.2351 | 0.2156 | 0.2737 | 0.3729 |
| 152 | 0.4788 | 0.3362 | 0.3073 | 0.2963 | 0.2551 | 0.1880 | 0.1370 | 0.1392 | 0.4153 | 0.4951 | 0.4927 | 0.4608 | 0.4096 | 0.3645 | 0.3410 | 0.3551 | 0.3779 |
| 168 | 0.3787 | 0.2801 | 0.2756 | 0.2756 | 0.2481 | 0.2005 | 0.1687 | 0.1882 | 0.4827 | 0.5276 | 0.5209 | 0.5031 | 0.4812 | 0.4698 | 0.4670 | 0.4405 | 0.3897 |

## Difference Image




There are two calculations performed in this case. One gives a difference image(s) which are pseudo colored such that where the experiment and simulation agree within one standard deviation, the pixel is black, less than 1.5 standard deviations, the pixel is colored green, and outside the pixels are shown in




shades of red or blue
depending on whether the values in the simulation are lower or higher than those in the experiment.

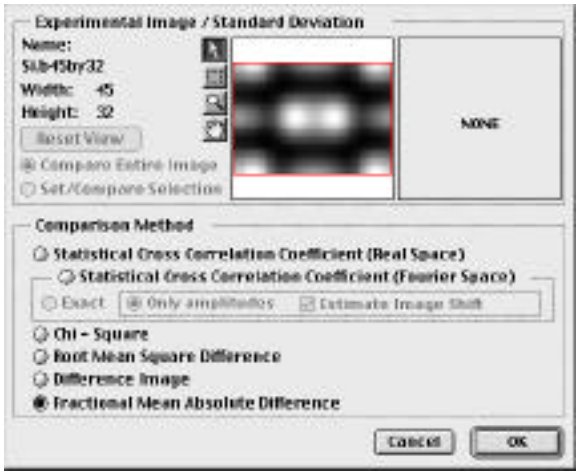
In addition to the difference image(s), the chi-squared value is also computed for each image and shown in its own table.

RMSD

| | -300 | -350 | -400 | -450 | -500 | -550 | -600 | -650 | -700 | -750 | -800 | -850 | -900 | -950 | -1000 | -1050 | -1100 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 0.6512 | 0.6889 | 0.7110 | 0.7239 | 0.7195 | 0.6468 | 0.4129 | 0.1257 | 0.2806 | 0.4421 | 0.4808 | 0.4461 | 0.3627 | 0.2737 | 0.2292 | 0.2885 | 0.5240 |
| 24 | 0.6452 | 0.6812 | 0.7035 | 0.7162 | 0.7018 | 0.5786 | 0.3091 | 0.0771 | 0.2536 | 0.4256 | 0.4670 | 0.4249 | 0.3309 | 0.2427 | 0.2064 | 0.2674 | 0.4945 |
| 40 | 0.6391 | 0.6723 | 0.6939 | 0.7054 | 0.6768 | 0.4976 | 0.2382 | 0.0488 | 0.2312 | 0.4085 | 0.4527 | 0.4040 | 0.3002 | 0.2146 | 0.1859 | 0.2467 | 0.4672 |
| 56 | 0.6326 | 0.6610 | 0.6792 | 0.6864 | 0.6327 | 0.4025 | 0.1815 | 0.0264 | 0.2137 | 0.3895 | 0.4346 | 0.3779 | 0.2645 | 0.1852 | 0.1656 | 0.2253 | 0.4430 |
| 72 | 0.6244 | 0.6435 | 0.6516 | 0.6436 | 0.5414 | 0.2988 | 0.1319 | **0.0114** | 0.2026 | 0.3691 | 0.4082 | 0.3373 | 0.2114 | 0.1473 | 0.1429 | 0.2016 | 0.4182 |
| 88 | 0.6157 | 0.6223 | 0.6128 | 0.5782 | 0.4411 | 0.2344 | 0.1039 | 0.0220 | 0.2047 | 0.3608 | 0.3874 | 0.2972 | 0.1535 | 0.1106 | 0.1255 | 0.1870 | 0.3997 |
| 104 | 0.6036 | 0.5900 | 0.5525 | 0.4897 | 0.3578 | 0.1967 | 0.0901 | 0.0409 | 0.2245 | 0.3714 | 0.3845 | 0.2800 | 0.1090 | 0.0803 | 0.1159 | 0.1860 | 0.3848 |
| 120 | 0.5808 | 0.5253 | 0.4540 | 0.3916 | 0.2981 | 0.1797 | 0.0935 | 0.0687 | 0.2764 | 0.4107 | 0.4164 | 0.3324 | 0.1867 | 0.1236 | 0.1389 | 0.2154 | 0.3743 |
| 136 | 0.5455 | 0.4353 | 0.3680 | 0.3327 | 0.2702 | 0.1801 | 0.1110 | 0.0997 | 0.3420 | 0.4545 | 0.4566 | 0.4027 | 0.3076 | 0.2351 | 0.2156 | 0.2737 | 0.3729 |
| 152 | 0.4788 | 0.3362 | 0.3073 | 0.2963 | 0.2551 | 0.1880 | 0.1370 | 0.1392 | 0.4153 | 0.4951 | 0.4927 | 0.4608 | 0.4096 | 0.3645 | 0.3410 | 0.3551 | 0.3779 |
| 168 | 0.3787 | 0.2801 | 0.2756 | 0.2756 | 0.2481 | 0.2005 | 0.1687 | 0.1882 | 0.4827 | 0.5276 | 0.5209 | 0.5031 | 0.4812 | 0.4698 | 0.4670 | 0.4405 | 0.3897 |

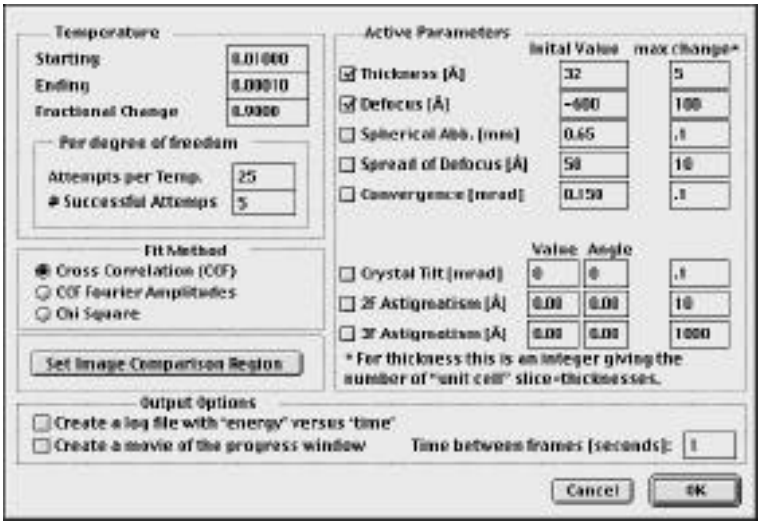
### Fractional Mean Absolute Difference

This calculates the fractional mean absolute difference between the experimental data and the simulated data.




**Refine Parameters**

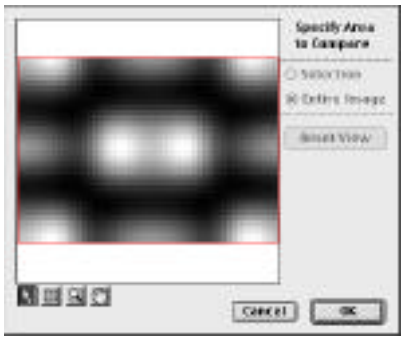
Refine Parameters... will attempt to find the image simulation parameters that produce a simulated image that gives the “best” fit between the experiment and the theory. The search routine is based on the concept of “Simulated Thermal Annealing” and requires a starting configuration of parameters, a starting temperature and an ending temperature, a maximum change in parameters and a goodness of fit criteria that measures the “Energy” of the system. For further explanation of Simulated Thermal Annealing, see the last chapter in this manual. Invoking the command brings up the following dialog which is used to give the input parameters to the algorithm.




**Setting Image Comparison region**

The area to be used for the comparison is set using the button

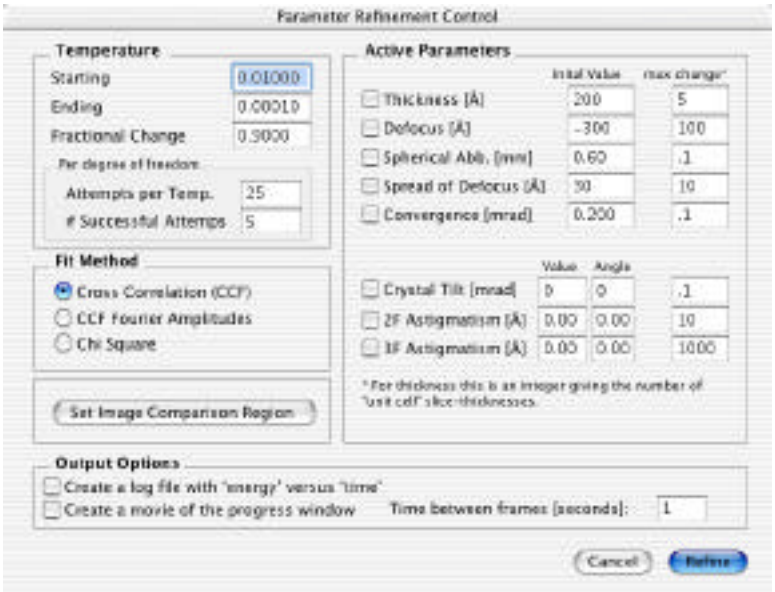
"Set Image Comparison Region"




Selecting the image region is done in the same fashion as under comparing images in the previous section.

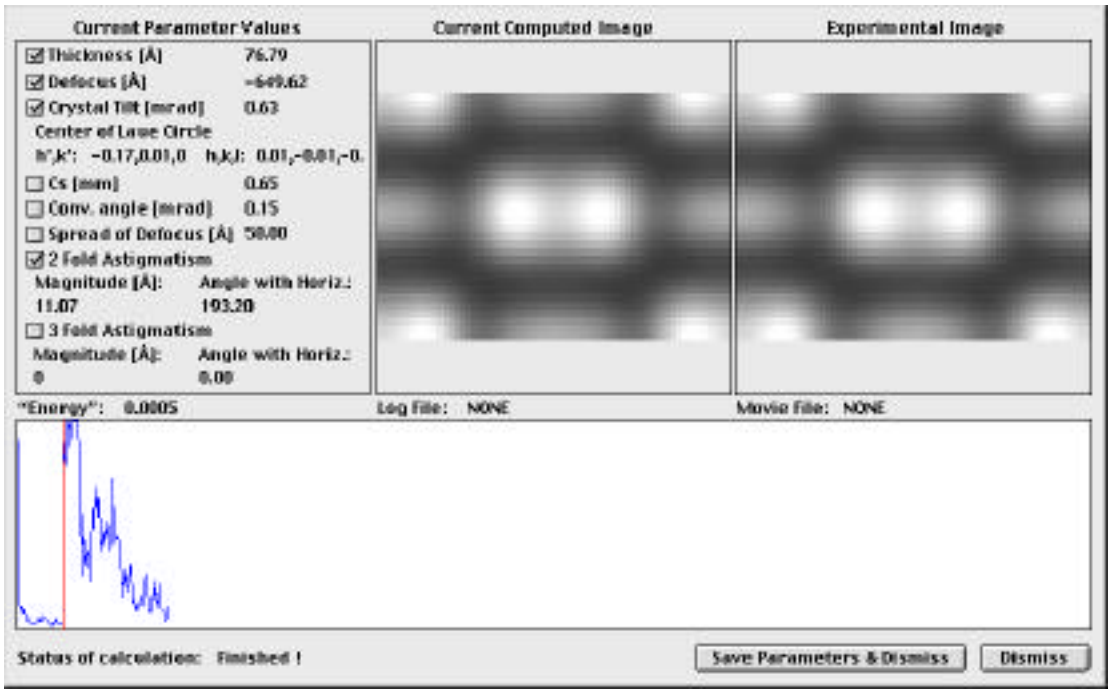
**Running the parameter refinement**

After selecting the area (not needed if the entire image is compared, which is the default) and selecting the parameters to be refined and clicking OK, a progress window for the parameter




refinement appears. If the refinement is not progressing in a satisfactory way, the computation can be canceled by hitting the

Apple-Command Key together with the Period. Optionally, a



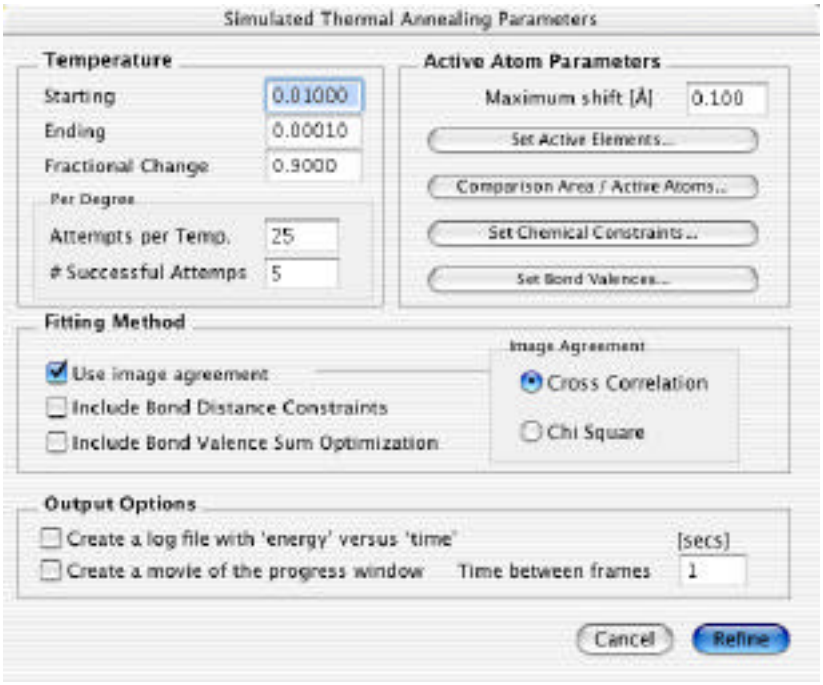

log file can be written so that the “energy” as a function of time/temperature can be plotted and also a Movie can be produced and played back. The number of frames/second for output can be set.

