Main contributions to X-ray and neutron diffraction.

Nicolae C. Popa

Internet search (ISI, Scopus, Google scholar, Google books):

Popa N. C. or Popa N.

1. **Extinction in the Framework of Transfer Equations for General-Type Crystals**. - N. C. Popa, *Acta Cryst.,* (1987) **A43,** 304-316

   Theoretical paper deriving a new analytical formula for the secondary extinction correction in the structure determination by single crystal diffraction. Working in large ranges of scattering angle, absorption coefficient and diffraction strengths, the formula covers all cases of extinction, from anisotropic type I to anisotropic type II where the traditional corrections fail.

   The paper was included under the title "Popa formalism", in the book "*Precision X-ray diffraction experiment*" edited in Russia in 1989 by Aslanov, a known crystallographer (former editor to Acta Crystallographica A)

   Two computer programs for structure determination from single crystal diffraction data, namely *PPXA* (*J. Appl. Cryst.* (1992) **25,** 451-454) and *ASTRA* (*J. Appl. Cryst.*(2007) **40,** 602-608) coded this extinction formula as an alternative to the traditional Zachariasen (1967), Coppens & Hamilton (1970) and Becker & Coppens (1974, 1975) extinction correction.

2. **Texture in Rietveld Refinement.** - N. C. Popa, *J. Appl. Cryst.,* (1992) **25,** 611-616.

   Theoretical and experimental paper reporting the implementation in the Rietveld refinement of the general description of texture by spherical harmonics. The reputed experts in texture analysis Matthies, Lutterotti and Wenk considered the paper "the first attempt to introduce modern texture analysis in the Rietveld method" (*J. Appl. Cryst.* (1997) **30,** 31-42).

   Following this idea R. B. Von Dreele from Los Alamos National Laboratory introduced this texture representation in "General Structure Analysis System" (*GSAS*), the most popular Rietveld code today, extending the applicability of the Rietveld method to quantitative texture analysis (*J. Appl. Cryst.* (1997) **30,** 517-525). Later the same representation was also implemented in the *TOPAS* codes of Brucker.

   A number of 67 explicit citations at this moment to which must add all users of *GSAS* and *TOPAS* performing texture analysis by this method but non-citing the original source show the high impact of the paper.

3. **Thermal Diffuse Scattering in Time-of-Flight Neutron Diffractometry.-** N.C. Popa & B.T.M. Willis, *Acta Cryst.,* (1994) A50, 57-63

4. **Correction for Thermal Diffuse Scattering in the Time-of-Flight Neutron Diffraction. -** N.C. Popa & B.T.M. Willis, *Acta Cryst.,* (1997) A53, 537-545

5. **Thermal Diffuse Scattering in Angular-Dispersive Neutron Diffraction. -** N.C. Popa & B.T.M. Willis, *Acta Cryst.,* (1998) A54, 1006-1013

A suite of papers giving for the first time the theory and the mathematical algorithm for calculating the correction of neutron diffraction peaks for the thermal diffuse scattering (TDS) on acoustic phonons, essential for accurate determination of the thermal parameters from single crystal diffraction data.

The importance of carrying out our TDS correction was firstly (and specially) proved experimentally by Prof. Jauch & Dr. Peters from Hahn-Meitner Institute, Berlin (*J. Appl. Cryst.* (2001) **34,** 493-495)) by using diffraction data recorded at the spallation neutron source IPNS – Argonne. The computer program that we provided was included in the programs library at Argonne National Laboratory.

