Crystal Quality – A Practical Guide

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Suitability for Charge Density Analysis

The suitability factor *S*, which defines how likely you are to obtain a satisfactory charge density analysis from a particular compound, has been quantified by Coppens :

$$S = \frac{V}{\sum n_{core}^2}$$

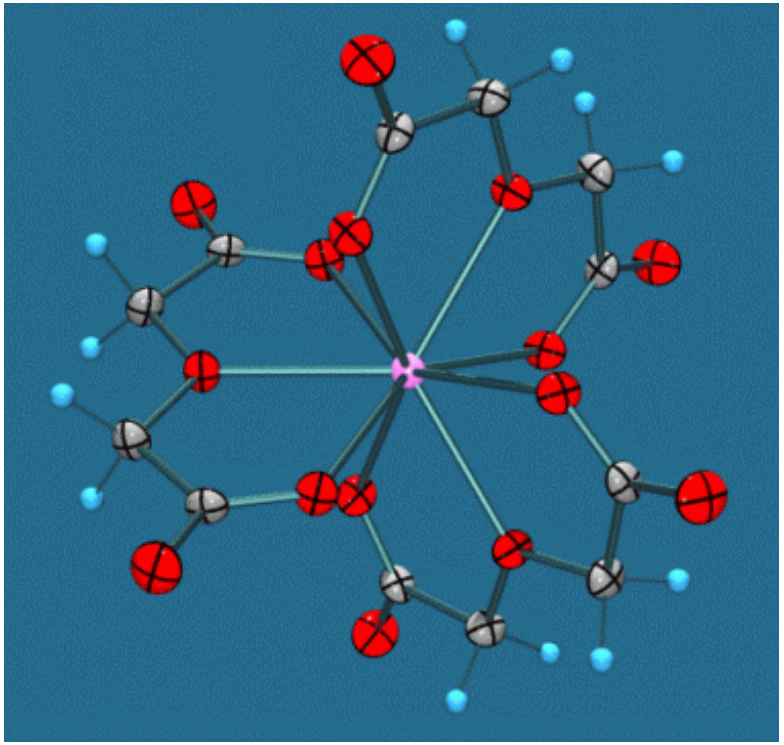
S = 3 – 5 for organic crystals
S ~ 0.5 for 1st row transition metal complexes

S ~ 0.1-0.2 for metals and alloys

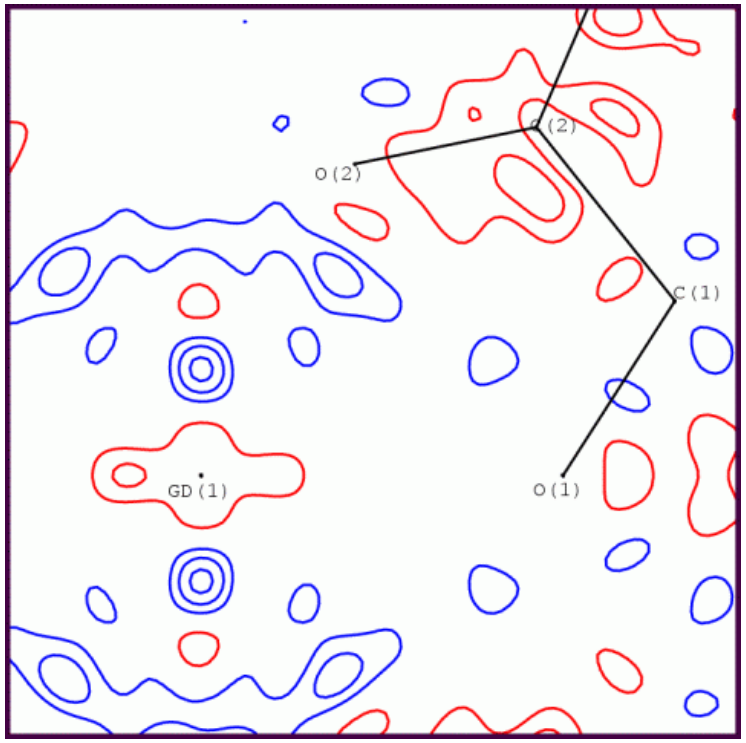
E. D. Stephens & P. Coppens (1976) *Acta Cryst.* **A32**, 915

