

## DEVELOPMENT AND USE OF ELECTRON DIFFRACTION IN NANOSTRUCTURAL MINERALOGY

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### INTRODUCTION

In less than one Century X-ray crystallography has described the atomic structure of millions of phases, both organic and inorganic, with a resolution otherwise impossible for conventional optical instruments. Unfortunately, even with synchrotron sources, single crystal X-ray diffraction is possible only for crystals with of some microns. Actually, smaller crystals do not guarantee a sufficient diffracting volume. Moreover, it is not possible to focus the X-ray beam on single nanocrystals. Consequently, it is not possible to use X-rays to investigate single nanocrystals in a polyphasic mixture or aggregate, such as a rock (see for instance Buseck, 1992).

In many cases it is possible to solve and refine structures by X-ray powder diffraction. However this technique is strongly affected by the monodimensional reduction of data, which involves overlapping of peaks and difficulties in determining the correct space group and the real intensity reflections. Moreover, powder diffraction is strongly affected by experimental factors not easily predictable or properly modelable, such preferential orientation of grains or fragments of anomalous dimensions. Finally this technique is difficultously applicable to polyphasic mixtures and high defectual materials.

The first attempt of quantitative structural analysis from electron diffraction data dates back to more than 70 years ago (Rigamonti, 1936). Despite this early attempt, electron crystallography was for a long time regarded as an unreliable technique, since it was demonstrated that the measured intensities significantly differ from values predicted by kinematic theory, *i.e.* assuming a single diffraction event inside the crystal. Nevertheless, since the second half of the 70s, electron crystallography has attracted a growing interest, especially after the demonstration that direct methods can be applied successfully to electronic diffraction data set (Dorset & Hauptman, 1976).

Electron crystallography electronic presents important advantages. First, it is possible to gain information from single nanocrystals. Indeed, unlike X-rays, electrons are easily deflected by magnetic fields. Today, technological development allows to assemble transmission electron microscope (TEM) able to focus the beam in spot less than 0.5 nm. The interaction of electrons with matter is about  $10^6$  times higher than for X-rays making possible to get diffraction patterns from nanovolumes.

At the same time, the ratio between diffusion coefficients of heavy and light atoms is relatively small, thus ensuring a better resolution for light atoms and in particular for H (Dorset, 1996). Moreover, getting electron diffraction patterns requires only few seconds and the large curvature of the Ewald sphere allows to collect more reflections with a single orientation of the sample. At last, it is possible to collect diffraction patterns in different setting: diffraction collected with a parallel beam by inserting an area diaphragm (SAED), diffraction from a pseudo-parallel nanobeam, diffraction from a convergent beam, diffraction from a precessed beam (Vincent & Midgley, 1994).

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Unfortunately, the main drawback of electron crystallography derives from its own strengths. The strong interaction of electrons with matter and the simultaneous diffraction of many reflections, as well as the lack of mosaicity in single nanocrystals, generate not-negligible dynamic effects of diffusion. The electron beam can be diffracted several times travelling the crystal, while each diffracted beam may in turn give rise to more diffraction events. These dynamic effects turn the intensities of reflections off the expected kinematic ones, jeopardizing any structural solution and refinement. The mathematical models able to describe this phenomenon are very complex and are insufficient in the presence of defects or lateral variations of thickness. Moreover, for their strict applications you should know in advance at least part of the investigated structure (Dorset, 1995, 1996).

The purpose of this thesis is to highlight the potential of electron diffraction for quantitative analysis in nanostructural mineralogy. Some of the difficulties encountered working with this kind of data are discussed and addressed. At last, we propose models and routines for structural solution and refinement of minerals, in presence of pseudo-kinematic and dynamic data set.

#### EMPLOYMENT OF SAED FOR ANALYSIS OF COMPLEX NONOSTRUCTURES: POLYGONAL SERPENTINE

Polygonal serpentine (PS) is a good example of a structure that could not be solved without high resolution TEM images and SAED. PS consists of polygonal fibers composed by different polytypes (Baronnet & Mellini, 1992; Baronnet & Devouard, 2005). With the only X-ray diffraction it was just possible to identify this phase by the presence of additional reflections in powder diffraction (Brindley & von Knorring, 1954), but nothing more could be said about the presence of different polytypes, their structures and their arrangement into the fiber (Mugnaioli *et al.*, 2007).

