Image Processing in High-Resolution Electron Microscopy using the Direct Method. II. Image Deconvolution*

By Han Fu-son, Fan Hai-fu† and Li Fang-hua

Institute of Physics, Academia Sinica, Beijing, China

Abstract

A new method is proposed to estimate the defocus (Δf) from a single electron micrograph (EM). The method has been tested by simulations using theoretical EM's calculated under different defocus conditions. The preliminary method is successful except when the EM is taken near the optimum defocus. This can be improved by making use of the information from the electron diffraction pattern. The method will be effective for radiation-sensitive materials.

Introduction

High-resolution electron microscopy (HREM) has made great progress in recent years. Many crystals important in science and technology are too small and imperfect for carrying out an X-ray single-crystal analysis, but are suitable for HREM observation. HREM is thus becoming more important in the determination of crystal structures. However, structure analysis by HREM is not as straightforward as X-ray single-crystal analysis, especially when the structure of the crystal is completely unknown. There are two difficulties with HREM. Firstly, an electron micrograph (EM) is not a true structure image of the object but rather a convolution of the projected potential distribution with the Fourier transform of the contrast transfer function. Secondly, the point-to-point resolution of an EM (~2 Å at present) is not enough to resolve individual atoms. The above defects may be overcome by introducing direct methods developed in X-ray crystallography into the image processing of HREM. It has been shown in the preceding paper (Fan Hai-fu, Zhong Zi-yang, Zheng Chao-de & Li Fang-hua, 1985) that the direct method can be used to improve the resolution of an EM. Here we describe a new procedure for image deconvolution using the Sayre equation as a criterion. The method is simple and does not rely on preliminary knowledge of the structure of the object. The present work is a continu-

ation of that of Li Fang-hua & Fan Hai-fu (1979), which was inspired by the work of Uyeda & Ishizuka (1974).

Principle of the method

Under the weak-phase-object approximation,‡ in which the dynamic diffraction effect is neglected, the Fourier transform of an EM can be expressed as

$$T(\mathbf{H}) = \delta(H) + 2\sigma F(\mathbf{H}) \sin \chi_1(H) \exp[-\chi_2(H)], \tag{1}$$

which can be rearranged to give

$$F(\mathbf{H}) = T(\mathbf{H})/2\sigma \sin \chi_1(H) \exp[-\chi_2(H)]. \tag{2}$$
$$\scriptstyle H \neq 0$$

Here $\sigma = \pi/\lambda U$, λ is the electron wavelength and U the accelerating voltage. $\mathbf{H}$ is the reciprocal vector within the resolution limit. $F(\mathbf{H})$ is the structure factor of electron diffraction, which is the Fourier transform of the potential distribution $\varphi(\mathbf{r})$ of the object.

$\sin \chi_1(H) \exp[-\chi_2(H)]$ is the contrast transfer function, in which

$$\chi_1(H) = \pi \Delta f \lambda H^2 + \tfrac{1}{2}(\pi C_s \lambda^3 H^4),$$

$$\chi_2(H) = \tfrac{1}{2}(\pi^2 \lambda^2 H^4 D^2).$$

Here Δf is the defocus value, C_s is the spherical aberration coefficient and D is the standard deviation of the Gaussian distribution of defocus due to the chromatic aberration (Fijes, 1977). The values of Δf, C_s and D should be found by image deconvolution. Of these three factors, C_s and D can be determined experimentally without much difficulty. Furthermore, C_s and D do not change much for each image in contrast to Δf. Hence the main problem is to evaluate Δf. With the estimated values of C_s and D, we can calculate a set of $F(\mathbf{H})$ from (2) for a given value of Δf. If this value is correct, the corresponding set of $F(\mathbf{H})$ should obey the Sayre equation (Sayre, 1952):

$$F(\mathbf{H}) = (\theta/V) \sum_{\mathbf{H}'} F(\mathbf{H}')F(\mathbf{H} - \mathbf{H}'), \tag{3}$$

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‡ The applicability of the weak-phase-object approximation has been demonstrated by Unwin & Henderson (1975) for biological specimens and by Klug (1978/79) for an inorganic compound.

where θ is the atomic form factor and V the volume of the unit cell. Hence the true Δf can be found by a systematic change of the trial Δf. The practical procedure should be as follows:

1. Calculate a set of $T(\mathbf{H})$ from an EM.

2. Assign trial values of Δf in a wide range with a small interval, say 10 Å. For each trial Δf, a set of $F(\mathbf{H})$ is calculated from $T(\mathbf{H})$ using (2). Reflections with $|\sin \chi_1(H) \exp [-\chi_2(H)]| \leq 0\cdot 2$ will be neglected.