Growing Crystals

The single most important factor in obtaining high quality data suitable for charge density analysis is the quality of the crystal. An example is the gadolinium complex $Na_5[GdL_3]^{3-}(BF_4^-)_2$



The anionic complex $[Gd(C_4H_4O_5)_3]^{3-}$.
Z = 64 !! S = 0.17



The difference Fourier map after multipole refinement. Contours at 0.05 eA^{-3}
R(F) = 0.65 % GOF = 1.26, no unobserved !!

Growing Crystals

Crystal growing is an art more than a science - *quality* not *quantity* is needed (not same as recrystallisation!).

Remember - *one crystal* is enough !

Some web sites with useful hints on crystal growing

- http://www.xray.ncsu.edu/GrowXtal.html
- http://www.cryst.chem.uu.nl/growing.html
- http://www.as.ysu.edu/~adhunter/Teaching/Chem832/ADHChXIV.pdf

The latter is a detailed guide

Growing Crystals

Crystals are best grown *slowly* - much more chance that they will be single. Crystal *quality* is the main determinant for any structure analysis.

Aim to have a size of ~ 0.3-0.5 mm in at least one dimension. X-ray diffracted intensities determined by the *volume* of crystal in the x-ray beam.

General techniques of crystal growing are :

- growing from solution - cooling, solvent diffusion, vapour diffusion
- sublimation - only suitable for compounds with significant vapour pressure
- crystallisation from melts - suitable for low melting compounds
- gel crysallisation - somewhat specialised but gives superb quality

Growing Crystals

Choice of solvent is very important - choose one in which the compound is *reasonably* soluble but not *too* soluble.

Better to use solvents which are not included in crystals - hexane or dichloromethane usually OK. Diethyl ether, acetonitrile or acetone often become included in crystals – problems with solvent loss and/or disorder.

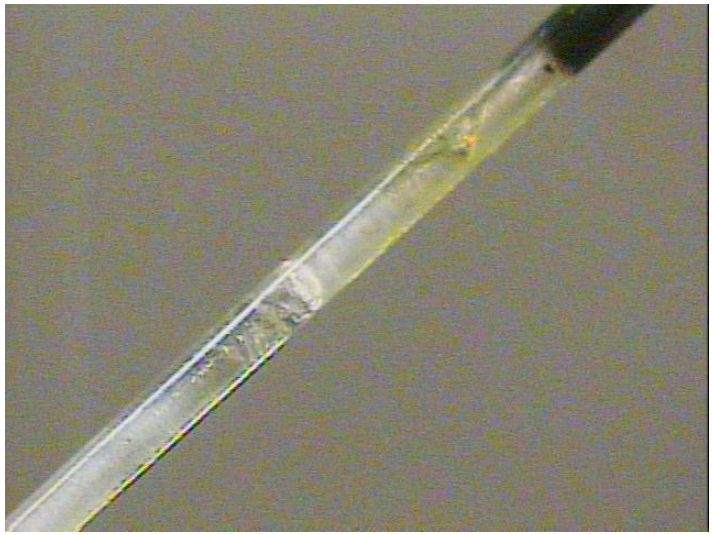
Aim to have as few nucleation sites as possible :

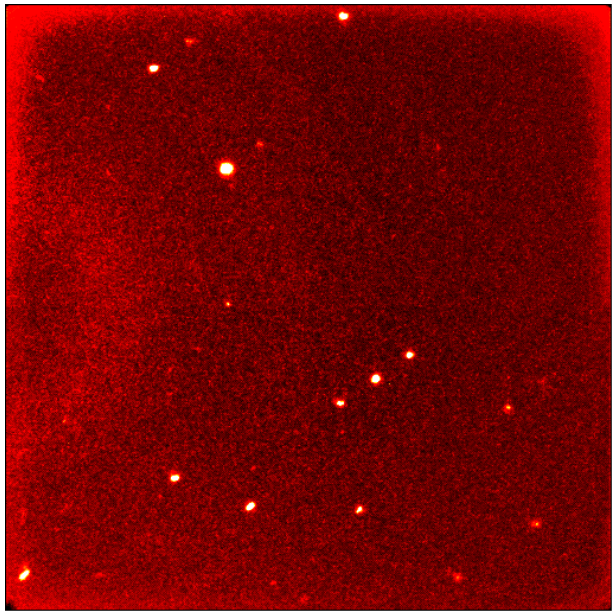
- use *clean glassware* - NMR tubes (teflon may be better!)
- filter solutions carefully to remove dust (or other) particles
- keep away from vibrations (such as vacuum pumps)

