Ultramicroscopy 155 (2015) 11–19

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

A complete comparison of simulated electron diffraction patterns using different parameterizations of the electron scattering factors

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ARTICLE INFO

Article history:
Received 13 November 2014
Received in revised form
12 March 2015
Accepted 23 March 2015
Available online 24 March 2015

Keywords:
Electron scattering factors
Electron diffraction
Phonons

ABSTRACT

The steadily improving experimental possibilities in instrumental resolution as in sensitivity and quantization of the data recording put increasingly higher demands on the precision of the scattering factors, which are the key ingredients for electron diffraction or high-resolution imaging simulation. In the present study, we will systematically investigate the accuracy of fitting of the main parameterizations of the electron scattering factor for the calculation of electron diffraction intensities. It is shown that the main parameterizations of the electron scattering factor are consistent to calculate electron diffraction intensities for thin specimens and low angle scattering. Parameterizations of the electron scattering factor with the correct asymptotic behavior (Lobato and Dyck [5], Kirkland [4], and Weickenmeier and Kohl [2]) produce similar results for both the undisplaced lattice model and the frozen phonon model, except for certain thicknesses and reflections.

1. Introduction

All the existing programs for quantitative simulations of experiments in electron microscopy and electron diffraction require the input of electron scattering factors for the atoms. In principle, the simulation programs could use the numerical values for the scattering factors and interpolate them to obtain the atomic electrostatic potential or scattering factor at the required points. But in order to reduce the data and improve the numerical accuracy, the electron scattering factors are parameterized by linear combination of simple basic functions. These parameterizations of the electron scattering factors are available from several publications [1–5] and are computed by fitting the scattering factors with discrete numerical results obtained from accurate ab initio quantum mechanical calculations [1,6,7,4].

Originally the electron scattering factors were parameterized by using a linear combination of Gaussian functions [8,9,1,3], which is sufficient for small spatial frequencies but cuts the scattering factors for large scattering angles. Weickenmeier and Kohl [2] used more complicated functions to fit the electron scattering factors to achieve a correct asymptotic behavior for large angles. Kirkland [4] used a combination of Lorentzians and Gaussians to fit the tabulated electron scattering data. The inclusion of the Lorentzians in this parameterization is needed to assure the correct asymptotic behavior for large angles. Lobato and Van Dyck [5] parameterized the electron scattering factors by using the analytic non-relativistic hydrogen electron scattering factors as basis functions. Moreover, this parameterization includes the correct physical constraints in the electron scattering factor and its derived quantities such as the x-ray scattering factor, the electron density distribution and the atomic electrostatic potential.

For simple routine simulations where precision is not so important most of these parameterizations are sufficiently adequate. However, the steadily improving experimental possibilities in instrumental resolution as in sensitivity and quantization of the data recording put increasingly higher demands on the precision of the scattering factors.

In the present study, we will systematically investigate the accuracy of fitting of the main parameterizations of the electron scattering factor for the calculation of electron diffraction intensities. To achieve this, we start by performing a full comparison in all ranges between the different parameterizations of the electron scattering factor and its derived quantities for copper ($Z=29$). After that, we perform accurate multislice calculations of the electron diffraction patterns of Cu-crystal for a range of thicknesses by using the undisplaced lattice and frozen phonon model. Next, the diffracted intensities as a function of thickness are compared for both Zero Laue zones (ZOLS) as Higher order Laue zones (HOLZ) reflections. And finally, the integrated diffuse scattering versus thickness is calculated by using the frozen phonon model. Comparison of all these results allows us to draw reliable conclusions about the range of applicability of these

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http://dx.doi.org/10.1016/j.ultramic.2015.03.018
0304-3991/© 2015 Published by Elsevier B.V.

parameterizations.

2. Parameterizations of the electron scattering factor and its derived quantities

Let us start with some definitions and formulas, which allow us to derive different quantities from the electron scattering factors [4].

For an atom with atomic number Z, the X-ray scattering factor is related to the electron scattering factor $f_e(g)$ via the inverse Mott–Bethe formula [10,11]

$$f_x(g) = Z - 2\pi^2 a_0 g^2 f_e(g), \tag{1}$$

where g is the magnitude of the three-dimensional vector in the reciprocal space and a_0 is the Bohr radius. $f_e(g)$ is in units of Å and $f_x(g)$ is a dimensionless quantity corresponding to the distribution of electrons. For neutral atoms $f_x(0) = Z$. The Mott–Bethe formula is equivalent to the solution of Poisson's equation in reciprocal space yielding the potential distribution from the charge distribution.

The electron charge distribution is related to the X-ray scattering factor by means of its inverse three-dimensional Fourier transform

$$\rho(\mathbf{r}) = \int f_x(\mathbf{g})\exp(2\pi\mathbf{g}\cdot\mathbf{r})\,d\mathbf{g}, \tag{2}$$

where $\mathbf{r}$ and $\mathbf{g}$ are the three-dimensional vector in the real and reciprocal space, respectively and the integration extends over all of space.