3. Calculate the figure of merit S for each set of $F(\mathbf{H})$ using the following formula (Debaerdemaeker, Tate & Woolfson, 1985):

$$S = \left[\sum_{\mathbf{H}} E^*(\mathbf{H}) \sum_{\mathbf{H'}} E(\mathbf{H} - \mathbf{H'}) \right]^2$$
$$\times \left\{ \left[\sum_{\mathbf{H}} |E(\mathbf{H})|^2 \right] \left[\sum_{\mathbf{H}} \left| \sum_{\mathbf{H'}} E(\mathbf{H'}) E(\mathbf{H} - \mathbf{H'}) \right|^2 \right] \right\}^{-1},$$
$$(4)$$

where $E(\mathbf{H})$ is the normalized structure factor, $E^*(\mathbf{H})$ is the conjugate of $E(\mathbf{H})$. S has a value between 0 and 1. The greater the value of S, the better the set of $F(\mathbf{H})$ fit the Sayre equation.

4. Find the greatest S and then Fourier transform the corresponding set of $F(\mathbf{H})$ to deconvolute the image.

Test results

A series of theoretical EM's at 2 Å resolution was generated for a model structure of copper per-chlorophthalocyanine ($C_{32}N_8Cl_{16}Cu$). Plane group of the projection along the c axis was cmm; unit-cell dimensions: $a = 19\cdot62$, $b = 26\cdot04$, $c = 3\cdot76$ Å and $\beta = 116\cdot5°$. Accelerating voltage = 500 kV; $C_s = 1$ mm; $D = 150$ Å and $\Delta f = \pm 1000$, ± 800, ± 600, ± 400, ± 200 Å. The calculated EM's are shown in the first and third columns of Fig. 1(b) and their Δf's are shown in Fig. 1(a). The results of Fig. 1(a) are summarized in Table 1.

The deconvolution was very successful in eight out of ten cases, for which the values of Δf were accu-
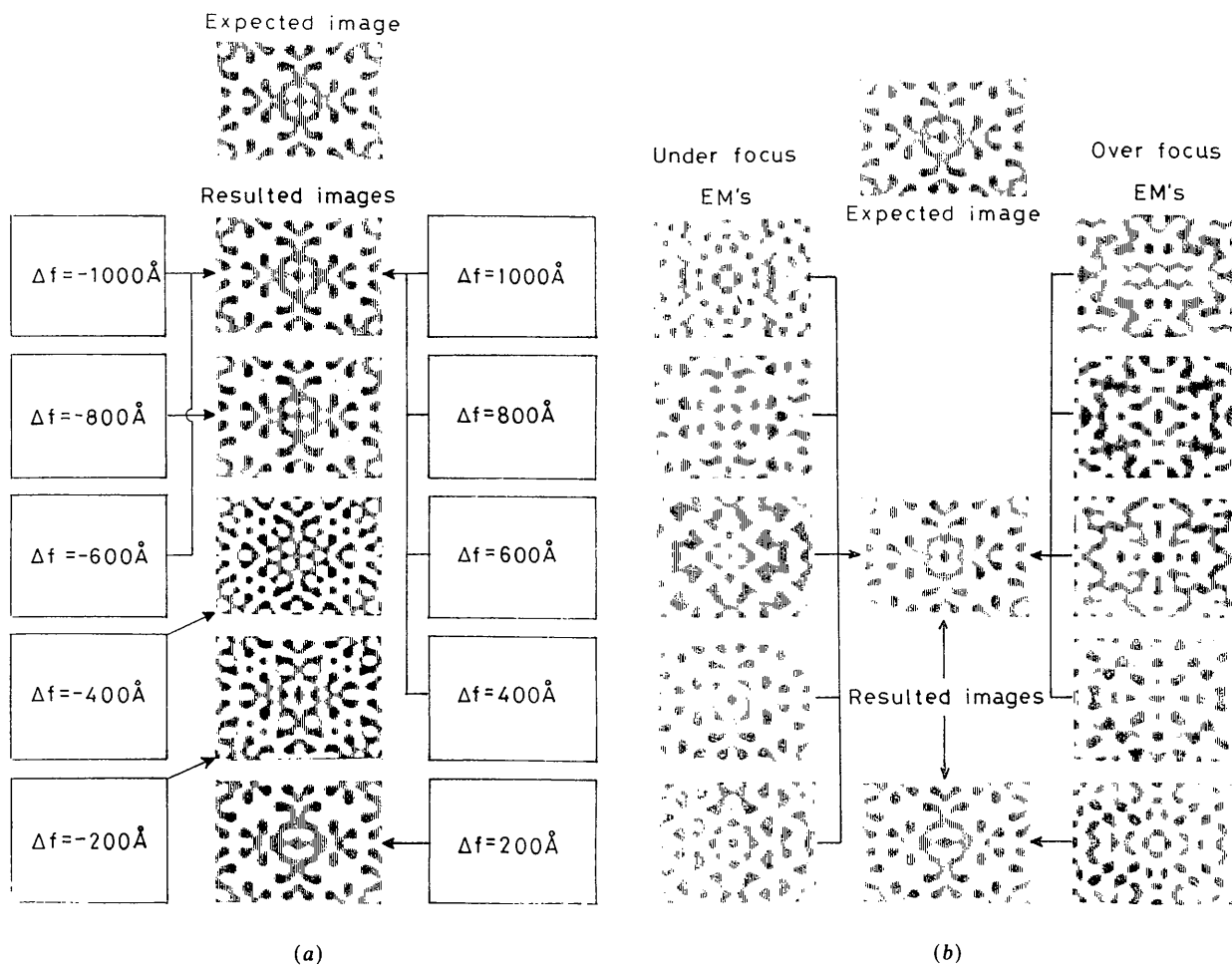