At the end of the run, the dialog box can be just dismissed and the final configuration of parameters will be discarded, or the parameters can be saved in the form of a new structure/simulation file.

**Refine Structure**

The structure refinement works in the same way as the parameter refinement. However, in this case it is the structure that is being varied, notably the coordinates of selected atoms and possibly debye-waller factors and occupancy. After invoking the

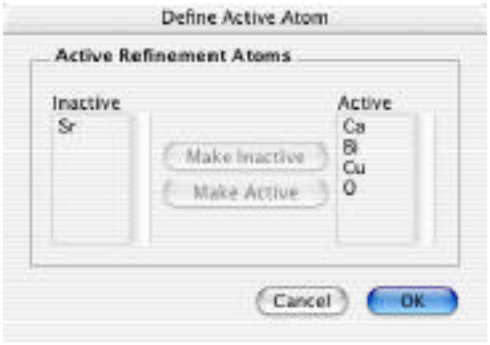
command, the following dialog box appears.




There are several options associated with the structure refinement, such as which elements are active, which coordinates to be varied, etc.. The standard parameters for the simulated thermal annealing need to be specified, together with the goodness of fit parameter. Output options such as a log file and movie are identical to that under parameter refinement. In addition, it is possible to include in the calculation of the “Configuration Energy” terms that depend on selected bond distances and selected bond valence sum.

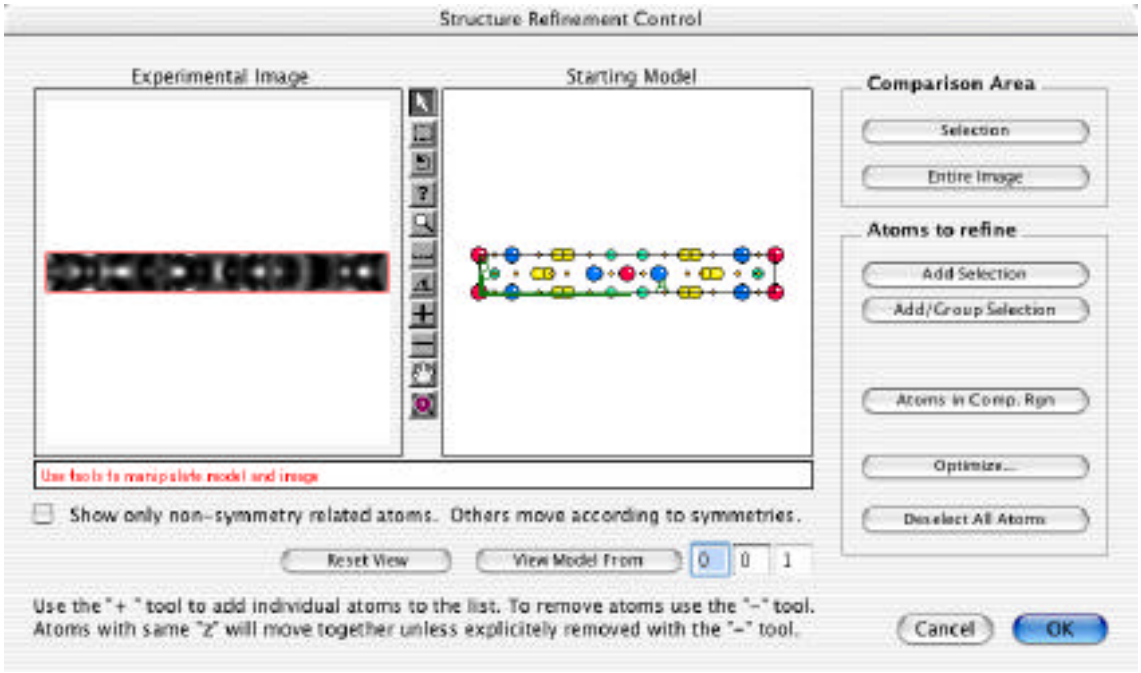
**Set Active Elements**
brings up the following dialog. By default all elements are active. Selecting an active element and clicking on the “Make inactive” button will move the selected element to the Inactive list. Just because an element is listed under active elements does

not mean that one of its types will be used in the refinement pro-




cedure. It is necessary to specify the area used for comparison and which atoms are to be optimized before the simulated thermal annealing is carried out.

**Set Are to Compare & Active Atoms**
is used to set the image comparison region (as previously explained) and to select atoms for refinement. The following window appears.




**Area used for comparison**

Selection
Sets the comparison region to the selection rectangle.
Entire Image
Sets the comparison region to the entire image.

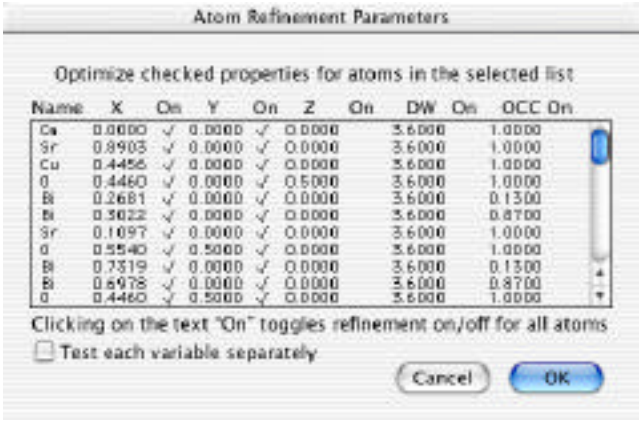
**Atoms to optimize**

Add Selection
Includes in the list of atoms the ones that fall within the selection rectangle set in the model window.

Add/Group Selection
Adds the atoms to the refinement list, but constrains all the atoms in this list to move as a unit.

Atoms Within the Comparison rectangle
Sets the refinement list to include the atoms that lie within the rectangle set for comparing images.

Optimize...
Specifies which properties of the selected atoms (those in the refinement list) that are varied. The following window appears.



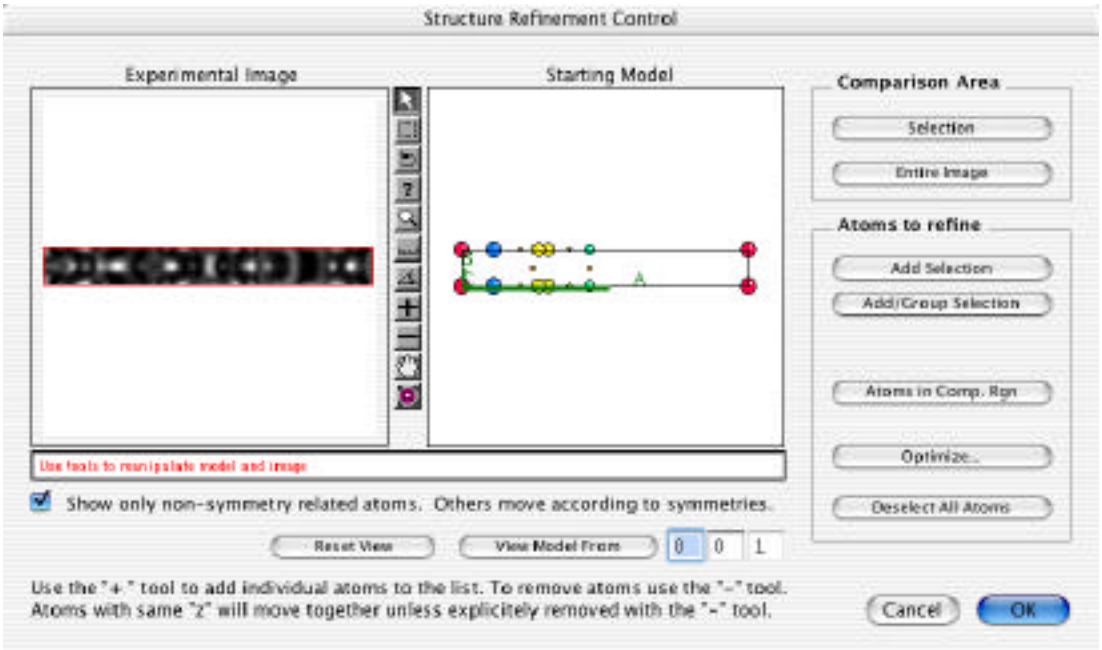

Normally varying the z-coordinate will not have any effect since the image simulation procedure uses a 2d projection of the atoms in the unit cell. However, in the case where symmetry operators are used, changing he z-position may result in changes in x and y for symmetry related atoms.

Each time an atom (or group) is varied, a new set of parameters for this atom/group is created and tested. If “Test each variable separately” is checked, each try will only vary one parameter. Thus if x and y are checked above, both x and y for an atom are changed at the same time unless “Test each....” is checked, in which case one time x is varied and another time y is varied.

Deselect All Atoms

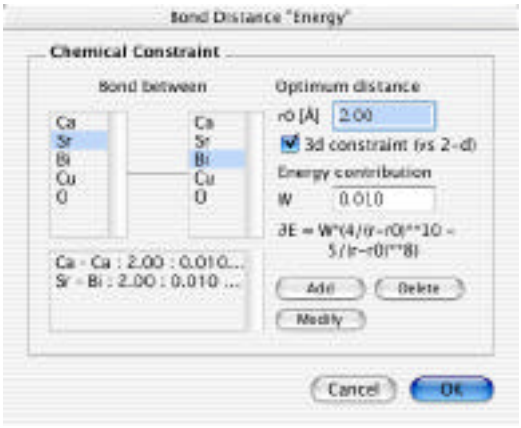
clears the refinement list and allows the user to start all over, defining the set of atoms to optimize.

**Show only symmetry related atoms/Use Symmetry elements**
If the structure is a perfect crystal defined by a set of basis atoms and a set of symmetry operators, it is possible to refine positions of the atoms in the basis and to move symmetry related atoms accordingly such as to preserve the crystalline spacegroup.
Checking this options will result in only atoms in the basis to be visible in the model. Thus the atoms to be refined is selected from the basis and any change in the basis is reflected in the entire structure.




**Set Chemical Constraints**

brings up the following window.

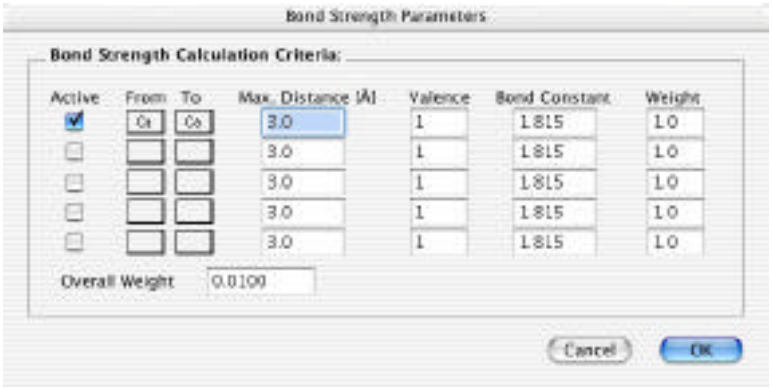



which can be used to specify a configuration energy that includes terms that depend on bond distances. It is possible to specify the optimum bond distance between two atoms, whether it is a 2d or 3d constraint, and to specify the weight of the term in the energy calculation. Even though bond distances have been defined, the inclusion of a bond-distance energy term can be turned off/on from the main “Refine Structure” window.

**Include Bond Valence Sum Optimization**

This allows the bond valence sum to be used to measure the energy of the configuration. It brings up the following window in which the active bonds are specified, the maximum distance between atoms for calculating the bond valence sum, the valence of the first atom in the atom-pair and the bond constant. Each “bond” has its own weight and the entire bond-valence

energy terms has an overall weight.