Growing Crystals from Melts

Many interesting compounds are liquids or gases at room temperature.
To obtain crystals it is necessary to grow them from melts.
Experimentally this is done by placing the sample into a capillary, which is mounted directly on the diffractometer. The sample is then crystallised in situ by means of a zone refinement technique using an infra-red laser and a cryo-cooling device.

Simon Parsons - Edinburgh





Crystal Quality

Ideal shape for a crystal specimen is a sphere (minimises absorption effects) - the more isotropic in shape the better.

Avoid plate-like crystals with a very thin plate direction.

May be necessary to cut crystals - but some crystals do not survive cutting.

Crystal *quality* can be ascertained in two main ways :

- Physical examination under a microscope - polarising microscopes are particularly useful in this respect but expensive.

- Examination of diffraction pattern on the diffractometer - very quick with area-detectors.

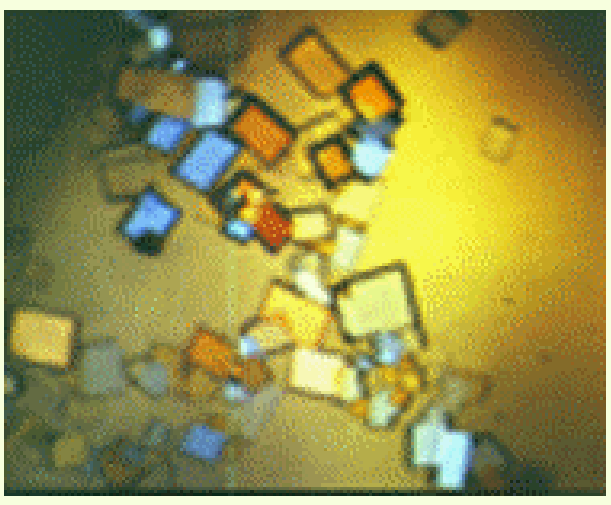
Physical examination under *normal light* is very important. Ideally a crystal should

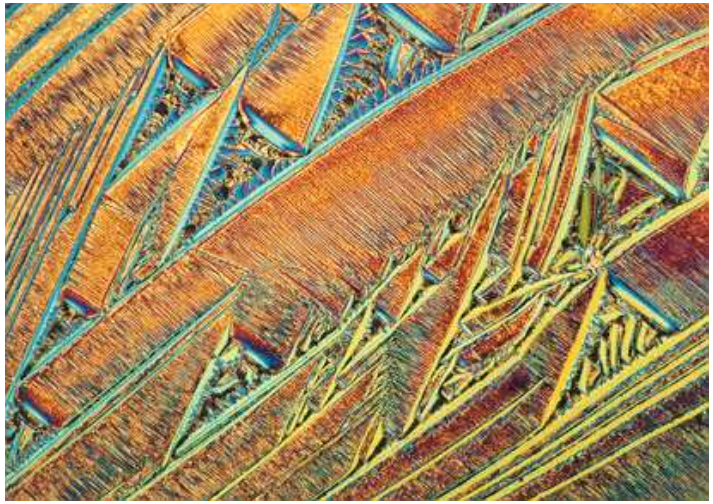
- have well formed faces
- should not be deformed or curved (may indicate internal stresses)
- should not be obviously twinned or grown together or have “babies”
- should not have re-entrant faces (may indicate possible twin)

Viewing Crystals under a Polarising Microscope

Physical examination under polarised light can be helpful - but …..