We develop a modeling program in order to index the complex [100] diffraction pattern and understand all its features, such rings, arcs and cusps (Fig. 1). At the same time we describe the geometric rules that regulate the lateral arrangement of polytypes and the stacking of polytypic successions in a single sector. In particular, it is possible to reduce all diffraction patterns to 11 admissible cases.

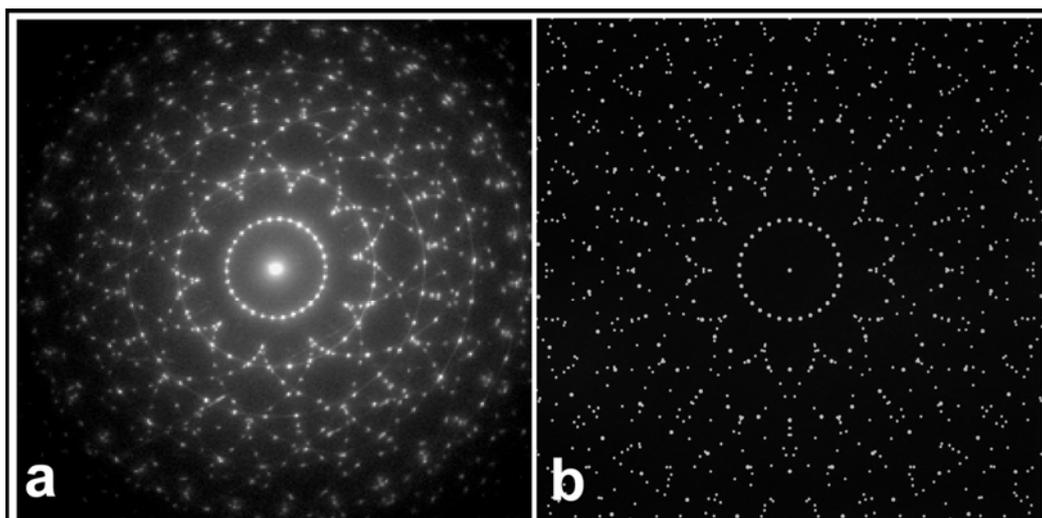


Fig 1 – (a) Experimental and (b) simulated [100] SAED of PS. In the simplest case the pattern consist of 10 cusps only.

Moreover, by combining such data with diffraction along the longitudinal projection of the fiber (*i.e.* [010]), we describe the structure of the 3 two-layer lizardite polytypes that compose the PS fiber. These polytypes were theoretically proposed by Dódony (1997), but never observed in nature: M5, M15 and M16. Actually, the satellite reflections observed by Brindley & von Knorring (1954) can be attributed to the overlap of at least two different reciprocal lattices, however linked by close dimensional and symmetry ties.

A correct understanding of the mineral structure make also possible to describe what happens at the sector boundaries. In intersector regions the continuity of 1:1 serpentine layers, sometimes put into doubt for high resolution images, and the shape of the curvature are emphasised by the continuous curvature of the streaks in SAED patterns.

#### PRECISE AND ACCURATE CELL PARAMETERS: CALIBRATION AND ELLIPTICAL DISTORTION

High resolution TEM images and SAED are usually considered just semi-quantitative techniques because the unreliability of scale factors of the presence of major distortions. Nevertheless, Capitani *et al.* (2006) pointed out that it is possible to establish a calibration and a model of distortion. In trying to deepen into these corrections and verify their time reproducibility, we used sampled of Au nanocrystals vaporized on different support. Two (001) sections of quartz and vesuvianite and different samples of mica were later used to estimate the precision and accuracy of our measurements before and after such corrections.

The nominal magnification, as well as the nominal camera lengths, usually does not allow to get structural measures with a precision and accuracy comparable to X-ray crystallography. Actually even within the same working session the reproducibility of the data is questioned. We point out that this strong variation derives mostly by not correctly set experimental parameters. In particular, changing the current in objective and intermediate lens (*i.e.* image and diffraction focus) strongly affect scale factors. With a correct setting of the microscope the calibration is reproducible within a 0.2-0.1% error.

