MOTT, N. F. & MASSEY, H. S. W. (1965). *The Theory of Atomic Collisions.* Oxford: Clarendon.
NAKAI, Y. (1970). *Acta Cryst.* A**26**, 459-460.
OHTSUKI, Y.-H. (1983). *Charged-Beam Interaction With Solids.* London: Taylor & Francis.
OKAMOTO, K., ICHINOKAWA, T. & OHTSUKI, Y.-H. (1971). *J. Phys. Soc. Jpn*, **30**, 1690-1701.
PLATZMAN, P. M. & WOLFF, P. A. (1973). *Waves and Interactions in Solid State Plasmas.* New York: Academic.
RADI, G. (1970). *Acta Cryst.* A**26**, 41-56.
REIMER, L. (1984). *Transmission Electron Microscopy. Springer Series in Optical Science*, Vol. 36. Berlin: Springer.
SERNEELS, R., VAN ROOST, C. & KNUYT, G. (1982). *Philos. Mag. A*, **45**, 677-684.
THOMAS, L. E. & HUMPHREYS, C. J. (1970). *Phys. Status Solidi A*, **3**, 599-615.
TOMAS, G. & GORINGE, M. J. (1979). *Transmission Electron Microscopy of Materials.* New York: Wiley.
UYEDA, R. & NONOYAMA, M. (1967). *Jpn. J. Appl. Phys.* **6**, 557-566.
UYEDA, R. & NONOYAMA, M. (1968). *Jpn. J. Appl. Phys.* **7**, 200-208.
WHELAN, M. J. (1965). *J. Appl. Phys.* **36**, 2099-2103, 2103-2110.
YOSHIOKA, H. (1957). *J. Phys. Soc. Jpn*, **12**, 618-628.

Acta Cryst. (1988). A**44**, 61-63

Image Processing in High-Resolution Electron Microscopy Using the Direct Method. III. Structure-Factor Extrapolation

BY LIU YI-WEI, FAN HAI-FU AND ZHENG CHAO-DE

Institute of Physics, Academia Sinica, Beijing, China

(*Received* 4 *April* 1987; *accepted* 25 *August* 1987)

Abstract

A resolution-enhancement method has been proposed which makes use of the Sayre equation [Sayre (1952). *Acta Cryst.* **5**, 60-65] to extrapolate both phases and magnitudes of structure factors. The starting point of the procedure is just a single deconvoluted electron microscopic image. No preliminary knowledge other than the chemical composition of the sample is necessary. A simulation on a theoretical image of copper perchlorophthalocyanine shows that the image resolution can be enhanced from 2 to 1 Å, resolving clearly individual atoms.

Introduction

Enhancement of the resolution of electron microscopic images by *a posteriori* processing techniques has long been attempted (Li Fang-hua, 1977; Ishizuka, Miyazaki & Uyeda, 1982; Fan Hai-fu, Zhong Zi-yang, Zheng Chao-de & Li Fang-hua, 1985). All the methods mentioned above rely on an additional electron diffraction pattern, which contains reflections corresponding to a higher resolution. Improvement in resolution can then be achieved simply by a phase extension procedure. However, without using the electron diffraction pattern, resolution enhancement is still possible. In X-ray crystallography, Fan Hai-fu & Zheng Qi-tai (1975) proposed a method using the Sayre equation (Sayre, 1952) to extrapolate both phases and magnitudes of structure factors. With this method a low-resolution image of a crystal structure can be enhanced to obtain a high-resolution picture without the necessity of collecting additional diffraction data in high-angle regions of reciprocal space. In this paper, the method has been improved and applied to high-resolution electron microscopy.