6. **The (hkl) Dependence of Diffraction-Line Broadening Caused by Strain and Size for All Laue Groups in Rietveld Refinement.** - N.C. Popa, *J. Appl. Cryst.* (1998) 31, 176-180 - a theoretical paper

   For size broadening the radius of the apparent crystallite is expanded in spherical harmonics, for strain some quartic forms in *hkl* are used, both fulfilling the necessary (and minimal) requirement to be invariant to the Laue group operations. These have been implemented in the Rietveld code "Material Analysis Using Diffraction" (*MAUD)* (http://www.ing.unitn.it/~maud) by L. Lutteroti soon after publication. Later have been implemented, fully or partially, named or not named, in other Rietveld codes: *MRIA, GSAS, TOPAS, FULLPROF*. Due to the numerous successful Rietveld refinements realized by using these models they become very popular, with a number of 120 citations at this moment, being frequently referred as "Popa models", "Popa rules", "Popa methods" or "Popa algorithm" (see e.g *J. Appl. Cryst.* (2005) **38,** 199-210; *J. Appl. Cryst.* (2005) **38,** 112-120; *Scripta Mat.* (2009) **60,** 520-523; and also various internet links found by using for example Google – English - advanced search - exact words).

7. **Diffraction-Line Shift Caused by Residual Stress in Polycrystal for All Laue Groups in Classical Approximations.** - N. C. Popa, *J. Appl. Cryst.* (2000) **33,** 103-107

8. **Elastic Strain and Stress Determination by Rietveld Refinement: Generalized Treatment for Textured Polycrystals for All Laue Classes.** - N.C. Popa & D. Balzar, *J. Appl. Cryst.* (2001) **34,** 187-195

Papers containing original contributions to the field of macrostrain and stress determination by diffraction.

In **7.** a complete list of the diffraction peak shift dependence on Miller indices in Reuss approximation was reported for the first time.

In **8** a new model based on symmetrized spherical harmonics is proposed that yields the average macrostrain and stress tensors as well as the intergranular strains/stresses in textured polycrystals. In comparison with other similar approaches our approach is extended for any sample and crystal symmetries and is suitable for implementation in Rietveld programs.

- For people not familiar with this problem a clarification is imposed.

  If the experimental technique in determination of macro strain/stress by diffraction had a spectacular development in the second half of twenty century the mathematical apparatus for data processing remained at the level of the years 1930 – 1950 (Voigt, Reuss, Hill or Kroner approximation). A promising, possible a revolutionary step ahead was produced in early 2000 by three groups using in various forms the approach of expansion in spherical harmonics of the strain and/or stress orientation distribution function: Wang *et al.* in USA (*Mater. Sci. Forum* (2000) **347-349**, 66-73), Behnken in Germany (*Phys. Status Solidi* (2000) **A177**, 401-418) and Popa & Balzar (*J. Appl. Cryst.* (2001) **34,** 187-195) – Romania & USA. To be reliable this method requires, in all variants, a large volume of diffraction data of high resolution which is time consuming. Possibly from this reason the diffraction community is still reserved in applying this method. But if intense spallation neutron source and high resolution diffractometer equipped with multiple detectors would be available the method becomes feasible.

- My contributions to the macro strain/ stress determination by diffraction and the texture in the Rietveld method are also described in a book chapter in a larger context: an exhaustive description of the state of art in the fields:

❑ **Microstructural Properties: Texture and Macrostress Effects** by Nicolae C. Popa, Chapter 12, pages 332 – 375 in **Powder Diffraction: Theory and Practice,** edited by R. E. Dinnebier and S. J. L. Billinge, RSC Publishing, Cambridge 2008

- It should be mentioned also:

❑ **Crystallite Size and Residual Strain/Stress Modeling in Rietveld Refinement** by D. Balzar and N. C. Popa, Chapter 5, pages 125 – 145 in **Diffraction Analysis of the Microstructure of Materials,** edited by E. J. Mittemeijer and P. Scardi, Springer 2004

9. **An analytical approximation for a size-broadened profile given by the lognormal and gamma distributions.** – N.C. Popa & D. Balzar, *J. Appl. Cryst.* (2002) **35,** 338-346.