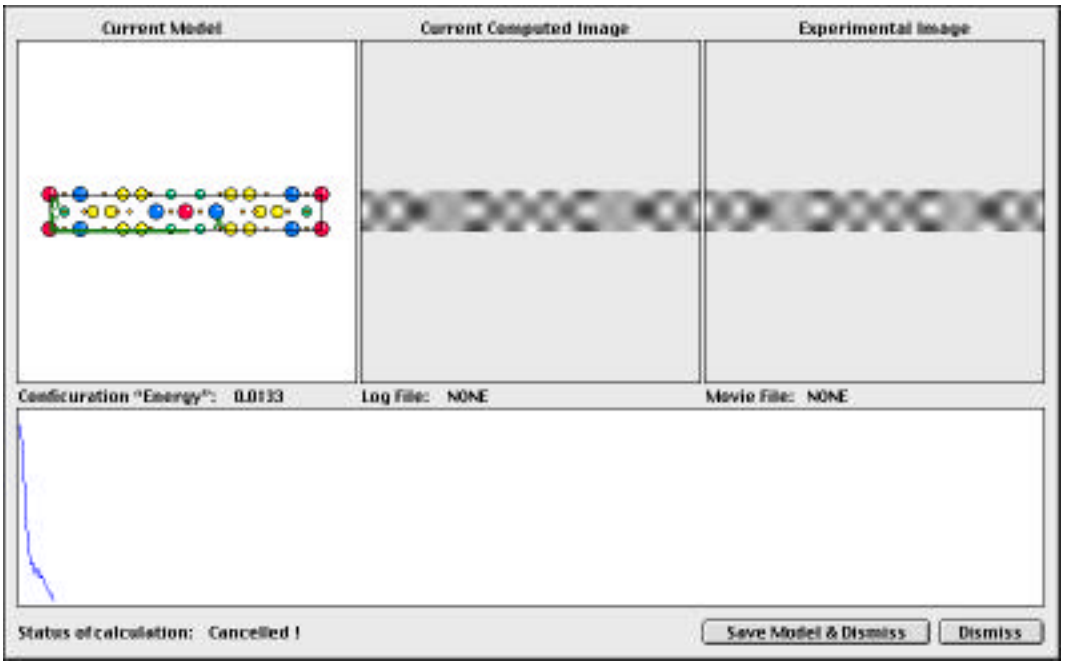



**Running the Refinement**

Once the parameters are set and OK has been clicked, a progress window appears. The current atomic configuration is shown together with the corresponding simulated energy. The energy as a function of “time/temperature” is shown in its own window and can be monitored to ensure that the system moves in a desirable fashion. It is important to understand that no specific recipe can be given to ensure that the system finds a meaningful minimum in the configuration energy. The success of the optimization depends on how far the starting configuration is from the “solution” and the choice of annealing parameters. It is not a straight forward, just run and you get the correct answer, black box approach. An understanding of the system, a good feel for choosing a reasonable starting structure and some experience in choosing “annealing parameters” is definitely a requirement in order to have confidence in the resulting ending configuration. Experimenting with different input parameters is advised.

As with refining simulation parameters, it is possible to save a log file or to produce a movie of the annealing process. Saving a movie can be very useful when the refinement takes hours/days and it is necessary to see how the system varied over time. It is important to realize that a movie file grows quickly in size and that the number of frames/second should be chosen appropri-

ately if the movie is to cover a period of many hours.




At the end of the run, the final structure can be dismissed or saved as a structure file for later use. The run can also be aborted by the normal “Apple + Period” key combination.

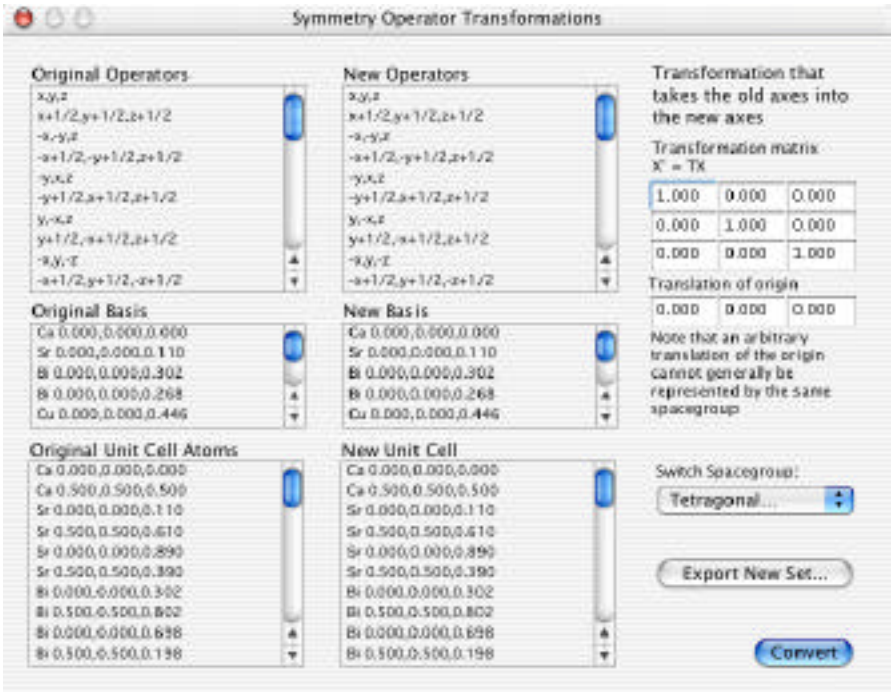
**Symmetry Transform Calculator**

Choosing the “Symmetry Transform Calculator” brings up a modal dialog window that can help the user find another set of symmetry operators and basis atom positions in the case of a change in axis and origin of the unit cell. Input is the original symmetry operators which come from the spacegroup that is in use together with the original basis atoms. The new unit cell axes **a’**,**b’** and **c’** are given by the transformation matrix T such

that

$$\begin{bmatrix} \boldsymbol{a}' \\ \boldsymbol{b}' \\ \boldsymbol{c}' \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix} \begin{bmatrix} \boldsymbol{a} \\ \boldsymbol{b} \\ \boldsymbol{c} \end{bmatrix}$$

together with a translation of the origin specified in the old unit cell system (fractional coordinates).
Invoking the command brings up the following window.




## Lists

*Original Operators*

This list shows the symmetry operators of the current space-group. Initially these are those of the crystal in use, but the spacegroup can be changed by the command “Switch Space-group”.

*Original Basis*

The basis atoms are the atoms of the current crystal.

*Original Unit Cell Atoms*

This list gives the atoms that are produce by the operation of the symmetry operators of the spacegroup in use on the original basis atoms.

*New Operators*

These operators are the result of applying the transformation operations that are given by the change in coordinate system together with a translation of the origin to the generators of the original spacegroup.

*New Basis*

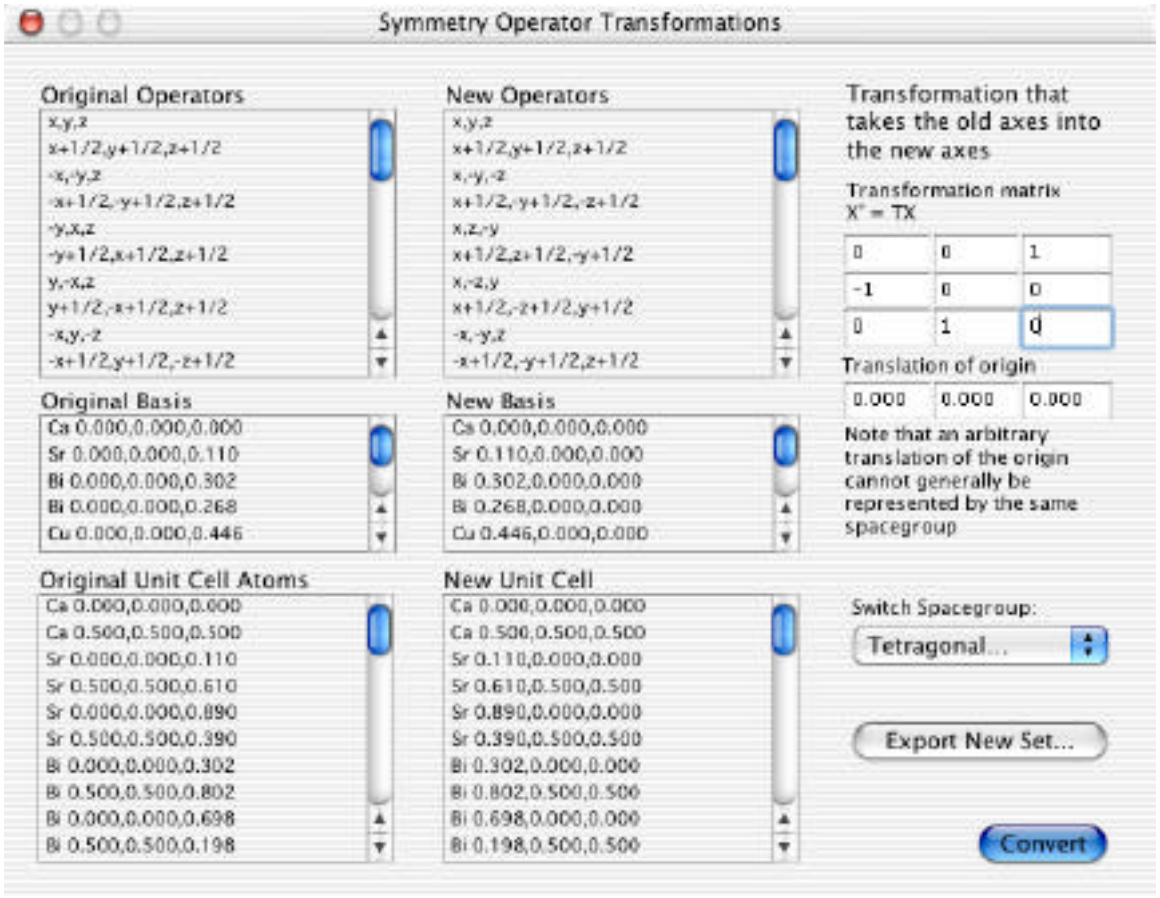
This is the transformed basis.

*Original Unit Cell Atoms*

This list gives the atoms that are produced by the operation of the new symmetry operators of the spacegroup used on the new set of basis atoms.

**Convert**

Clicking on this button initiates the computation of the transformed set of symmetry operators, the transformed basis and the new atomic positions.




Note:
It is important to realize that arbitrary input does not result in a symmetry which still can be presented by the same spacegroup with a change in symmetry operators.

**Export New Set**
Allows the user to export the new basis and the symmetry operators as a new structure file.

## Process Menu

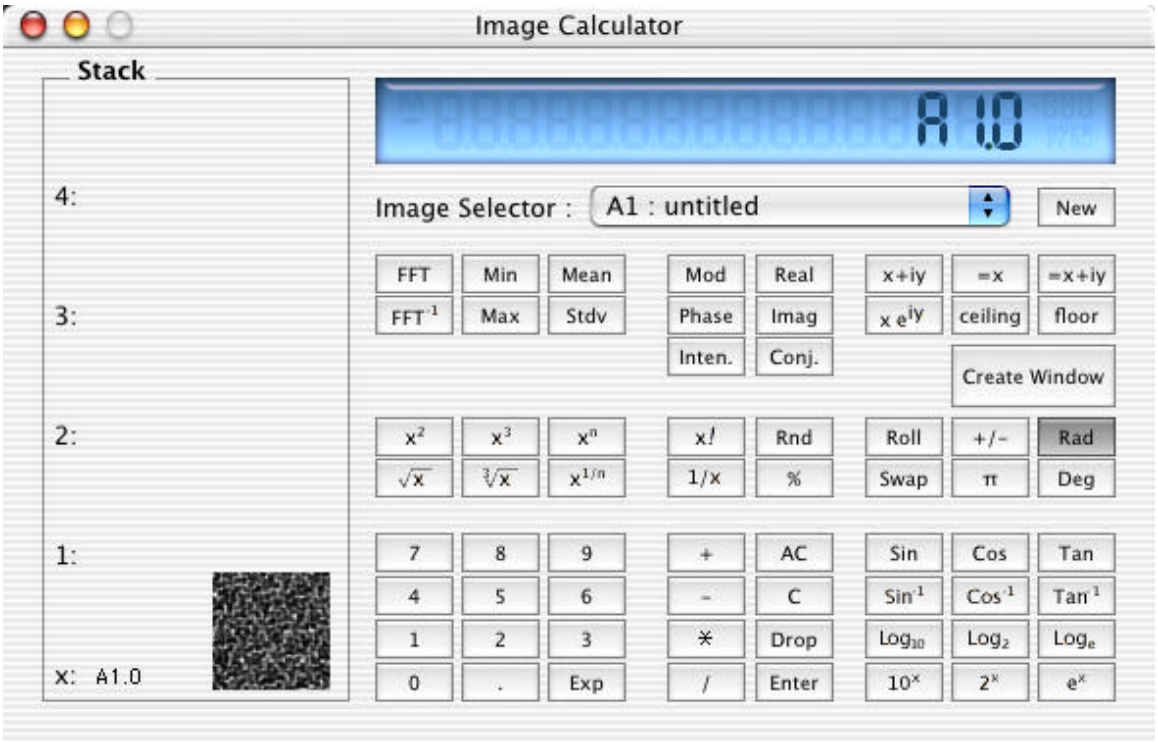
The Process menu is the largest menu and is the source of all

image processing functions. There are menu sub-menus as well.