The philosophy of the method is as follows: For a crystalline sample, suppose that there are N atoms in the asymmetric unit; then, in order to reveal the structure with sufficiently high resolution, we only have to solve the $2N$ positional parameters (in the two-dimensional case). Now if we have in hand a low-resolution image of the crystal structure, which in reciprocal space can yield more than $2N$ symmetrically independent structure factors wihin its resolution limit, then in principle we can set up enough simultaneous equations to solve the $2N$ parameters. This implies that high-resolution structural information may be extracted from a low-resolution image. The Sayre equation (1) may be used for this purpose.

$$\mathbf{F_H} = (\theta/V)\sum_{\mathbf{H'}} \mathbf{F_{H'}}\mathbf{F_{H-H'}}. \quad (1)$$

Structure factors beyond the resolution limit can be obtained from the left-hand side of (1) using a set of structure factors at low resolution on the right-hand side. A least-squares procedure based on (1) has accordingly been developed.

The least-squares procedure

Suppose that we have m known structure factors with reciprocal vectors all within a resolution limit H_L.

0108-7673/88/010061-03$03.00

We are going to derive n unknown structure factors beyond the resolution limit. Denote the known structure factors by $\mathbf{F}_\mathbf{H}$ and the unknown structure factors by $\mathbf{F}^0_\mathbf{H}+\Delta\mathbf{F}_\mathbf{H}$, where $\mathbf{F}^0_\mathbf{H}$ is the initial value input to each cycle of the least-squares procedure, and $\Delta\mathbf{F}_\mathbf{H}$ is the correction to $\mathbf{F}^0_\mathbf{H}$. From (1) we can set up m equations for the known structure factors and n equations for the unknown ones:

$$\mathbf{F}_\mathbf{H} \simeq (\theta/V)\sum_{\mathbf{H}'}^{m+n} \mathbf{F}_{\mathbf{H}'}\mathbf{F}_{\mathbf{H}-\mathbf{H}'} \equiv \mathbf{S}_\mathbf{H}(\mathbf{F}_{\text{unknown}}) \quad (2)$$

where $H \leq H_L$, and

$$\mathbf{F}^0_\mathbf{H}+\Delta\mathbf{F}_\mathbf{H} \simeq (\theta/V)\sum_{\mathbf{H}'}^{m+n} \mathbf{F}_{\mathbf{H}'}\mathbf{F}_{\mathbf{H}-\mathbf{H}'} \equiv \mathbf{S}_\mathbf{H}(\mathbf{F}_{\text{unknown}}) \quad (3)$$

where $H > H_L$.

A least-squares procedure was developed to solve the n unknown $\mathbf{F}_\mathbf{H}$'s by minimizing $\sum^m_\mathbf{H}|\mathbf{F}_\mathbf{H}-\mathbf{S}_\mathbf{H}|^2$ for $H \leq H_L$ and $\sum^n_\mathbf{H}|\Delta\mathbf{F}_\mathbf{H}-\mathrm{d}\mathbf{S}_\mathbf{H}|^2$ for $H > H_L$, where $\mathrm{d}\mathbf{S}_\mathbf{H}$ is the differential of $\mathbf{S}_\mathbf{H}$ with respect to $\mathbf{F}_\mathbf{H}$. The initial $\mathbf{F}^0_\mathbf{H}$'s in the first cycle are set to zero. A greater weight is given to the equations for $H \leq H_L$. The iteration will stop at the cycle when all $|\Delta\mathbf{F}_\mathbf{H}|$ become smaller than a given value. The $F(0,0)$ value used in (2) and (3) can be calculated from the known chemical composition.

Compensation for systematic errors

When dealing with electron microscopic images, the Sayre equation suffers from serious systematic errors, which come from the uncertainty of the absolute scale of $\mathbf{F}_\mathbf{H}$, the existence of unequal atoms, the truncation effect *etc.* These can be compensated in part by the following treatments.

Firstly, the coefficient θ of the Sayre equation (1) is expressed approximately as a linear function of H, *i.e.*

$$\theta = a - bH.$$

a and b are then treated as variables and modified in each cycle of the least-squares procedure. Hence $\mathbf{S}_\mathbf{H}$ in (2) and (3) becomes a function of $n+2$ variables, *i.e.* a function of a, b and n unknown $\mathbf{F}_\mathbf{H}$'s.