Capitani *et al.* (2006) highlight the presence of an elliptical distortion in high resolution images and SAED able of a distortion greater than 1%. Although negligible for many common applications, such a distortion may affect a proper determination of the lattice parameters and possibly of the crystal system. Anyway, this distortion is stable in time and for different camera lengths. Appropriately modeling the induced deformation and back-applying it to measurements, the difference among equivalent directions falls within the measurement accuracy.

When these corrections are applied to quartz and vesuvianite, precision and accuracy of measures fall in a range of 0.2-0.1%. The same corrections applied to mica lead to more scattered results. Actually it is hard to state if such samples are really more scattered or something during the ion-thinning or the observation inside the microscope affects the cell parameters of mica, or at least induce any surface effect.

The ability to perform accurate and precise measures is a powerful tool for nanostructural analysis. SAED could be used to identify size-dependent properties, surface effects and structural differences among minerals of different generations, or even among nanodomains inside the same crystal.

## AB INITIO SOLUTION FROM SAED: LIZARDITE-1T

The strong interaction between electrons and matter makes theoretically possible the collection of 3D structural data set from a single nanocrystal. Unfortunately, this strong interaction involves also the emergence of significant dynamic effects that undermine the use of electron diffraction for structural purposes. Nevertheless, Dorset (1996) highlights that for a structural solution there is no need for a tight fit of experimental data to kinematic intensities. In fact, the position of atoms is largely determined by phase pattern, rather than intensities of single reflections.

In X-ray crystallography direct methods are widely used for *ab initio* solution of structures (Giacovazzo *et al.*, 2002). Several authors succeed to apply this technique also to SAED data (Gemmi *et al.*, 2000; Weirich *et al.*, 2000). Following these authors, we apply direct methods to SAED data from lizardite-1T (Mellini, 1982; Mellini & Viti, 1994). The structure of lizardite-1T was chosen as a test structure because it is already known from previous single crystal X-ray refinements and could lead to interesting applications to other serpentine polytypes. Moreover, even if the structure of lizardite-1T consists of only 6 independent atoms, the presence of pseudosymmetries, as well as the lack of symmetry elements perpendicular to [001] and centrosymmetry, make non-trivial the solution of such structure.

Our analysis was carried out using a poor, but quite kinematic data set. Only 4 SAED collected on different crystals are used (Fig. 2), for a full data set of only 43 crystallographic independent reflections. Moreover, we used simulated SAED, calculated by the program NCEMSS (Kilaas, 1987), in order to estimate the correlation between thickness and dynamic effects and determine for which thickness a fully kinematic treatment can be sufficient.

Our results show that it is possible to determine a 3D lizardite-1T structure model starting from SAED data. However, we needed to estimate any solution proposed by the program with respect to expected bond lengths and geometry of single fragments.

In particular, for our experimental SAED a fully kinematic treatment provides the best results with the identification of all the atoms of the structure. Moreover, our experimental results match those obtained with simulated SAED for 2 nm thickness. For thicker samples, such as 5 nm, it seems more appropriate a dynamic treatment, using the approximation  $I \propto F$ .