Fig. 1. Results on image deconvolution for Cu(Clphthalocyanine) (a) starting from a single EM, (b) starting from a single EM and the corresponding electron diffraction pattern.

Table 1. *Estimation of defocus from a single EM*

Δf_{true} true defocus; Δf_{est} estimated value of defocus; S figure of merit corresponding to Δf_{est} calculated from (4).

Δf_{true}	1000	800	600	400	200	−200	−400	−600	−800	−1000
Δf_{est}	1000	800	600	400	210	−560	−520	−600	−810	−1000
S	0·9704	0·9704	0·9704	0·9704	0·9708	0·9704	0·9711	0·9704	0·9704	0·9704

Table 2. *Estimation of defocus from a single EM and the corresponding electron diffraction pattern*

Δf_{true}	1000	800	600	400	200	−200	−400	−600	−800	−1000
Δf_{est}	1000	800	600	400	210	−200	−420	−600	−800	−1000
S	0·9704	0·9704	0·9704	0·9704	0·9708	0·9704	0·9711	0·9704	0·9704	0·9704

rately determined and the deconvoluted images were almost the same as the expected one. The two EM's for which deconvolution failed have Δf values close to that of the optimum underfocus (about −400 Å). The failure may be due to two reasons:

1. When the value of Δf is close to that of the optimum underfocus, the contrast transfer function will not be sensitive to small changes of Δf. This results in a large error in the estimation of the defocus.

2. The Sayre equation was used without an observed set of $|F(\mathbf{H})|$. Hence the solution may not necessarily be unique. There are two ways to get rid of the above difficulty:

1. Use an overfocus EM rather than an underfocus one. As can be seen in Table 1 the deconvolution was successful for all overfocus EM's.

2. Use the corresponding electron diffractions to provide a set of $|F(\mathbf{H})|$. Then for the calculation of S, the phases derived from the EM using (2) and the magnitudes obtained from the electron diffraction can be combined to yield $E(\mathbf{H})$. Results on this modified procedure shown in the second column of Fig. 1(b) and summarized in Table 2 are much better than the previous ones, especially for the cases near the optimum underfocus.

The influence of the truncation effect

In practice, it is difficult to have an EM with resolution much better than 2 Å. Hence when using the Sayre equation in reciprocal space, the truncation effect will be much greater than in X-ray analysis. In order to reduce this effect, an artificially large temperature factor, $B = 50$, was used throughout the above test calculations. However, too large a temperature factor will cause the atoms partially to overlap each other, giving a non-negligible effect on the Sayre equation. Hence it is worthwhile to know the influence of the temperature factor on the deconvolution. From Table 3, it can be seen that in practice the temperature factor is not as important as expected. The worst Δf_{est} in Table 3 is −970 Å, which deviates only 30 Å from the true value. This yields the slightly degraded image shown in Fig. 2(c).

Table 3. *Test result on the effect of temperature factor*

B temperature factor; S figure of merit; Δf_{est} defocus (Å) estimated from (4); $\Delta f_{\text{true}} = -1000$ Å.