Secondly, the solution of the n unknown structure factors resulting from the least-squares procedure can give a best fit to the Sayre equation in the presence of systematic errors, but this is not the best solution for the true structure factors. A better result for $\mathbf{F}_\mathbf{H}$ $(H > H_L)$ can be obtained from the left-hand side of the Sayre equation by substituting the least-squares resultant $\mathbf{F}_\mathbf{H}$'s into the right-hand side.

Test and result

A theoretical image at 2 Å resolution of the model structure of copper perchlorophthalocyanine (Fig. 1*a*)* was used to test the procedure. By Fourier transformation of this image, a set of structure factors within 0·5 Å^{-1} were obtained. The least-squares procedure described above was then used to derive structure factors within the region from 0·5 to 1·0 Å^{-1}. In

---

* This image may be considered as the result of a theoretical electron microscopic image after suitable deconvolution [see paper II of this series (Han Fu-son, Fan Hai-fu & Li Fang-hua, 1986)].

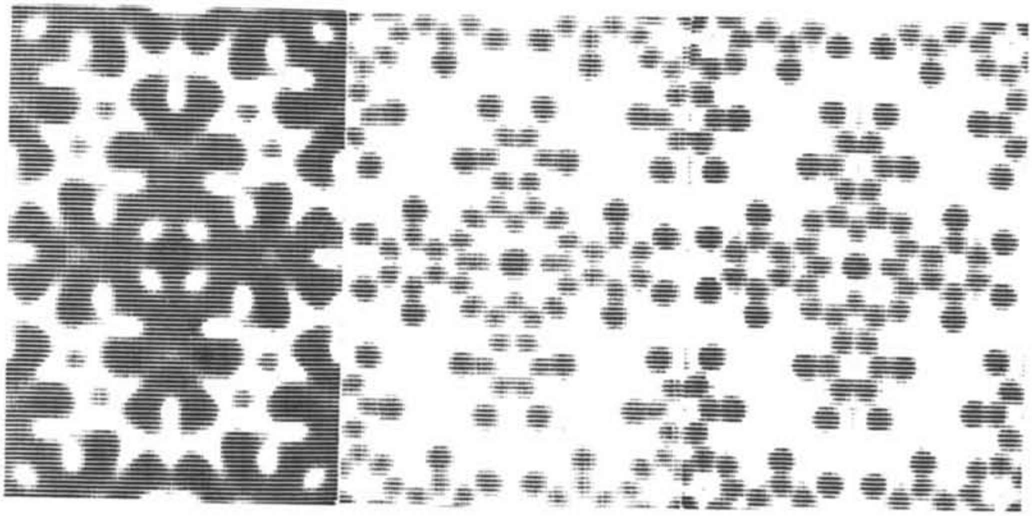
(*a*) (*b*) (*c*)

Fig. 1. Result of structure-factor extrapolation of copper perchlorophthalocyanine. Chemical formula: $C_{32}Cl_{16}CuN_8$. Unit cell: $a = 19{\cdot}62$, $b = 26{\cdot}04$, $c = 3{\cdot}76$ Å, $\beta = 116{\cdot}5°$. Plane group of the projection along the c axis: *cmm*. (*a*) Projection map of the theoretical potential distribution function along the c axis at 2 Å resolution. (*b*) Improved map obtained from (*a*) by structure-factor extrapolation. (*c*) Expected projection of the potential distribution at 1 Å resolution.

this example, the number of atomic parameters to be solved is 30, which is smaller than the number of known structure factors, 49. This implies that the problem is in principle solvable. Actually, instead of solving directly the atomic parameters, we derived 141 unknown structure factors beyond 2 Å resolution. The process stopped after 20 cycles of iteration. The discrepancy factor R for the m known structure factors dropped from 0·52 to 0·02, while that for the n unknown ones dropped from 1·0 to 0·36.* The resultant image is shown in Fig. 1(b), which shows a prominent enhancement of resolution revealing all the individual atoms. The expected image at 1 Å resolution is shown in Fig. 1(c) for comparison.

