

TOPICAL REVIEW

Direct methods for surface crystallography

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Online at stacks.iop.org/JPhysCM/20/304208**Abstract**

In the most developed branches of crystallography, structure solution proceeds by two distinct steps: first, an approximate model of the structure is deduced *directly* from the measured data by an algorithm which assumes no preconceived model; second, a process of structure refinement simulates the experimental data for systematic variations of the parameters of such a model and determines a final structure to be that which agrees best with the data. The developments of direct methods for surface crystallography are aimed at enabling the first of these steps to be performed by an objective algorithm applied directly to the experimental data, in order to avoid the (fallible) human guesswork that has been largely applied up to the present to postulate structural models for subsequent refinement.

(Some figures in this article are in colour only in the electronic version)

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1. Introduction

Crystallography is the science of the determination of the atomic-scale structure of repeat units (or *unit cells*) of a crystal from the distribution of the scattering of radiation incident on it. If we restrict our attention initially to the far-field measurement of weak scattering (or single scattering) of an incident plane wave (as is usually the case with x-ray

scattering), the complex amplitudes of the scattered radiation may be regarded as a set of Fourier coefficients of the distribution of scattering matter within each unit cell. If these complex amplitudes may be measured, the recovery of the structure of the unit cell would simply require performing an inverse Fourier transform of those amplitudes. Unfortunately, usual crystallographic experiments measure not these complex amplitudes, but rather their square moduli in the form of diffracted *intensities*. The square roots of these measured intensities are proportional to the (real) amplitudes of the scattered radiation, but the corresponding *phases* are not measured directly.

A major challenge of crystallography is the determination of these phases. In the crystallography of bulk samples, there are two main classes of techniques: those which require information extraneous to the intensities from the diffraction of radiation of a single wavelength, and those which require no further information. In the former class fall three techniques commonly used in protein crystallography, namely multiple isomorphous replacement (MIR) (Green *et al* 1954, Blow and Crick 1959) which requires extra experimental data from related compounds with heavy-atom substitutions; multi-wavelength anomalous dispersion (MAD) (Hendrickson 1991, Leahy *et al* 1992) which requires extra diffraction data from x-rays of wavelengths close to absorption edges of atoms of the sample; and the technique of molecular replacement (Rossman and Blow 1962) which requires a knowledge of the structure

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