B	50	35	25	10	0
S	0·952	0·941	0·930	0·905	0·857
Δf_{est}	−1000	−970	−970	−970	−970

The influence of $F(000)$

In the calculation of S according to (4), we need the term $F(000)$. However, unlike X-ray analysis, it is often difficult to obtain an accurate $F(000)$ before the structure has been solved. Hence we have to omit the term $F(000)$ or use an approximate value for it. In all the above calculations, an approximate value, $F(000) = 300$, was used instead of the true value of 367. Table 4 shows the effect of different values used for $F(000)$ on the calculation of S and Δf_{est}. It can
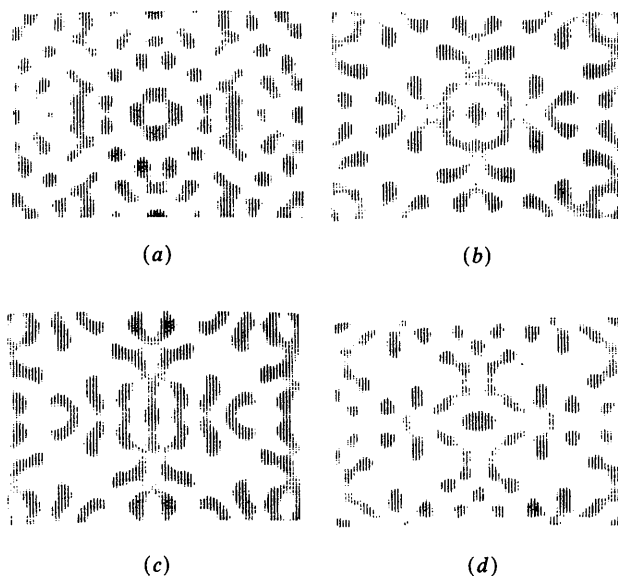

Fig. 2. Image deconvolution with different Δf_{est} values; $\Delta f_{\text{true}} = -1000$. (a) 2 Å EM of Pt(Clphthalocyanine) before deconvolution. (b) Deconvolution result using $\Delta f = -1000$ Å (expected image). (c) Deconvolution result using $\Delta f = -970$ Å. (d) Deconvolution result using $\Delta f = -940$ Å.

Table 4. *Test result on the effect of* $F(000)$

$B = 50$; $\Delta f_{true} = -1000$; $F(000)_{true} = 367$.

$F(000)$	0	200	367	400	500
S	0·460	0·878	0·970	0·975	0·985
Δf_{est}	−1000	−1000	−1000	−1000	−1000

be seen that $F(000)$ has a significant influence on the value of S, but has little effect on Δf_{est}. Hence we could omit the term $F(000)$ in the calculation of S.

Influence of the presence of heavy atoms

In principle, the Sayre equation is not valid for structures simultaneously containing light and heavy atoms. However, the results shown above on the test structure containing different kinds of atoms like C, N, Cl and Cu demonstrate that the Sayre equation could give satisfactory results. To see the effect of heavy atoms, the copper of the test structure was replaced by platinum. From Table 5, we can see that in the case of platinum perchlorophthalocyanine. Δf_{est} is −940 Å for $\Delta f = -1000$ Å giving the resultant image shown in Fig. 2(d), which is still acceptable. A better result was obtained by using the equation of Woolfson (1958) instead of Sayre's. Here Δf_{est} is −970 Å and an image like Fig. 2(c) was obtained.

Concluding remarks

The procedure proposed in this paper has been shown to be successful in processing theoretical images

Table 5. *Test result on the effect of a heavy atom*

$B = 50$; $F(000) = 300$; $\Delta f_{true} = -1000$ Å.

Sample	Pt(Clphthalocyanine)		Cu(Clphthalo-cyanine)
Equation used	Sayre equation	Woolfson's equation	Sayre equation
S	0·903	0·959	0·952
Δf_{est}	−940	−970	−1000

without preliminary structural information. In addition, it has been shown that the procedure is not sensitive to errors in the temperature factor and $F(000)$ or to the presence of heavy atoms. The next step in the investigation is to apply the method to experimental EM's. Another important task still to be begun is the extension of the method to include the dynamical diffraction effect.

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Positional Parameters Obtained With Anharmonic Temperature Factors

BY C. SCHERINGER

Institut für Mineralogie der Universität Marburg, D-3550 Marburg/Lahn, Federal Republic of Germany

Abstract

Comparisons of distances between the positions obtained from harmonic and anharmonic refinements lead to the conclusion that the positional parameters may have different physical meanings for the two cases. The mean positions are obtained if the temperature factor (t.f.) has no first-order terms in the reciprocal-lattice vector $\mathbf{Q}$ (harmonic t.f., Fourier transforms of the Gram–Charlier series); if there are first-order terms in $\mathbf{Q}$, other positions will be obtained whose meaning needs to be established. The advantages associated with the mean positions are described, and the disadvantages associated with other positions are illustrated with an example from the literature. A procedure is described in which the physical meaning (if there is any) of a non-mean position can be established and the mean position calculated. The problem of parameter bias is analyzed and numerical results are discussed for three