**Image Calculator**

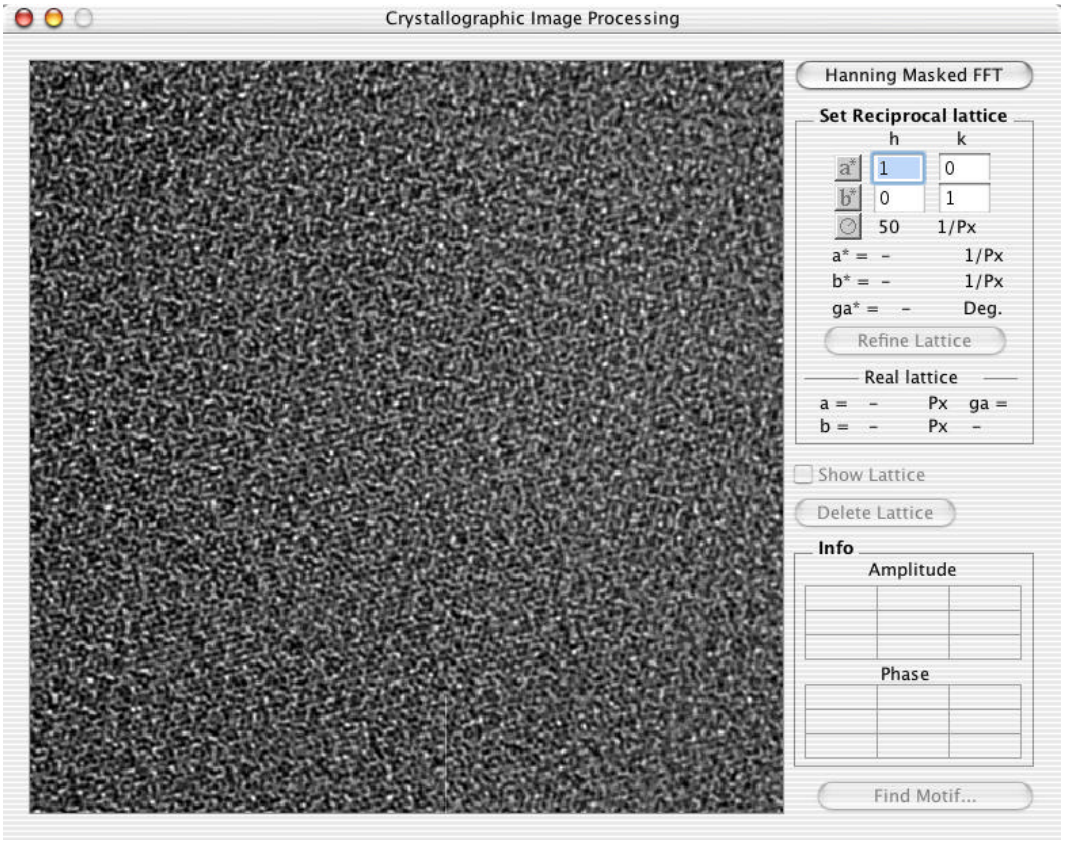
This is a general image and number calculator using reverse

polish notation (HP style calculator).



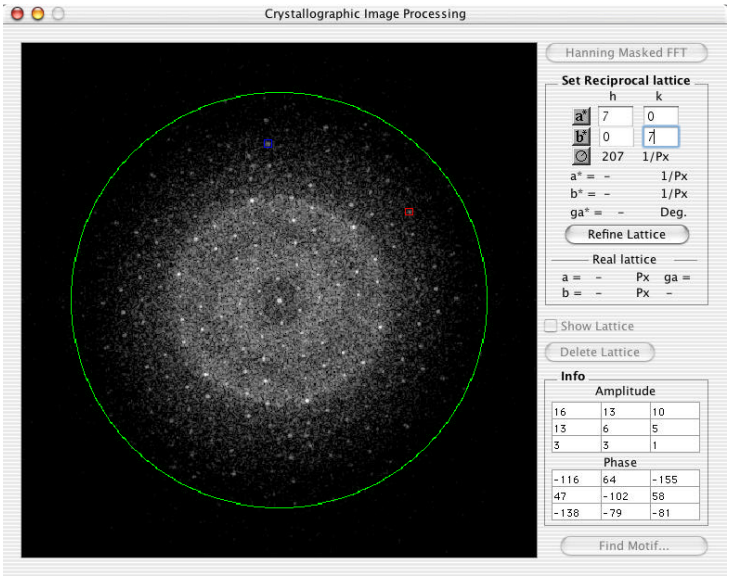

**Crystallographic Image Processing...**
Can be invoked on a real space image which is square or has a

square selection. In order to get started, the Hanning Masked

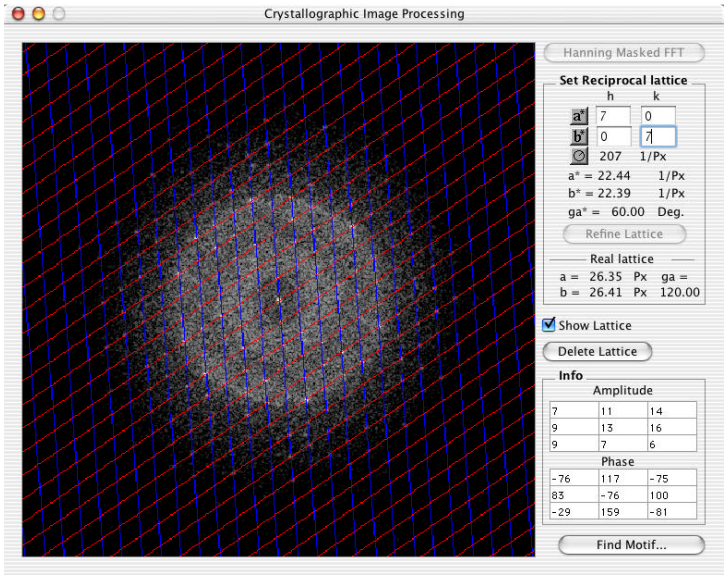



Fourier transform need to be calculated. Once the Fourier transform has been calculated, the reciprocal space lattice needs to be set using the a* and b* tools and clicking on two consecutive

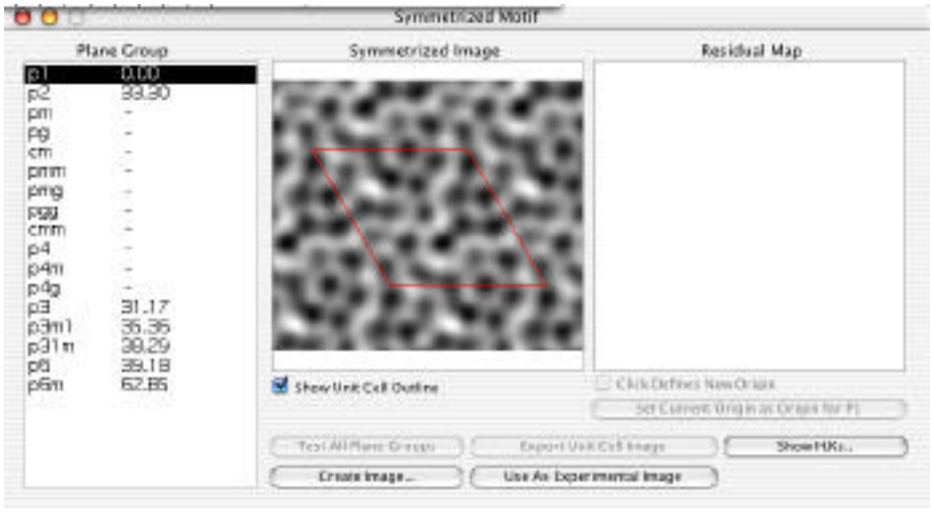
reflections that defines the reciprocal space. The number of



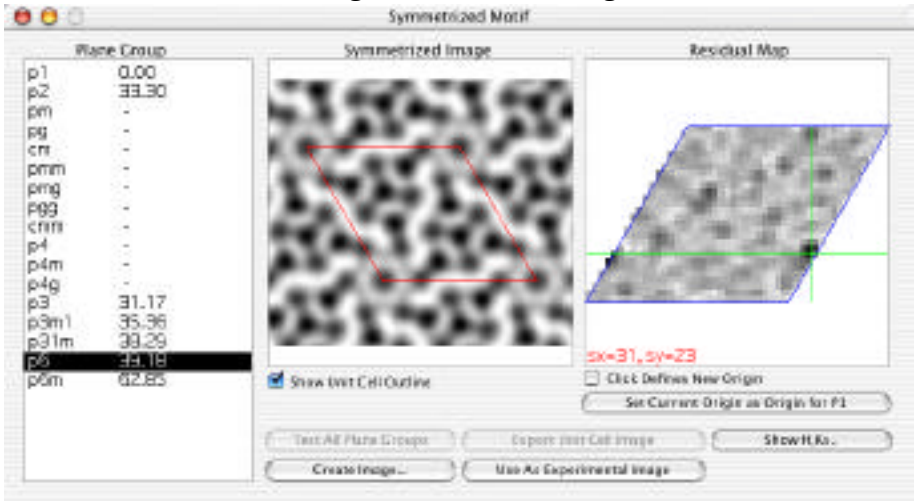

reflections used in the lattice refinement and information extraction can be limited by the circular aperture tool. Once the lattice reflections have been marked, the next action is to invoke the command “Refine Lattice”.



After the lattice has been refined, click on “Find Motif”. This will extract all the phases and amplitudes from the Fourier transform at the lattice points and one can test for possible symmetries of the motif.



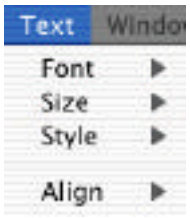

Each symmetry can be tested and imposed on the reflections to form a new unit cell motif. The origin of the unit cell motif is dhown on the right and can be changed.




Once a solution has been chosen, a new image can be created with the imposed symmetry and can be used as an image to compare with simulation.

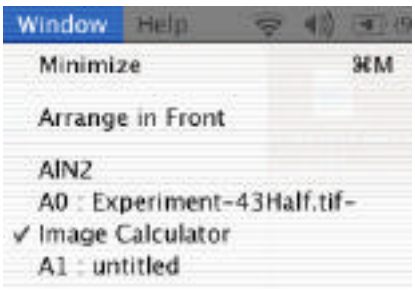
## Text Menu

This menu determines the appearance of text drawn in the MacTempas image window. The following text attributes can be set:




## Windows Menu

Use this menu to bring a window to the top of the screen in case it has been completely covered by another window.



Chapter 7

# *Input File Format*

The structure file created by New... in the File Menu is a file of type ‘TEXT’ and can be produced by a text editor. At times it is desirable to edit the file directly, rather than using MacTempas to create this file. In fact the user may sometimes want to write a program to generate the data in the structure file. For that purpose in particular, the format of the structure file <structure-name>.at is given below:

| Line # | Parameter(s) | Meaning |
|---|---|---|
| 1 | Title | Arbitrary description of this structure |
| 2 | SpaceGroupNumber | Just as is says, one of the 230 spacegroups, (1-230). |
| 3 | a b c a b g | The lattice parameters and angles |
| 4 | Gmax | The maximum reciprocal lattice vector in the multislice calculation. The potential is evaluated out to twice this value, units Å-1. |
| 5 | iu iv iw | The direction of the electron beam in units of the real space crystal lattice vectors. |
| 6 | NSymops Nslices (I3d) | Number of symmetry operators, number of slices per unit cell, and a flag indicating 2d (0) or 3d (1) potential calculation only if Nslices is different from 1. |

| Line # | Parameter(s) | Meaning |
|---|---|---|
| 7 | NBasis Ntypes | The number of atoms in the basis, the number of different types of atoms. A different type is associated with a different chemical symbol or a different Debye-Waller factor. |
| 8 | it symb x y z dw occf | The type of atoms (a number from 1 - NTypes), Chemical symbol, x-,y-,z coordinates in relative units of the lattice vectors, Debye-Waller factor and occupancy factor. |
| 9 | The same as line 8 for atom number 2. | |
| 10 | The same as line 8 for atom number 3. | |
| . | | |
| 8+NBasis | MicName Cs Del Th | The name of the microscope, the spherical aberration (mm), the spread of defocus (Å) and semi-angle of divergence (mrad). |
| 9+NBasis | Voltage | Accelerating voltage (kVolt). |
| 10+NBasis | Lh Lk | The center of the Laue circle in units of the h and k of the transformed reciprocal unit cell. (Real numbers). |

| **Line # Parameter(s)** | **Meaning** |
|---|---|
| 11+NBasis | |
| Thickness | The specimen thickness or T1,T2,DT First thickness, last thickness, increm. The commas are required. |
| 12+NBasis | |
| IPlot | Amplitudes to be stored as for possible plotting, (YES/NO). |
| 13+NBasis | |
| ih ik il | The indices of the reflection to be stored, or if IPlot == NO then : |
| Defocus | Objective lens defocus or |
| D1,D2,DD | First defocus, last defocus, increment. The commas are required. |
| 14+NBasis +NAmp | |
| ApertureRad. | Radius of the objective lens Aperture in units of Å-1. |
| 15+NBasis +NAmp | |
| Ah Ak | The center of the objective lens aperture in units of h,k of the transformed reciprocal unit cell. |
| 16+NBasis +Namp | |
| Oh Ok | The center of the optic axes in the same units as Ah,Ak. |

| Line # Parameter(s) | Meaning |
|---|---|
| 17+NBasis<br>+Namp<br>s1,s2,s3 | Symmetry operator number 1. An example is x+1/3,y+5/6,z+1/3. The commas are required. |
| .<br>17+NBasis<br>+Namp<br>+NSymop<br>istat | The calculation status of this structure. For a new structure this should be 1 |
| 18+NBasis<br>+Namp<br>+NSymop<br>Vibration | Halfwidth of mechanical Vibration in A. |

**Note:** If different wordprocessing software is used, Microsoft Word, Write Now etc., make sure that the text file is saved at the end as type TEXT.

Chapter 8

# *Sample Calculation*

As an example of a calculation using MacTempas we consider a BCSCO super-conductor structure. Using the structure determined by Tarascon et al (1988), we show the steps necessary to input the model structure, examine it, compute the diffraction pattern and simulated images, and display and print them.