- crystal must be opaque to light
- cubic crystals no good or tetragonal,trigonal/hexagonal along high symmetry axis also opaque
- single crystals should extinguish sharply every 90^{o} - if not, a possible twin !



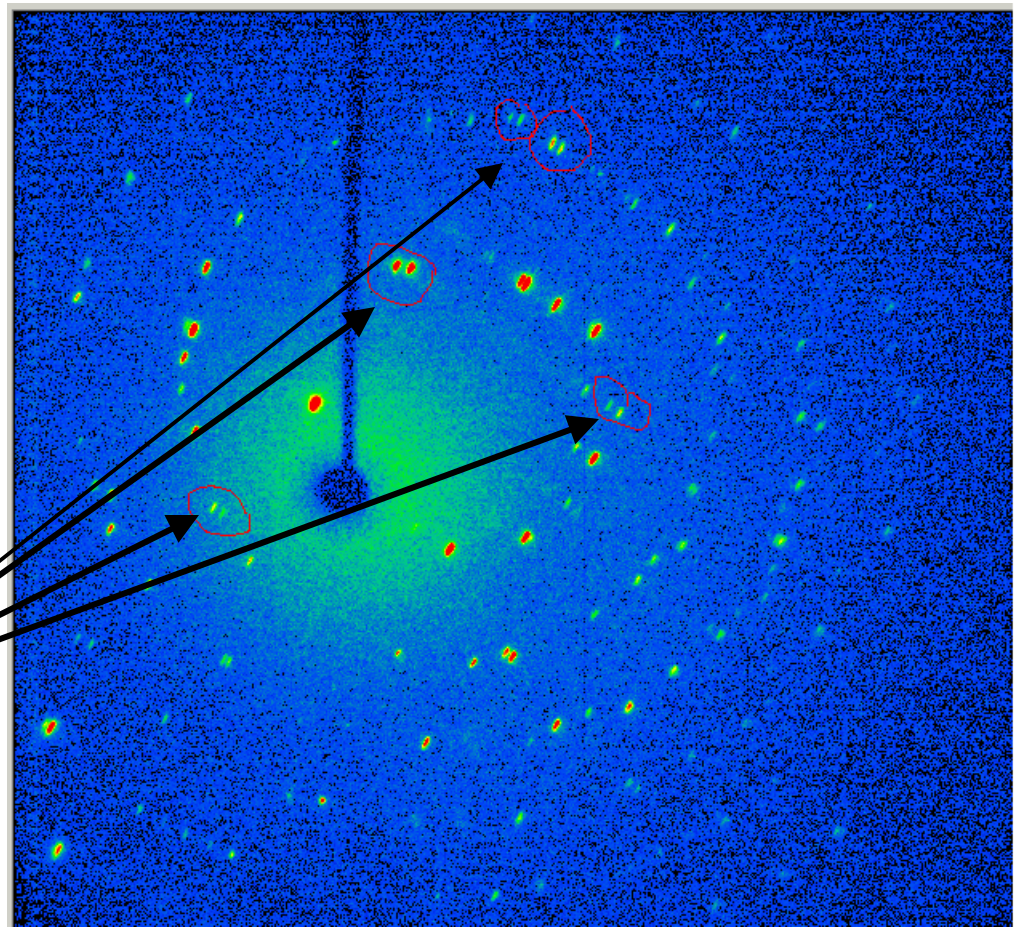


Crystal Quality on Diffractometer

Examination on diffractometer is most common nowadays.

With area detectors it is possible to screen crystals very rapidly.