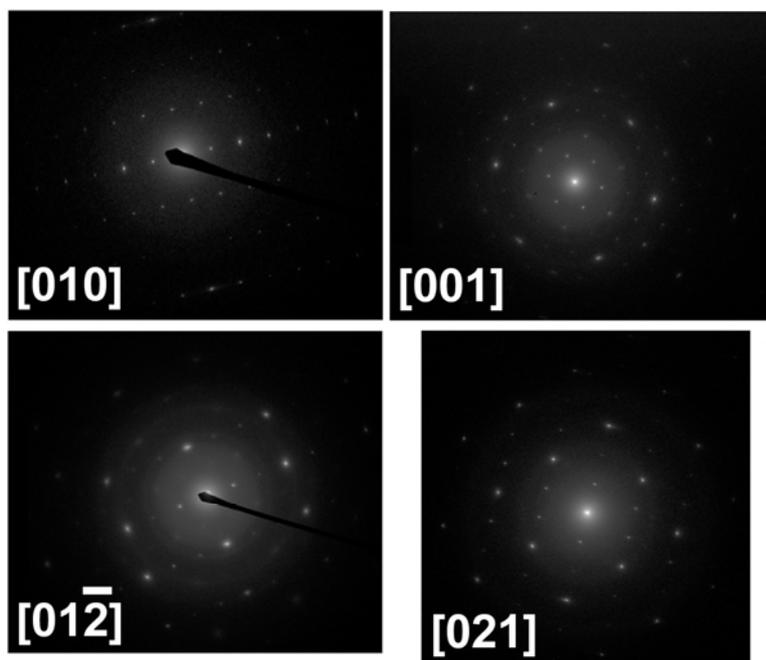


Figure 2. SAED used for structure solution and refinement of lizardite-1T.

## REFINEMENT FROM SAED: LIZARDITE-1T

Finally, SAED are used to refine the structure of lizardite-1T employing the program SHELXL97 (Sheldrick, 1997). Corrections for dynamical effects and excitation error are discussed and estimated, as well as the improvements brought by restraints on bond distances.

Our experiments show that it is possible to refine the structure of lizardite-1T up to a result comparable to that obtained with X-ray data. However, such a result is possible only if the data come from portions of the sample extremely thin and SAED do not show major experimental defects. This means that the crucial difficulty lies in recognizing when a SAED can be considered good enough for a kinematic refinement. A possible estimation can rely on the parameter EXTI of SHELXL97. As an indication, a value around 1000-5000 is an index of sufficiently good data, while higher values indicate that the result is significantly less reliable.

Whatever the case, even if the geometry is close to that refined via X-rays, all the agreement indexes, whether R1, wR2 or GooF, never get to the values typical of X-ray crystallography. However, this doesn't mean that the structure has to be rejected. Therefore the comparison  $F_c - F_o$  does not look as a sufficient parameter to determine the goodness of refinement, as already emphasized by Dorset (1996) and Weirich (2004).

In conclusion, the best outcome was obtained without applying any corrections for excitation error and dynamic effects, but imposing restraints to distances Si-O and Mg-O. This suggests the possibility of an immediate kinematic refinement for silicates, when SAED are collected in optimal experimental conditions and samples thinner than 5 nm.

## CONCLUSIONS

This work highlights on quantitative employment of SAED, and more generally TEM data, for crystallographic analyses of nanocrystals, pointing out strengths and limits of such data set. In fact, many materials are present only in the form of polyphasic nanocrystalline aggregates or mixtures that cannot be analysed individually through conventional optical microscopy techniques or X-ray diffraction.

After the application of a reliable calibration and a correction for lens distortion, the use of SAED for *ab initio* solution and refinement is quite promising. For lizardite-1T, all the atoms of the structures were found by just SAED data, and the refinement led to a structure close to that obtained from X-rays, although characterized by a higher residual.

Although the kinematic approach is limited on areas of the sample extremely thin and at present we lack a system of automated data collection, there is growing interest in the development of experimental and analytical techniques that can face these limitations (Vincent & Midgley, 1994; Kolb *et al.*, 2007).

The electronic crystallography is still in rapid development. From a passive description of theoretical and technical difficulties, we have passed to proposals for systematic solutions of problems. Furthermore, the development of a wide enough case is leading to the first investigations of unknown structures.

On the other hand, getting reliable results from electron crystallography is the only way to investigate individual nanophases in polyphasic aggregates and powders. This would to investigate nanotwinned materials, modular structures, and micro- and meso-porous materials, glass and nanoprecipitates such as catalysts, pharmaceuticals, pigments and thin films. The use of electronic

diffraction is also advantageous compared with HRTEM because allows a low dose of light on the sample, with possible applications on organic or strongly polymerised materials. Important repercussions may therefore affect different scientific fields, such as mineralogy, petrography, inorganic chemistry, materials science, nanotechnology and structural biology.

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