## The Structure

As published by Tarascon et al in Phys. Rev. B 37 (1988) p.9382-9389, the tetragonal structure has the following parameters -

Space group: I4/mmm

Cell parameters: a=b=3.814Å, c=30.52Å, a=b=g=90

with nine atom positions in the basis:

| Atom | Wyckoff notation | x | y | z | Occupancy |
|---|---|---|---|---|---|
| Ca | 2a | 0 | 0 | 0 | 1 |
| Sr | 4e | 0 | 0 | 0.1097 | 1 |
| Bi | 4e | 0 | 0 | 0.3022 | 0.87 |
| Bi | 4e | 0 | 0 | 0.2681 | 0.13 |
| Cu | 4e | 0 | 0 | 0.4456 | 1 |
| O(1) | 8g | 0.5 | 0 | 0.446 | 1 |
| O(2) | 4e | 0 | 0 | 0.375 | 1 |
| O(3) | 4e | 0 | 0 | 0.205 | 1 |
| O(4) | 4d | 0.5 | 0 | 0.25 | 0.065 |

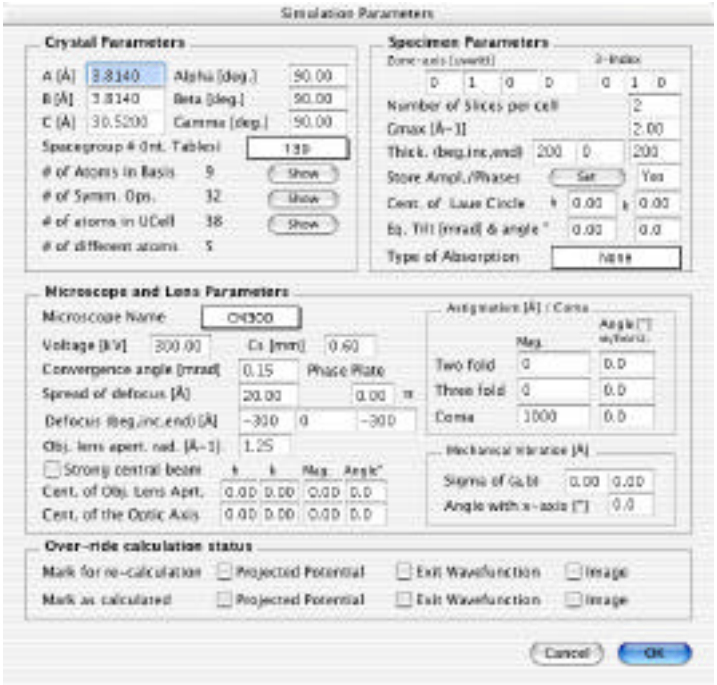
Isotropic thermal parameters for all atoms are fixed at 3.6 $Å^2$.

## Entering the Structure

To enter a new structure into MacTempas, we first go to the **FILE menu** (Section 3.3), and select **New Structure File...** After entering a filename in the New File dialog, MacTempas will put up a dialog into which the relevant information must be entered. Note that the program shows a default cubic structure. We need to change the data to reflect that of our structure.

**Filename** BCSCO

Specify a filename under which to file the input data. It should be descriptive enough to be easily remembered when you need to open it later. Make sure you use no extension.




**Space group #** 139

From the structure information, we know that the cell is tetrago-

nal with a space group I4/mmm. From Table 6.2.1 of the International Tables for Crystallography, we find that the space group number for I4/mmm is 139. Choose the correct space-group from the popup menu.

**a** 3.814

Enter the correct value for the lattice parameter a. In this example MacTempas knows that **b** is equal to **a** for the tetragonal space group #139, and so enters **b** automatically once **a** has been set. Similarly, MacTempas puts in the correct unit cell angles, since they are defined by the space group (in this particular example). Note that cell parameters are input in Å, not in nm.

**c** 30.52

The value of the C cell parameter is input in Å.

**Gmax** (default=2)

Gmax is the size of the "multislice aperture" and defines how far out in reciprocal space the diffraction calculation will extend. The value of $\mathbf{G}_{max}$ is automatically set to 2.0 reciprocal Ångstrøm units, so that MacTempas will compute all of the dynamically-diffracted scattered beams out to this value, by considering all their interactions with phase-grating coefficients out to twice $\mathbf{G}_{max}$ (a default of 4.0 reciprocal Ångstrøm units). Note that these default values (2 for the multislice and 4 for the phase-grating) are normally large enough to ensure that all significant contributions to the dynamic scattering are included; however $\mathbf{G}_{max}$ is displayed in the MacTempas menu so that it can be set to a larger value if greater precision is required with a structure that includes heavy atoms.

**Zone Axis** 0,1,0

The correct response is the set of three integers that defines the direction of the electron beam with respect to the specimen (or the specimen orientation with respect to the incident electron beam direction). In this example we choose to enter 0,1,0 in order to image the specimen down the b-axis.

**Number of slices per unit cell** (default=1)
This value will be computed by MacTempas from the repeat distance of the structure in the beam direction and the current value of $\mathbf{G}_{max}$. This number can be changed if desired (as, of course, can all the parameters entered in response to the prompts listed in this chapter).

**Show (Basis**) 9
Click on the command to bring up the dialog box for entering the information regarding the number of atoms in the basis. We enter the nine different atom positions listed for the basis atoms. For each of the atoms in the basis, MacTempas requires the chemical symbol, x,y,z coordinates, DW factor and occupancy factor. From the information given above, we use the following information for the nine atoms that are given in the structural basis.

| | |
|---|---|
| **Chemical Symbol** | Ca |
| **x,y,z** | 0,0,0 |
| **Debye-Waller Factor** | 3.6 |
| **Occupancy** | 1 |

The data for the first atom include the chemical symbol for calcium (used by MacTempas to select the correct scattering factor table), the atom coordinates, the temperature factor (or Debye-Waller factor), and the occupancy factor.

The second atom position is entered in the same way with responses of -

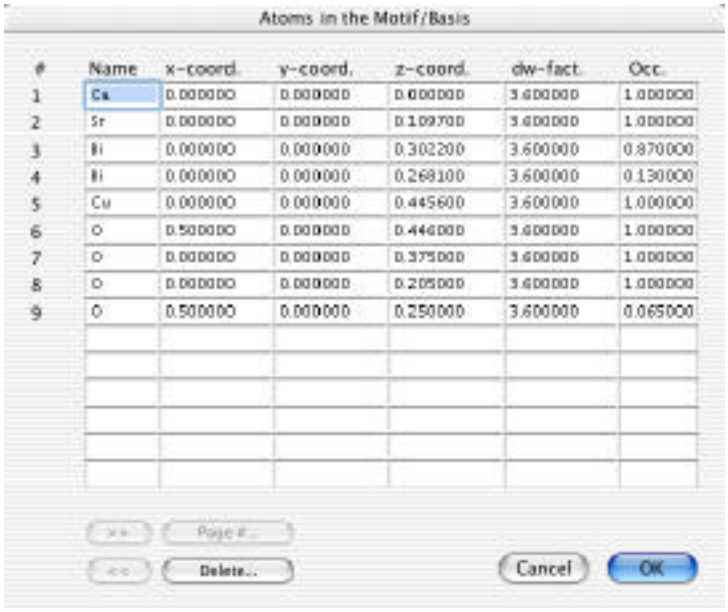
| | |
|---|---|
| **Chemical Symbol** | Sr |
| **x,y,z** | 0,0,0.1097 |
| **Debye-Waller Factor** | 3.6 |
| **Occupancy** | 1 |

The third atom position is similar, except that the occupancy is set at 0.87 -

| | |
|---|---|
| **Chemical Symbol:** | Bi |
| **x,y,z:** | 0,0,0.3022 |

**B Factor:** 3.6
**Occupancy:** 0.87

After all nine atom positions have been entered, MacTempas will need the parameters of the electron microscope for which to compute the simulation.




**Microscope** 4000EX

If the input microscope name is listed in MacTempas's microscope file, various operating parameters will be set automatically. If the entered name is unknown to MacTempas, values will need to be given for each of the operating parameters. In this example, we use 4000EX, and find that MacTempas sets the spherical aberration coefficient to 1.0mm, the Gaussian half-width of depth of focus to 80Å, and the semi-angle of beam convergence to 0.5milliradian.

**Specimen Thickness** 40 20 80

The foil thickness response may be in one of two forms, either a single value in Ångstrøm units, or a construction combining a starting and ending thickness with an incremental value. The

construct that we have entered requests MacTempas to store diffraction results for thicknesses starting at 40Å and continuing through 80Å in steps of 20Å. That is, at specimen thicknesses of 40Å, 60Å and 80Å.

**Store Ampl./Phases** No

As well as storing all the beam amplitudes at specified specimen thicknesses, MacTempas can store a selected few beam amplitudes at each single-slice increment in thickness, then plot amplitude (or intensity) and phase as a function of thickness for any of the stored beams. To store beams for plotting, click on the command to enter the indices for the reflections that will be stored. In this starting example we will not be entering any information here.

**Voltage** (400)

The voltage would need to be entered if an unknown microscope type were selected. Since we have selected a 4000ex, MacTempas will choose a value of 400keV.

**Center of the Laue Circle** 0,0

The pair of values specified as the Laue circle center are used by MacTempas to define the direction and amount by which the specimen is tilted from the exact zone-axis orientation specified above, and, in fact, specify the center of the Laue circle in units of the h and k coordinates in the diffraction plane. Note that the values supplied need not be integers, but should not define a tilt of more than a few degrees. The default values of 0,0 specify exact zone-axis orientation.

**Objective Lens Defocus** -200 -200 -800

So far, we have supplied all the information MacTempas requires to carry out the dynamical diffraction part of the simulation; now we input the imaging conditions. The first imaging-condition prompt is for the objective lens defocus. We choose to enter four values of defocus by specifying defocus values from -200Å to -800Å in steps of -200Å. Note that a negative value denotes an objective lens weakened from the Gaussian condi-

tion; that is, underfocus is negative.

**Aperture Radius** 0.67
The value for the radius of the objective aperture should correspond to the radius in reciprocal Ångstrøm units, as measured from a diffraction pattern exposed with the aperture superimposed. We will enter 0.67 to represent a typical value.

**Center of the Objective Aperture** 0,0
In order to simulate dark-field images, MacTempas provides for an objective aperture displaced from the center of the diffraction pattern. As for the Laue circle center, the aperture center is defined in units of h and k. We leave the default values of 0,0.

**Center of the Optic Axis** 0,0
To provide for microscope misalignment, or for conditions of tilted-beam imaging, the coordinates of the diffraction pattern at which the optic axis lies can be specified in the same manner as the center of the aperture. Again, we use default values of 0,0.

## Verifying the Input

After the response to the last data-entry prompt, MacTempas draws the windows it uses. To re-display the input information click on the "Main Parameters" in the **Parameters** menu. At this stage any desired changes can be made by using the mouse to move the cursor to the desired parameter, and making the change.

When all the data in the top field are satisfactory, we go to "Atomic Basis" in the **parameters** menu to check that all atom parameters have been entered correctly. At this stage it is also worthwhile getting MacTempas to display a model of the structure by.going to the **Commands** menu and clicking on "Draw the Unit Cell".

## Running the Calculation

When we are satisfied that all data are correct, we run the simu-

lation by.clicking on "Full Calculation" in the **calculate** menu. Note that MacTempas displays the current status of the calculation in the Status Window. First, MacTempas computes the phase-grating for the structure (the status window shows the number of coefficients generated so far), then the dynamical diffraction for each slice of the specimen (current slice number is shown in the Status Window), then four images are computed at each of the three specimen thicknesses that we specified (the image number is shown in the window).

## Displaying the Results

Once MacTempas has finished the computation, the results (diffraction patterns, images and diffractograms) can be displayed. (Also beam amplitude and phase plots if any of these has been stored).

To display the images, we.go to the **Display Window** and select "IMAGE", then "DISPLAY". MacTempas will ask which of the 12 images is to be displayed, then display the requested image in the center of the screen. The image can be moved around with the pointer tool

To get all 12 images onto the display screen simultaneously, select the **options** menu and the "Montage" option. Back in the **source** window, set "ZOOM" to 0.5 (to reduce the image magnification in order to fit all 12 images on the screen), then "DISPLAY".

Now go back to the montage option and deselect "Montage".

To display the projected potential for comparison with images, select "PROJ.POT" in the **source** window, then "DISPLAY".

To display the diffraction patterns at the stored specimen thicknesses, select "DIFFR.PATT" in the **source** window, then "DISPLAY". To change the size of the patterns, choose "Diffr. Patt". from the **Options** Menu and choose a different camera length.

The size of the diffraction spots also depend on the divergence angle set in the main parameters. It may be necessary to adjust both the camera length and the divergence angle to get a suitable display of the diffraction pattern.

To display the power spectrum of one of the images, we choose "IMAGE" from the **source** window. Respond by answering which image and then choose "FFT" from the **operand** window. Finally click on "DISPLAY" to view the power spectrum. The options for the power spectrum are the same as those for display of diffraction patterns. The circle drawn in diffraction patterns and power spectra corresponds to the objective aperture and can be turned off from the diffraction option.

Chapter 9

# *The Weak Phase Object Approximation*

The Weak Phase Object (WPO) approximation is a useful tool to find out what kind of information about a specific structure may be revealed at different levels of resolution.
The WPO approximation has already been described earlier, and some of that information is repeated here.There are two important assumptions that are made in the WPO approximation.

## Wavefunction Approximations

The wavefunction of the electron can be written as

$$\Psi(x, y) = 1 - i\sigma t\Phi(x, y)$$

where $\Psi(x, y)$ is the electron wavefunction at a point (x,y) and $\Phi(x, y)$ is the projected electrostatic potential at the same point. Sigma is the interaction parameter between the electron and the potential of the atoms and t is the specimen thickness. This first approximation is good for very thin specimens containing light atoms.

## Ideal Scherzer Lens

An ideal Scherzer lens is a lens that transfers all diffracted beams with a g-vector that is less or equal to 1/resolution, and blocks all diffracted beams with a larger g-vector. In addition it adds a phaseshift of 90 degrees (relative to the central beam) to all beams passing through the lens. This in addition to the 90 degree phaseshift introduced by the scattering event itself (the 'i' in the equation for $\Psi(x, y)$ above) causes all scattered beams that pass through the lens to be 180 degrees out of phase

with the central beam.