Easy to spot twinned crystals

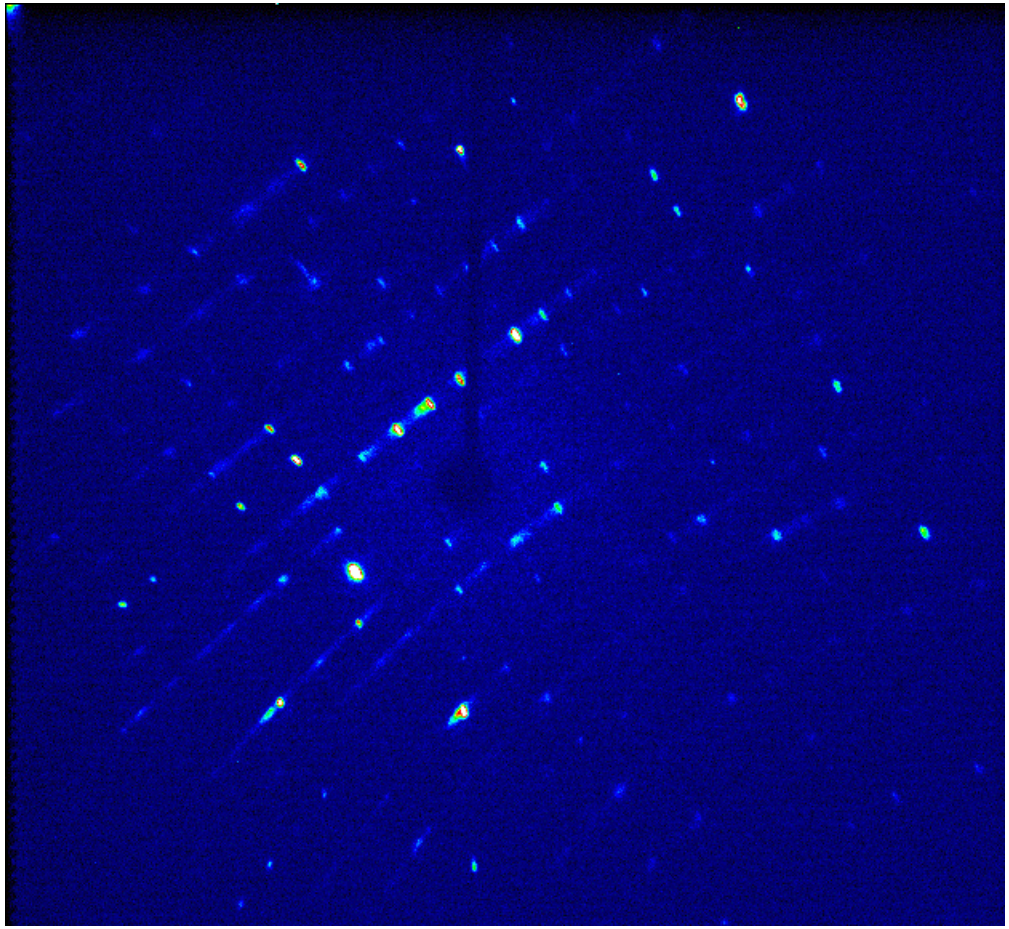


Spots here are all doubled

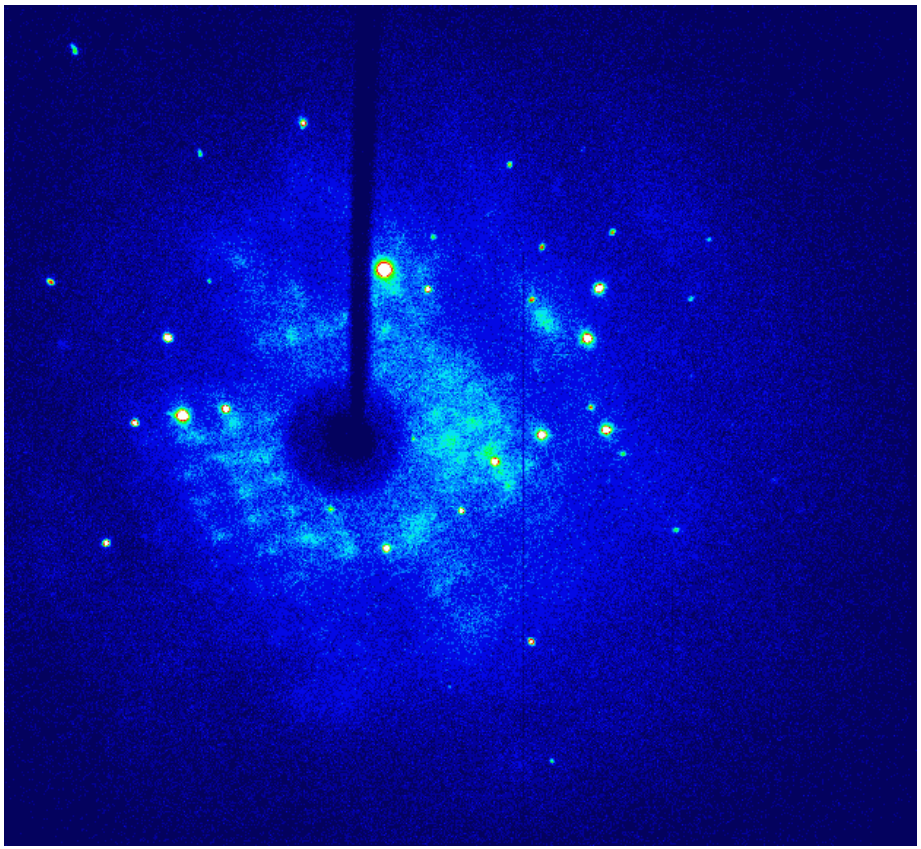
Crystal Quality on Diffractometer

This crystal shows streaks along the layer lines