Concluding remarks

The present work confirms the possibility of extracting high-resolution structural information from a low-resolution image. This will be useful not only in electron microscopy but also in diffraction analysis.

An advantage of the method described here is that it does not need any experimental electron diffraction data in addition to an electron micrograph. This is important for radiation-sensitive materials since it makes the experiment simpler to implement. This is also important for enabling the method to be used, at least in theory, for non-crystalline samples.

---

* The R factor is defined as

$$R=\sum_{\mathbf{H}}|\mathbf{F}_{\mathbf{H}\,\mathrm{true}}-\mathbf{F}_{\mathbf{H}\,\mathrm{estimated}}|\Big/\sum_{\mathbf{H}}|\mathbf{F}_{\mathbf{H}\,\mathrm{true}}|,$$

where $H\leq H_L$ for the known structure factors and $H>H_L$ for the unknown structure factors. Values of $\mathbf{F}_{\mathbf{H}\,\mathrm{true}}$ are those obtained from Fourier transformation of the structure, while values of $\mathbf{F}_{\mathbf{H}\,\mathrm{estimated}}$ are calculated each cyle from the Sayre equation. The initial $\mathbf{F}_{\mathbf{H}\,\mathrm{estimated}}$ values for the unknown structure factors are all set to zero.

References

FAN HAI-FU & ZHENG QI-TAI (1975). *Acta Phys. Sin.* **24**, 97-104.
FAN HAI-FU, ZHONG ZI-YANG, ZHENG CHAO-DE & LI FANG-HUA (1985). *Acta Cryst.* A**41**, 163-165.
HAN FU-SON, FAN HAI-FU & LI FANG-HUA (1986). *Acta Cryst.* A**42**, 353-356.
ISHIZUKA, K., MIYAZAKI, M. & UYEDA, N. (1982). *Acta Cryst.* A**38**, 408-413.
LI FANG-HUA (1977). *Acta Phys. Sin.* **26**, 193-198.
SAYRE, D. (1952). *Acta Cryst.* **5**, 60-65.

Acta Cryst. (1988). A**44**, 63-70

Phase Determination Using High-Order Multiple Diffraction of X-rays

BY SHIH-LIN CHANG, HSUEH-HSING HONG, SHAU-WEN LUH, HIASO-HSI PAN AND MAU-CHU TANG

Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30043

AND JOSÉ MARCOS SASAKI

Instituo de Física, Universidade Estadual de Campinas, Campinas, São Paulo, 13100 *Brazil*

(*Received* 8 *June* 1987; *accepted* 27 *August* 1987)

Abstract

The effect of invariant phases on the intensity profiles of high-order N-beam X-ray diffractions, with $N>3$, is investigated. Theoretically, the second-order Bethe approximation and the graphic analysis of the structure-factor multiplets involved in the dispersion equation of the dynamical theory of X-ray diffraction are employed to reveal the dominant invariant phases in the multiple diffraction processes. It is shown that the phases of the triplets or the quartets are the effective phases which affect the multiply diffracted intensities. Experimentally, the intensity profiles of four-, five-, six- and eight-beam cases provide clear evidence to support the theoretical considerations.

1. Introduction

N-beam multiple diffraction, with $N>2$, occurs when N reciprocal-lattice points are brought simultaneously onto the surface of the Ewald sphere. The interaction of the N diffracted beams gives rise to a modification of the intensity background of any diffracted beam involved in this N-beam case. Intensity variation near a three-beam X-ray or electron diffraction has been investigated and used to reveal the phase dependence of the diffraction intensities in transmission geometry (Kambe & Miyake, 1954; Hart & Lang, 1961; Post, 1977; Jagodzinski, 1980; Høier & Aanestad, 1981) and in reflection geometry (Colella, 1974; Chapman, Yoder & Colella,

0108-7673/88/010063-08$03.00