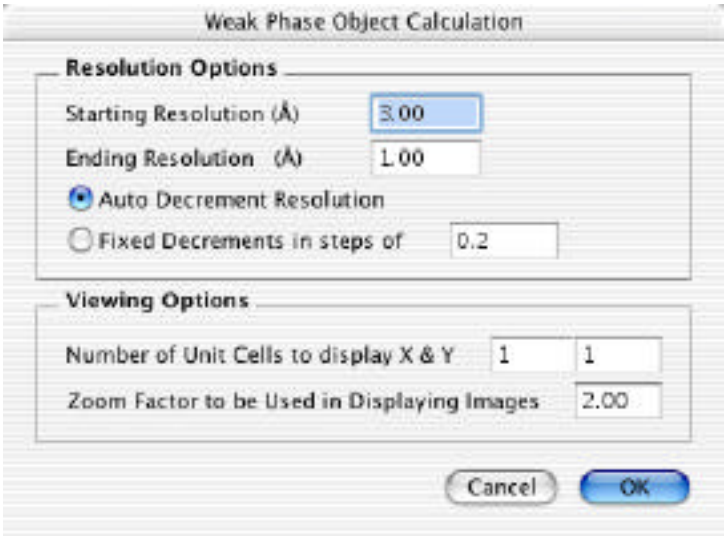
Under the two assumptions above, the image intensity in the WPO approximation can be written as

$$\Psi(x, y) = 1 - i\sigma t\Phi(x, y)$$

such that the image intensity is low in areas of high electrostatic potential, the location of atoms. Atoms of higher atomic number show up as larger and darker regions in the image. This type of image will often be similar in appearance to images calculated by a full multislice calculation for equivalent resolution for a thin specimen for Scherzer defocus.

The WPO approximation is invoked from the menu bar in the same fashion as the multislice calculation. The input to the WPO calculation is a starting resolution in Å and an ending resolution. The steps in resolution can be fixed (user determined) or automatic. When automatic steps are chosen, the program will calculate the first image corresponding to the reflections that lie within 1/BeginningResolution and each new image will be calculated for the next set of reflections corresponding to a higher resolution until the end resolution is

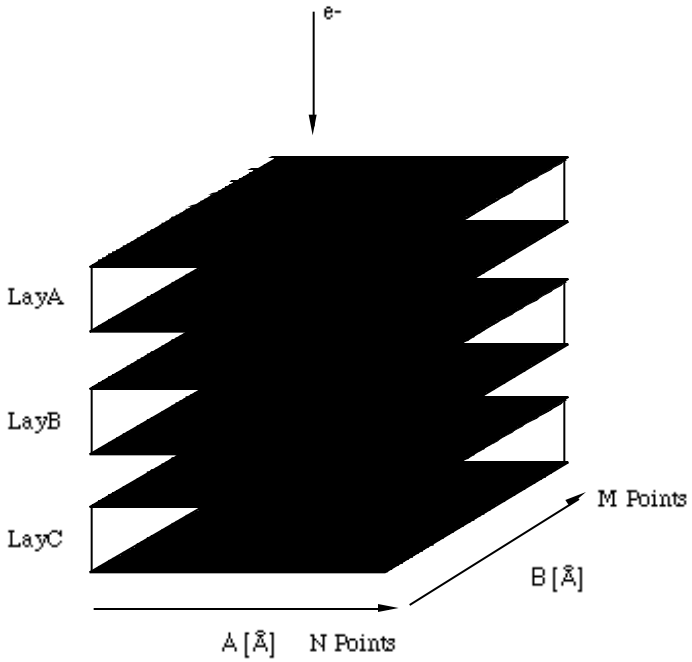
reached.


Weak Phase Object Calculation
Resolution Options
Starting Resolution (Å)
3.00
Ending Resolution (Å)
1.00
Auto Decrement Resolution
Fixed Decrements in steps of
0.2
Viewing Options
Number of Unit Cells to display X & Y
1
1
Zoom Factor to be Used in Displaying Images
2.00
Cancel
OK

Chapter 10

# *Creating a Layered Structure*

A layered Structure is a special type of “structure” where the composition varies in the direction of the electron beam. An example of this would be a crystalline material having surface layers of amorphous material. Another example would be a crystalline structure where the repeat distance in the electron beam direction is too large for the repeat to be used as the slice-thickness and the unit cell must be sub-divided into several



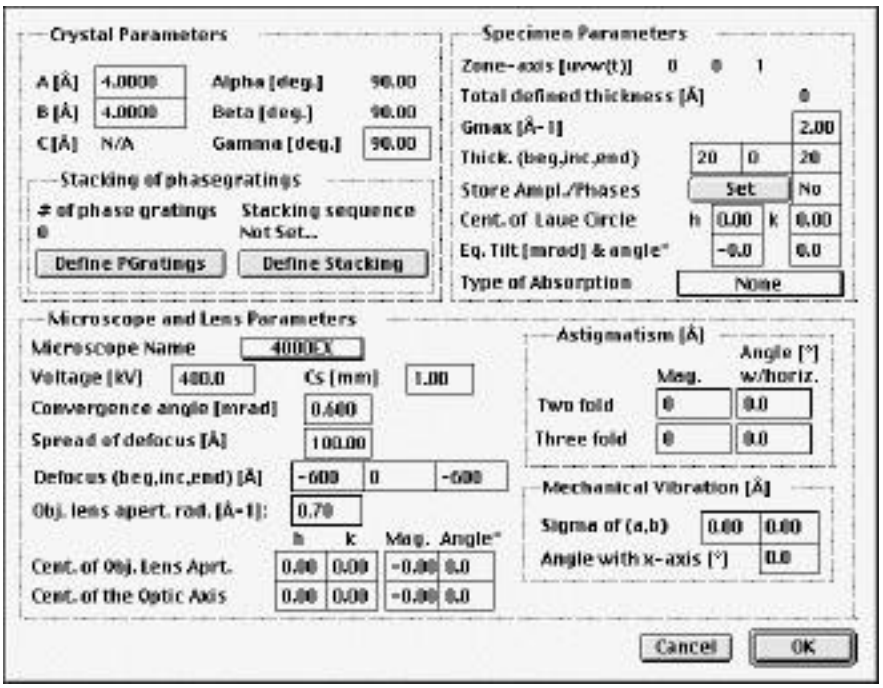
slices with different atomic content. As an example we will work with three layers which we will call LayA, LayB and LayC. Each of these "layers" are what we would call a "single" structure. That means they are defined as a unit cell with lattice parameters and atomic content. The one thing they have in common is that the lattice parameters A and B with respect to the electron beam are the same and that we will use identical sampling in each case, see figure above.
The idea of the layered structure is that the 3 layers can be arranged in any chosen sequence to make up the total structure. The steps in creating and calculating the image for a "**layered**" structure are as follows.

1) Define the 3 layers LayA, LayB and LayC as single structures with the same unit cell dimensions perpendicular to the electron beam (A and B).

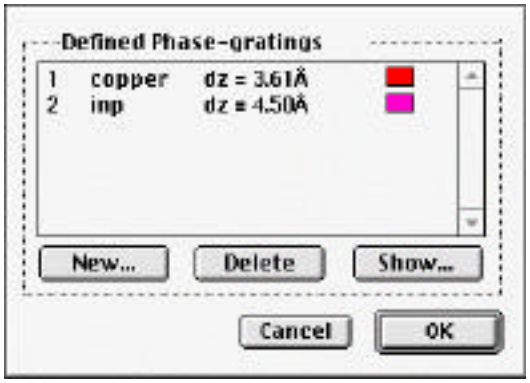
2) Calculate the phasegrating for each structure LayA, LayB and LayC using the same value for Gmax.

3) Now create a "**New**" Structure in MacTempas using the

option "**Layered Structure**". You will be asked to fill out infor-

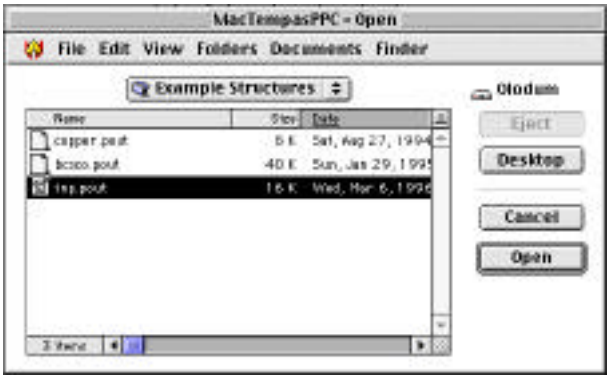



mation regarding the lattice parameters A and B etc. There are no input for atoms, because a layered structure has no atom information per se. Even though you are asked to fill out a specimen thickness, this value has no meaning at this time, because the content of the structure has not been defined. The values of A and B come from the structures LayA, LayB and

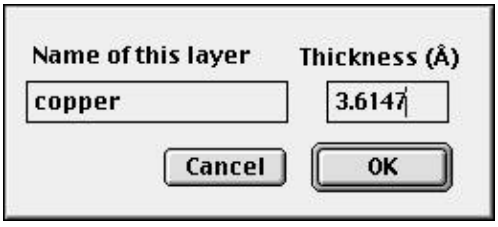


LayC. When you create the layered structure, a default value of 2 $Å^{-1}$ is supplied and you must change it in the main parameters if a different value was used in calculating the phase-gratings for LayA, LayB and LayC.

4) Once the information in 3) has been filled out, the file is created and you must define the "structural" or "phasegrating" content of the layered structure. This is done by going to the Command Menu and executing the command "**Stack Phasegratings**". If this is a new file, there will be no phasegratings listed and the command "**New**" must be used to define the layers. By invoking "**New**", you get a list of the available phaseg-



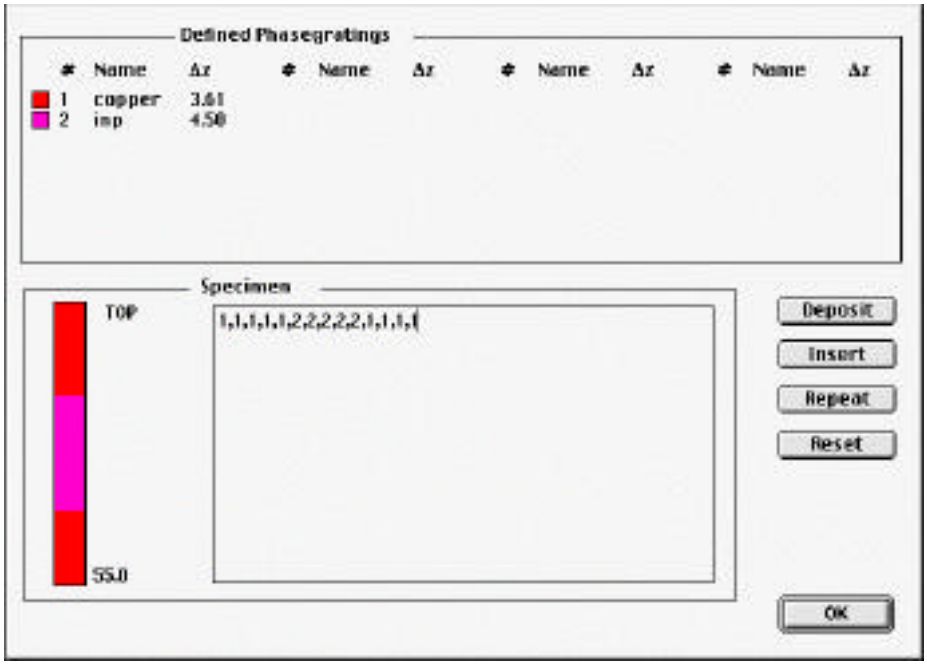

rating files (—.**pout**). Double Click on LayA.pout and fill in the value for the slice-thickness that was used in the calculation of LayA.pout. Continue and do the same for LayB and LayC.




Now the program has information as to which phase-gratings it can use and the final part is to define the sequence of these phasegratings up to the desired thickness. Use "**Stack**" and the sequence can be defined in different ways. One way is to type

in the sequence as

1,1,1,1,1,1,1,2,2,2,2,2,2,23,3,3,3,3,3,1,1,1 where 1 stands for LayA, 2 for LayB and 3 for LayC. One can also use the commands to define the sequence. At all times the specimen is drawn as a colored bar at the left. Once this is done, you have defined the structure.




5)Now check the Main Parameters to see that everything is correct and finally run the calculation. The calculation will begin with multislice.

Chapter 11

# *HOLZ Interactions & Sub-slicing*

With suitable algorithms, it is possible to include in the diffraction calculation the effects of out-of-zone scatterings, or non-zero (or higher-order) Laue zone (HOLZ) interactions. Basically, there are four ways to produce the set of phasegratings (or projected potentials) that describe the "multisliced" crystal. For structures with short repeat distances in the beam direction, the simplest method is to use one slice per unit cell. For structures with large repeats in the beam direction, several methods may be used, three of which rely on sub-dividing the slice into "sub-slices". Any of the four methods can be used in MacTempas.

### Identical slices with only one sub-slice per unit cell repeat distance

A multislice computation in which every slice is identical contains no information about the variation in structure along the incident beam direction, and includes scattering interactions with only the zero-order Laue zone (ZOLZ) layers. For structures with short repeat distances in the beam direction such a computation is adequate, since the Ewald sphere will not approach the (relatively distant) high-order zones.