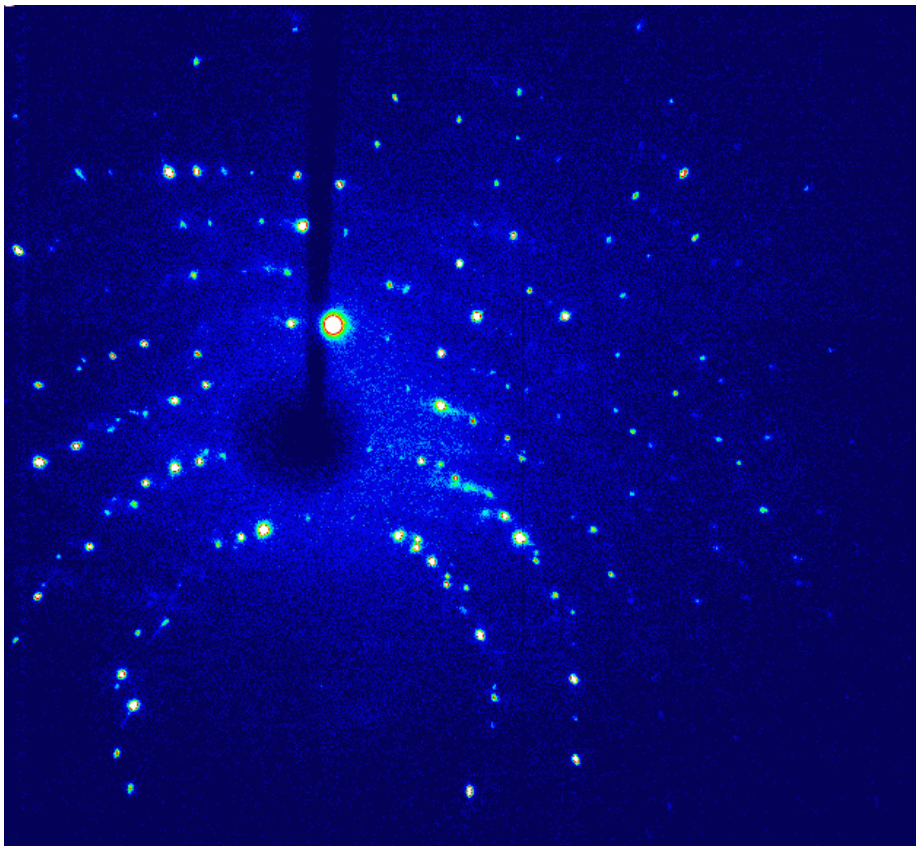
and high mosaicity ...



Crystal Quality on Diffractometer



Room temp



100 K

$Fe_3(CO)_{12}$ showing diffuse scattering due to disorder and phase change