By definition the atomic electrostatic potential is related to the electron scattering factor $f_e(g)$ by means of the inverse three dimensional Fourier transform

$$\mathrm{V}(\mathbf{r}) = \frac{1}{\kappa}\int f_e(\mathbf{g})\exp(2\pi\mathbf{g}\cdot\mathbf{r})\,d\mathbf{g}, \tag{3}$$

where $\kappa = 4\pi\varepsilon_0/2\pi a_0 e$, e is the electron charge, ε_0 is the vacuum permittivity and a_0 is the Bohr radius.

If we know the parameterization of the electron scattering factor, we can use the above definitions and formulas to derive the X-ray scattering factor, the electron density distribution and the atomic electrostatic potential.

In Refs. [8,9,1,3] the electron scattering factors were parameterized by using a linear combination of Gaussian functions. Although this parameterization is sufficient for small spatial frequencies, it cuts the scattering factors for large scattering angles, which is inappropriate for dynamical calculations that involve large scattering angles or for the proper calculation of the thermal diffuse scattering (TDS). The most accurate Gaussian parameterization is given by Peng et al. [3]. They used five Gaussians to fit the tabulated electron scattering data and perform a nonlinear least squares fitting by using simulated annealing (SA) optimization [12]. For this parameterization the electron scattering factor and its derived quantities can be written as

$$f_e(g) = \sum_{i=1}^{5} a_i \exp\left(-b_i g^2\right), \tag{4}$$

$$f_x(g) = Z - \sum_{i=1}^{5} 2\pi^2 a_0 a_i g^2 \exp\left(-b_i g^2\right), \tag{5}$$

$$\rho(r) = Z\delta(r) + \sum_{i=1}^{5} \frac{\pi^{11/2} a_0 a_i}{b_i^{7/2}}\left(2r^2 - \frac{3b_i}{\pi^2}\right)\exp\left(-\frac{\pi^2 r^2}{b_i}\right), \tag{6}$$

$$\mathrm{V}(r) = \sum_{i=1}^{5} \frac{\pi^{3/2} a_i}{\kappa b_i^{3/2}} \exp\left(-\frac{\pi^2 r^2}{b_i}\right). \tag{7}$$

where a_i and b_i have units of Å and Å^2, respectively.

Weickenmeier and Kohl [2] used five more complicated functions to fit the electron scattering data to achieve the correct asymptotic behavior of the electron scattering factors at large values of g. In this parameterization, the nonlinear minimization procedure was carried out by using the Levenberg–Marquardt algorithm (LMA) [13]. The drawback of the LMA is that it only finds a local minimum, which means that the result of fitting parameters depends sensitively on their initial assigned values. For this parameterization the electron scattering factor and its derived quantities can be written as

$$f_e(g) = \sum_{i=1}^{5} a_i \frac{\left(1 - \exp\left(-b_i g^2\right)\right)}{g^2} \tag{8}$$

$$f_x(g) = \sum_{i=1}^{5} 2\pi^2 a_0 a_i \exp\left(-b_i g^2\right) \tag{9}$$

$$\rho(r) = \sum_{i=1}^{5} \frac{2\pi^{7/2} a_0 a_i}{b_i^{3/2}} \exp\left(-\frac{\pi^2 r^2}{b_i}\right) \tag{10}$$

$$V(r) = \sum_{i=1}^{5} \frac{\pi a_i}{\kappa} \frac{Erfc\left(\frac{\pi r}{b_i}\right)}{r}. \tag{11}$$

where a_i and b_i have units of Å^{-1} and Å^2, respectively.

To obtained the correct asymptotic behavior of the electron scattering factors at high angles, Kirkland [4] used a combination of three Lorentzians and three Gaussians to fit the tabulated electron scattering data. Although Kirkland used LMA for the nonlinear minimization procedure, his fit was improved by trying several different starting points and keeping only the best one. This parameterization allows us to express the electron scattering factor and its derived quantities as

$$f_e(g) = \sum_{i=1}^{3} \frac{a_i}{b_i + g^2} + \sum_{i=1}^{3} c_i \exp\left(-d_i g^2\right) \tag{12}$$

$$f_x(g) = Z - \sum_{i=1}^{3} \frac{2\pi^2 a_0 a_i g^2}{b_i + g^2} - \sum_{i=1}^{3} 2\pi^2 a_0 c_i g^2 \exp\left(-d_i g^2\right) \tag{13}$$

$$\rho(r) = \left(Z - \sum_{i=1}^{3} 2\pi^2 a_0 a_i\right)\delta(r) + \sum_{i=1}^{3} 2\pi^3 a_0 a_i b_i \frac{\exp\left(-2\pi\sqrt{b_i}\,r\right)}{r} + \sum_{i=1}^{3} \frac{\pi^{11/2} a_0 c_i}{d_i^{7/2}}\left(2r^2 - \frac{3d_i}{\pi^2}\right)\exp\left(-\frac{\pi^2 r^2}{d_i}\right) \tag{14}$$

$$\mathrm{V}(r) = \sum_{i=1}^{3} \frac{\pi a_i}{\kappa} \frac{\exp\left(-\frac{2\pi r}{\sqrt{b_i}}\right)}{r} + \sum_{i=1}^{3} \frac{\pi^{3/2} c_i}{\kappa d_i^{3/2}} \exp\left(-\frac{\pi^2 r^2}{d_i}\right). \tag{15}$$