### Identical sub-slices with n sub-slices per unit cell repeat distance

For structures with large repeats in the beam direction, a method of sub-dividing the slice is required in order to compute the electron scattering with sufficient accuracy. The simplest, but most approximate method, is to compute the projected

potential for the full repeat period then use 1/n of the projected potential to form a phase-grating function that can be applied n times to complete the slice. This method avoids interaction with any "pseudo-upper-layer-line" (Goodman and Moodie, 1974), but ignores real HOLZ layers.

### Sub-slices based on atom positions

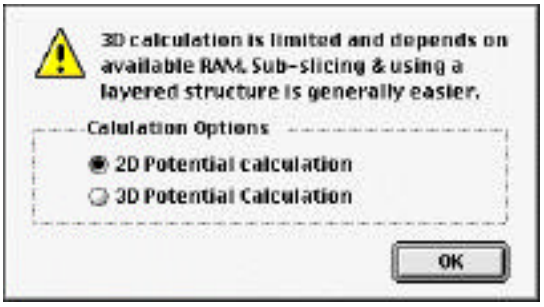
An improvement on sub-dividing the projected potential is to sub-divide the unit cell atom positions. In this procedure the list of atom positions within the unit cell is divided into n groups depending upon the atom position in the incident beam direction. From these sub-sliced groups, different projected potentials are produced to form n different phase-gratings, which are applied successively to produce the scattering from the full slice.

### Sub-slices based on the three-dimensional potential

A further improvement on sub-dividing the atom positions, is to sub-divide the three-dimensional potential of the full slice, since an atom with a position within one sub-slice can have a potential field that extends into the next sub-slice. Rather than compute a full three-dimensional potential and then integrate over appropriate sub-slices (a 128x128x128 potential would require over two million samples to be stored), it is possible to derive an analytical expression for the potential within the sub-slice $z_0 \pm \partial z$ projected onto the plane at $z_0$ (Self et al., 1983). It is possible to apply this method routinely to structures with large repeats in the beam direction, thus generating several different phase-gratings for successive application, and even to structures (perhaps with defects) that are aperiodic in the beam direction and require a large number of individual non-repeating phase-gratings (Kilaas et al., 1987).

## MacTempas sub-slicing

While ensuring that the calculation remains sufficiently accurate, MacTempas will normally choose the simplest (and quickest) method of specifying how slices are defined for any particular combination of specimen, zone axis, accelerating voltage, and maximum g. To this end, the user can choose to neglect HOLZ interactions if these are judged to be unimportant. If HOLZ interactions are important, then the user should select the "3D-Potential Calculation" radiobutton in the Options menu, rather than "2D-Potential Calculation".




When a two-dimensional calculation is selected, MacTempas will use one slice per cell if the cell repeat distance in the beam direction is small. If the repeat distance is too large for one slice per unit cell, MacTempas will avoid pseudo-upper-layer-lines by producing n identical sub-slices.

When a three-dimensional calculation is selected, (3D-Potential Calculation activated), MacTempas uses a sub-divided three-dimensional potential when the repeat distance is large, and defaults to one slice per cell if the distance is small enough. Note that the number of sub-slices per unit cell can be forced to be greater than one by setting it explicitly in the Parameter menu; this will ensure that any HOLZ interactions are included even for small repeat distances. Of course, if the repeat distance is very small, leading to a distant HOLZ in reciprocal space, both the calculation and the experiment it is modeling will interact only very weakly with the HOLZ reflections.

Use of the Layered Structure option to produce the scattering from a structure that is layered or aperiodic in the incident beam direction is effectively an application of the method of sub-slicing based on atom positions. Thus the user could create a number of sub-slices by assigning selected atoms to different structure files, then forming a phasegrating for each sub-slice, and using the Stack Phasegratings command to specify how the sub-slices are to be used to describe the specimen structure. This is the suggested method to try first if upper Laue layers are to be included or 3-dimensional effects are important as it is much faster than using a complete 3D calculation.

**Other methods**

Van Dyck has proposed other methods to include the effects of HOLZ layers, including the second-order multislice with potential eccentricity (Van Dyck, 1980) and the improved phase-grating method (Van Dyck, 1983). Tests of these procedures show that the extra computation involved in using potential eccentricity may be worthwhile, but that the improved phase-grating method diverges too easily to be useful.

Goodman P, Moodie AF (1974) Numerical evaluation of N-beam wave functions in electron scattering by the multislice method. Acta Cryst. A30, 322-324.

Kilaas R, O'Keefe MA, Krishnan KM (1987) On the inclusion of upper Laue layers in computational methods in high resolution transmission electron microscopy. Ultramicroscopy 21, 47-62.

Self PG, O'Keefe MA, Buseck PR, Spargo AEC (1983) Practical computation of amplitudes and phases in electron diffraction. Ultramicroscopy 11, 35-52.

Van Dyck D (1980) Fast computational procedures for the sim-

ulation of structure images in complex or disordered crystals: A new approach. J. Microscopy 119, 141-152.

Van Dyck D (1983) High-speed computation techniques for the simulation of high resolution electron micrographs. J. Microscopy 132, 31-42.

Chapter 12

# *Structure Refinement Through Matching of Experimental and Simulated HRTEM Images*

## 12.1.Introduction

The goal of performing simulation of HRTEM images is to compare these with the experimental data in order to determine the structure. In practice this means that various models are proposed and that images are calculated until a match is found. At that point, the structure is presumed to be known (atomic positions and atomic numbers) with some given uncertainty. Alternatively, one starts with a given model and varies the model in a systematic fashion searching for a global maximum in the fit between experiment and simulation. This entails that one needs an efficient method to compare the experimental and the calculated image. It also requires knowledge of the uncertainty in the measurement (image intensities in the experimental image) and a way to relate this uncertainty to the uncertainty in chemical composition and atomic positions. This area of quantitative electron microscopy is fairly new and most images are still compared visually. However, it is an active area of research and many techniques from statistics are just now beginning to be used in HRTEM.

## 12.2.Acquiring quantitative data

In order to extract quantitative information from electron micrographs, the data must be represented by a set of numbers. Usually, images from TEMs are brought into a digital representation by one of the following methods.

i)Recording the image on a photographic plate and using a scanner to convert the film density into numbers which are stored in a computer.

ii)Recording the image on an image plate.

iii)Recording the image on a slow scan CCD camera with read-out of deposited charge into a computer.

The first approach yields data that is not directly comparable to computer calculations because of the non-linear response of the film. It is however possible to calibrate the response of the film based upon a sequence of controlled exposures using varying exposure times and mapping the resulting scan values versus electron dosage[1]. The image plate and the CCD camera both yield numbers that are linear with respect to the electron dosage and only require a scaling of the data in order to compare to computed values[2]. There has been much discussion about the relative merits of the various recording media above and each has its own advantage. The CCD camera is currently limited to 2K by 2K pixels, although it may be possible to go to 6K by 6K by using multiple chips in the near future. Since its Modulation Transfer Function (MTF) can be characterized, it is straight forward to use deconvolution to compensate for the drop in high frequency response due to spread of electrons and due to spill over of charge to neighboring cells[3]. The image plate has many of the advantages of the CCD camera and covers a larger image area. However, the imaging plate is not gaining as much popularity as the CCD camera. Many laboratories are now starting to do much of the recording on CCD cameras, while still retaining the use of film.

### 12.3.Pre-processing of data

Once the image data has been converted to numbers, any necessary processing or transformation of the data can take place. The required pre-processing of the data depends on the nature of the information that is sought and thus there is no one optimal method, but rather a number of possible options.

#### 12.3.1Sampling and resampling of data

If the image is distorted over the image field of view, either by the action of the imaging system or the recording system, the data can be re-transformed by a warping transformation of the image. This can be done if the transformation can be determined by imaging a perfectly crystalline material and noting deviations from where the atoms are known to be and where they are imaged[4]. On some systems, i.e. the Gatan Imaging Filter, the distortions are measured by recording the image of a square grid of circular holes.

An image of a crystalline material can be resampled onto lattice relative coordinates, such that the unit cell dimensions are represented by an integer number of pixels and commensurate with the dimensions of the final image. This will eliminate streaking in the Fourier transform of the image which is due to the truncation of the image by the edges on boundaries that do not represent a periodic continuation of the image. Streaking can be reduced by multiplying the image with a circular mask. The mask is represented by a circle of pixels with value 1 up to a specified radius and then falling off gradually to 0 within 5 to 10 pixels close to the borders of the image. A side-effect of masking is the increase in noise in the Fourier transform which is discussed below.

If only the image of a single unit cell of the crystalline material need to be determined and compared with the image obtained through an image simulation calculation, the image of the unit cell can be resampled onto the coordinate system and sampling interval used in the computation. This is equivalent to determining the matrix M defined through the equations

$\mathbf{a}_s = M\mathbf{a}_e$ 1)

$\mathbf{b}_s = M\mathbf{b}_e$

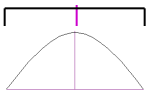
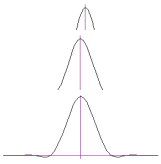
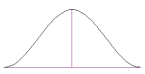
Two steps are necessary; the rotation /scaling required to make the lattice base vectors identical; and secondly the determination of a common origin.

Finding the common origin between experimental and calculated image is determined by cross-correlation between the simulated and the experimental image[5].

### 12.3.2Fourier transforms and masking

The Fourier transform of HRTEM images of crystalline materials provides useful information about lattice spacings and can also be used to compare experimental Fourier amplitudes with theoretical calculations. Because the image being transformed is rarely a periodic function in W (width) and H (height), the Fourier transform of the image of a pure crystalline material is the convolution of the Fourier transform of a perfectly periodic signal (the crystal) with the transform of a window the size of the image dimensions, making a Bragg peak take on the shape of the transform of the window.

**Table 1:**

| name | window | function | transform | peak profile | falloff | rel. noise level |
|---|---|---|---|---|---|---|
| none | $1$ |  | $\frac{\sin(\pi k)}{\pi k}$ |  | $\frac{1}{k}$ | 1 |
| cosine | $\frac{\pi}{2}\cos\left(\frac{\pi x}{2}\right)$ |  | $\frac{\cos(\pi k)}{1-4k^2}$ | | $\frac{1}{k^2}$ | 1.23 |
| Von Hann | $1+\cos(\pi x)$ | | $\frac{\sin(\pi k)}{\pi k(1-k^2)}$ | | $\frac{1}{k^3}$ | 1.5 |

The use of a mask changes the transform of the window and can be used to make the peak profiles decay faster, but at the expense of increasing the noise level. This is illustrated above,

showing the effects of employing masks on a 1-dimensional signal[6]. This also has an effect on locating peak positions in order to determine lattice spacings and on the estimate of the amplitude of the Fourier component. The standard error in both estimates increases as a function of applying a mask, with the cosine window being a good compromise.

### 12.3.3Noise reduction

In addition to reducing noise, it is also important to have an estimate for amount of noise present and to quote a signal to noise ratio. From two equivalent regions, the noise can be estimated from obtaining the cross-correlation coefficient for two regions. Given a cross-correlation coefficient ccf, the signal to noise ratio can be estimated as

$$S/N \approx \frac{CCF}{1 - CCF} \quad 2)$$

In order to reduce noise and to obtain a statistical average of the image of a single unit cell (motif), the positions of individual motifs can be determined by cross-correlation. Once these are found, statistically equivalent regions can be averaged to find the average motif and to determine the signal to noise ratio associated with individual pixels as a function of position within the unit cell. This determines a standard deviation for each pixel i and can be used to set confidence levels associated with matching of the experimentally averaged image with a calculated image[7].

$$\sigma^2(i) = \frac{1}{M-1}\sum_{j=1}^{M}(I_j^2(i) - \langle I(i)\rangle^2) \quad 3)$$

where M is the number of equivalent regions being averaged. Using a low pass filter to perform a smoothing of the image may be effective depending on the noise level present, particularly when averaging over statistically equivalent regions can not be performed. Smoothing helps the eye see features more clearly; but has the disadvantage that it causes correlation between image pixels, which may distort the significance threshold of simulation mismatch criteria.

Averaging can also be performed through symmetrization which is to average the motif with copies of itself to which symmetry operations known to be present are performed. This will reduce noise levels by a further factor of $1/\sqrt{M}$ when M symmetry related copies are averaged, but may also just disguise defects in imaging conditions.

### 12.4. Matching experimental and simulated images

There are a number of various ways to measure similarity or mismatch between two images. Below are a few of these[8].
The mean square difference:

$$D^2 = \left\langle \left(I_1 - I_2\right)^2 \right\rangle = \frac{1}{N} \sum \left(I_1 - I_2\right)^2 \quad 4)$$

The Root Mean Square Difference:

$$D_{rms} = \sqrt{D^2} \quad 5)$$

The mean modulus difference:

$$D_{mmd} = \left\langle \left| I_1 - I_2 \right| \right\rangle = \frac{1}{N} \sum_i \left| I_1 - I_2 \right| \quad 6)$$

The Cross-correlation Coefficient:

$$CCF = \frac{\sum_i (I_1(i) - \bar{I}_1)\ (I_2(i) - \bar{I}_2)}{\sqrt{\sum (I_1(i) - \bar{I}_1)^2 \sum (I_2(i) - \bar{I}_2)^2}} \quad 7)$$

The brackets <> all indicate the mean of the enclosed quantity. In each of these equations, the sum is over all the pixels i in the image and N is the total number of pixels. The cross-correlation coefficient above is a normalized coefficient where the images are normalized to zero mean.
The CCF (which measures similarity rather than difference) can also be interpreted as the cross-product between two n-dimensional vectors (n being the number of pixels in the image). In that case, one can associate an angle with the CCF, $CCF = \cos\vartheta$, in the general interpretation of an inner product between two vectors as $I_1 \cdot I_2 = |I_1|\ |I_2| \cos\vartheta$ with the angle

being $\vartheta = \cos^{-1}(CCF)$ .This angle is zero for identical images. If the images are normalized to zero mean and unit length as in the definition of the normalized cross-correlation coefficient above, the angle is 180 deg. for a reversal in contrast between the two images $I_1$ and $I_2$.

### 12.4.1Significance and Noise

Each of the above criteria must be tested for the significance of the measured value.

$D^2$ can be compared to the mean square intensity (or intensity deviation due to noise) in either image.

$D_{rms}$ can be compared with standard deviation of the intensity in either image

A good way to test for the mismatch between two images, is to use a statistical measure for the probability of two images being equal given knowledge of the noise in the images. If one assumes Gaussian uncorrelated noise for each pixel in the experimental image, the optimum statistical measure is given by

$$\chi^2 = \frac{1}{N}\sum \frac{\left(I_1(i) - I_2(i)\right)^2}{\sigma^2(i)} \quad 8)$$

where N is the number of pixels in the image[9]. The value $\sigma^2(i)$ is the standard deviation associated with the pixel *i* and can be found as described above from a number of equivalent regions. If an experimental image $I_e$ is compared to a calculated image $I_c$ and there are M adjustable parameters in the calculation, the equivalent expression becomes[7]

$$\chi^2 = \frac{1}{(N-M)}\sum \frac{\left(I_e(i) - I_c(i)\right)^2}{\sigma_e^2(i)} \quad 9)$$

A mismatch by one standard deviation adds one to the sum in the expressions above and a value of $\chi^2$ of 1 implies that the two images are identical within the uncertainty given by the noise. The expected value for statistically equivalent images consisting of N points is 1 and random deviations from this value by more than $2/\sqrt{N}$ are considered unlikely.

Writing

$$\chi^2 = \frac{1}{N}\sum \frac{\left(I_1(i) - I_2(i)\right)^2}{\sigma^2(i)} = \frac{1}{N}\sum f^2(i) \quad 10)$$

leads to the definition of a Residual Image $f(i)$ [10] which is used to visualize and to quantify the (mis)match between two images. It has the advantage that instead of presenting a single number for how well two images match, it is a two-dimensional mapping of the local fit. Thus a difference image will more clearly reveal areas of greater mismatch. The optimum match is still defined by minimizing $\chi^2$.
It is important to note that the fitting parameters can also be applied to the Fourier transforms of the images which sometimes will lead to a reduction in the number of the data-points to be compared[11]. In the case of images of crystalline material containing no defects, the Fourier components will be non-zero only for frequencies corresponding to Bragg-reflections of the lattice, although this is strictly only true if the motif has been averaged over many repeating regions and resampled onto lattice coordinates such that streaking due to discontinuities at the boundaries is eliminated. The complex values for the Fourier coefficients take the place of the image intensities.
It is interesting to note that the use of different matching criteria can lead to slightly different values for optimized parameters[12].

### 12.4.2 Adjusting for different means and contrast levels

Since absolute values for image intensities are not known and an experimental image may be linearly related to a calculated image, a useful way of normalizing the image intensities is to subtract the mean and divide by the standard deviation. This ensures that $D^2 = 0$ for linearly related images and a value of around 2 for unrelated data.
Similarly, the Cross-correlation coefficient will lie in the range from -1 to 1, taking the extreme values when the two images are linearly related and being near 0 for unrelated data.
Another approach is to scale the images to the same mean. This is done as follows

$$I_{calc} = \frac{I_{calc}}{\langle I_{calc} \rangle} \langle I_{\exp} \rangle \quad 11)$$

where the calculated image is scaled to the mean of the experimental image.
In order to understand how the mean value, contrast and image pattern affect the image matching criteria, it is useful to consider how the Root Mean Squared Difference $D_{rms}$ can be separated into three terms[13].

$$D_{rm} = \sqrt{\langle (I_1 - I_2)^2 \rangle} = (\langle I_1 \rangle - \langle I_2 \rangle)^2 + [\sigma_1 - \sigma_2]^2 + 2(1 - \rho)\sigma_1\sigma_2 \quad 12)$$

where

$$\sigma_{1,2} = \sqrt{\langle I_{1,2}{}^2 \rangle - \langle I_{1,2} \rangle^2} \quad 13)$$

and

$$\rho = \frac{\langle I_1 I_2 \rangle - \langle I_1 \rangle \langle I_2 \rangle}{\sigma_1 \sigma_2} \quad 14)$$

The first term measures the difference in the mean of the two images and vanishes if both images are normalized to the same mean value. The second term measures the difference in contrast between the two images, while the third term (where is the same as the normalized cross correlation coefficient) measures the difference (similarity) in the pattern of the two images. Thus it is important to note that the normalized cross correlation coefficient CCF only measures similarity in patterns and ignores variation in contrast and differences in mean levels. It is generally found that most of the mismatch between experimental and computer simulated images is due to the difference in contrast[14]. The difference in contrast can be an order of magnitude and the cause is generally attributed to the following factors.
misalignment
specimen vibration
inelastic scattering

specimen damage

There is however an ongoing debate as to the nature of the discrepancy in contrast as calculations indicate that the factors above are not sufficient to resolve the disparity. A possible explanation is that there is a general background in experimental images that is not accounted for.

### 12.4.3 Effect of noise on matching criteria

In order for two images to be considered equal, we need to consider the effect of the uncertainty or error in the matching criteria due to noise and the parameters determining the image.
A study of the effect of noise on the cross-correlation factor reveals that in the presence of noise, the cross-correlation coefficient *CCF* for the two images $I_1$ and $I_2+\eta$, where $\eta$ represent random noise superimposed on image $I_2$, can be written as[13]

$$CCF(I_1, I_2, \eta) = CCF(I_1, I_2) \Big/ \sqrt{1 + \frac{\sigma^2(\eta)}{\sigma^2(I_2)}} = CCF(I_1, I_2) \Big/ \sqrt{1 + \vartheta_n^2} \quad 15)$$

with

$$\vartheta_\eta^2 \equiv \frac{\sigma^2(\eta)}{\sigma^2(I)} \quad 16)$$

The effect on the hyper-angle $\vartheta = \cos^{-1}(CCF)$ is in the small angle approximation

$$\vartheta(I_1.I_2, \eta) \approx \sqrt{\vartheta^2(I_1.I_2) + \vartheta_\eta^2} \quad 17)$$

If two images are identical except for a small error in one of the image-formation parameters (defocus, thickness, etc.) the error in the angle $\vartheta$ is proportional to the parameter error. The error in the angle due to independent parameter errors is

$$\theta = \sqrt{\sum \vartheta_i^2} \quad 18)$$

Typical mismatches in CCF (pattern matching) due to parameter errors are

**Table 2:**

| Parametet | Error | theta(mrad) |
|---|---|---|
| Noise | | 0.06 |
| Composition | ±0.03 | 0.02 |
| Thickness | ±2nm | 0.2 |
| Defocus | ±15nm | 0.4 |
| Beam Tilt | <1.5mrad | 0.8 |
| Astigmatism | <15nm | 0.2 |
| Crystal Tilt | <2mrad | 0.6 |
| Beam Diverg. | <0.3mrad | 0.1 |
| Focal Spread | <5nm | 0.15 |
| Vibration | <0.04nm | 0.2 |

### 12.4.4Chi-Square or Chi-based criteria

Although all the methods above measure either the match or mismatch between two images, the important questions is not to what degree do they match, but how well do they match given systematic and non-systematic errors. Thus the fitting parameter must take into account the statistical nature of the data and the accuracy to which we know the data-points. Thus the fitting parameter should depend on a maximum-likelihood (probability) model and be a measure of the probability that A is equal to B, given knowledge of the probability distribution of the data-points. In the presence of Gaussian distribution of uncorrelated noise, each data point has a Gaussian probability distribution with the noise in one pixel uncorrelated to the noise in adjacent pixels, which leads to a $\chi^2$ criteria. The criteria takes into

account the number of adjustable parameters and the error in each data point.
As mentioned above, any data point lying one sigma away from the expected value will add 1 to the sum in $\chi^2$.
Similarly, any data point which has only 1% probability of being measured given A = B, adds a value of 6.63 to the sum in $\chi^2$. Thus values of $\chi^2$ greater than about 6 states that there is less than 1% probability that A is equal to B.
The fitting parameter depends on the model of the distribution of data-points due to statistical noise with a Gaussian distribution of uncorrelated noise leading to the criteria. However, it is important to determine the statistical nature of the noise in the image. This can be done by examining the noise distribution determined from a large number of image regions considered to be equivalent except for noise. A non-Gaussian distribution will lead to a modified criteria, but still based upon [7].

### 12.5. Structure determination

In order to determine the "unknown" structure, it is necessary to perform a comparison between calculated images, exit wavefunctions or diffraction patterns and experimentally obtained data. As described above the comparison can be done using different matching/mismatching criteria. Ideally, the determination of the structure is done by modifying the structure until the mismatch between the experimental and calculated data is within the error in the experimental data. In principle the imaging parameters themselves can be allowed to vary together with the atomic coordinates. However, in practice the imaging parameters are optimized separately if possible. This reduces the complexity of the problem and reduces the number of steps involved in the search for a solution which optimizes the matching criteria. In cases involving unknown defects in the presence of a "known" structure, the imaging parameters and specimen thickness are first determined from the known structure.
Determination of an unknown set of input parameters requires the following
1)An image (in real or reciprocal space) obtained from the experimental data.

2)A computational method yielding an image to be compared to the 1).
3)A method for comparing 1) and 2)
4)A criteria based upon 3) for when 1) and 2) are statistically equivalent.
5)An initial set of adjustable input parameters which are to be optimized so that the final configuration results in satisfying 4)
6)A method for varying the adjustable parameters so that the final configuration is found within finite time.
There is an essential assumption being made above, which states that the computational method used in 2) will produce the image in 1) given the correct choice of input parameters. This is a separate issue which will not be addressed here. The validity of this assumption can be debated and it is acknowledged that computational methods are in need of further refinement. However, in what follows, the assumption is presumed to be valid.

### 12.5.1Matching Images or Exit Wavefunctions

In order to compare calculation with experiment, one can compare either images or diffraction patterns. For perfect structures it may be beneficial to compare diffraction patterns since the number of data points to compare are given by the possible Bragg reflections of the structure[11]. However, for defect structures, the information that describes the defect is located in the diffuse scattering between Bragg spots, and it is more efficient to compare images. The entire discussion relates to both real space and reciprocal space, although only real space images will be referred to.

### 12.5.2Simulated Thermal Annealing

Simulated thermal annealing is a relatively new technique for finding the global minimum of a multivariate function[15]. The algorithm is based upon assigning an energy to the system which is a function of the parameters being varied, with the optimum configuration of the system being the minimum energy state, the ground state. A temperature is also assigned to the system and the temperature is slowly being reduced as the configuration is changed. From the initial configuration

$E_0(x_1,x_2,....x_n)$, the parameters are varied in a random fashion and for each variation the new energy $E_j(x_1,x_2,....x_n)$ is calculated. The new configuration is always accepted if $\Delta E = E_j(x_1,x_2,....x_n) - E_{j-1}(x_1,x_2,....x_n) < 0$. Otherwise the new configuration has a probability P of being accepted, where

$$P = e^{-\Delta E/T} \qquad 19)$$

E and T being dimensionless quantities.
For each temperature, the system undergoes a given number of variations, accepting or rejecting the new configuration based upon the above criteria. When a specified number of successful transitions have taken place, the temperature is lowered by a certain amount, and the parameters are changed again. As a function of iterations, the energy of the system decreases towards what is hoped to be the minimum energy configuration and the process is terminated when either no more successful variations are made for a given number of attempts or the temperature reaches a lower limit.
When comparing calculated and experimental images, the energy of the system can be chosen to be $\chi^2$ or any of the other quantities that measures image-mismatch. When basing the comparison on the cross-correlation coefficient, the energy can be taken as 1-CCF.
Simulated thermal annealing is a straight forward technique that has proven to be very powerful for finding global minimum without getting trapped in local minima. It is sensitive to the starting conditions and the choice of starting temperature and some experimentation may be required. Near the minimum, it tends to be less optimal than search techniques based upon gradient methods and switching to a different search algorithm may be an alternative once the simulated annealing algorithm has terminated.

### 12.5.3Simulated Evolution

Simulated evolution is another technique for obtaining the global minima which is modeled after Darwin’s principle of "survival of the fittest"[16] It starts with an initial configuration of

all the variables to be fitted and produces a number of sets l from the initial set using a random generator (mutation generator). This set l represents the first generation of children. The algorithm proceeds in the following way:
i)Evaluate a quality function Q (goodness of fit) for all l children.
ii)Select a subset ($\mu < l$) of survivors which will be he parents of the next generation.
iii)Create a new generation by applying the random generator, after selecting and mixing a part of the parent's parameter vectors.
iv)Loop back to i) until one of the following criteria are met: a) a maximum number of generations have been reached or b) a critical goodness-of-fit has been reached.

### 12.5.4Other Techniques

There are other ways to do the refinement which is based upon changing the input parameters so that the system moves in a path where the gradient with respect to the fit is the largest[17]. Each method has its advantages. Simulated thermal annealing and simulated evolution are good techniques for getting close to the optimum fit. Once close to the minimum, gradient methods may be used for further refinement until the match is within the uncertainty of the measurement.

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