10. **Size-strain line-broadening analysis of the ceria round-robin sample**. – D. Balzar, N. Audebrand, M.R. Daymond, A. Fitch, A. Hewat, J.I. Langford, A. Le Bail, D. Louer, O. Masson, C.N. McCowan, N.C. Popa, P.W. Stephens and B. H. Toby, *J. Appl. Cryst.* (2004) **37**, 911-924 (**note various authors colors**)

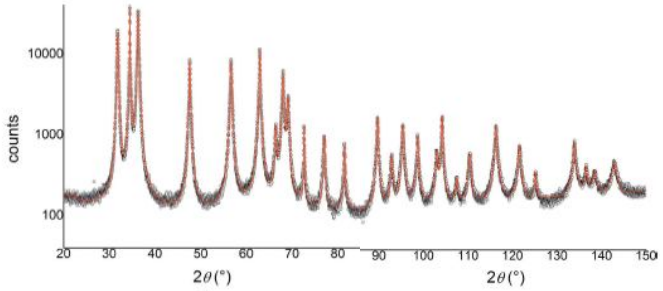
11. **Size-broadening anisotropy in whole powder pattern fitting. Application to zinc oxide and interpretation of the apparent crystallites in terms of physical models** - N.C. Popa & D. Balzar, *J. Appl. Cryst.* (2008). **41**, 615–627

- In paper **9** from this suite dedicated to the peak profile in powder diffraction are reported analytical approximations for the diffraction line profile caused by crystallites with lognormal and gamma distribution of size, suitable for an easy implementation in the whole pattern fitting programs, Rietveld in particular, and allowing a direct refinement of the size distribution parameters.

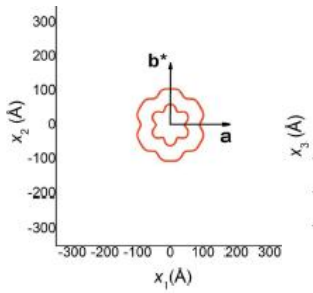
- The new method reported in the paper **9** namely the part concerning the lognormal size distribution was one of the three methods used as reference in the project "Size Strain Round Robin" which results were reported in the paper **10**. The other two methods were the classical Warren – Averbach method and the Rietveld method. The project was initiated by Commission of Powder Diffraction of the International Union of Crystallography and leaded by Davor Balzar**.** My job was to hand the method described in **9** for all patterns used in project. The sample of cerium dioxide and that used for the instrumental profile have been prepared at Rennes University by D. Louer and N. Audebrand and examined by SEM by C.N. McCowan at NIST. Seven diffraction pattern were recorded in leading laboratory in the world by renewed scientists – authors in pink: two X-ray laboratory (Birmingham and Le Mans), two X –ray synchrotron (Brookhaven and ESRF) two neutron patterns at stationary reactors (NIST and ILL Grenoble) and one time-of-flight neutron pattern (ISIS).

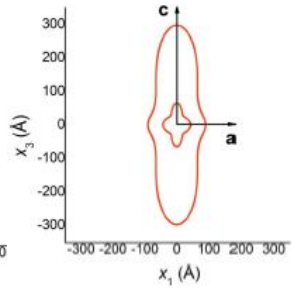
  Both papers, **9** and **10** become guides for people interested in microstructure determination by diffraction. Citations at this moment: 42 and 44 respectively.

- The third paper in the suite recently published (2008) describes a new phenomenological size – broadening model constructed by combining the spherical harmonics representation of the apparent crystallite (paper # 6 from 1998) with the analytical profile due to the lognormal size distribution (paper # 9 from 2002). The new model is convenient for implementation into the Rietveld programs and allows determination of both, volume and area apparent crystallites which is essential for estimation of real crystallites and their distribution (possible if some *apriori* information is available). The model effectiveness was demonstrated on a ZnO powder pattern exhibiting strongly anisotropic size broadening and pronounced super-Lorentzian peak shape.



Pawley fit of a difficult ZnO pattern





Cross-sections through the apparent crystallites: volume averaged (outer); area averaged (inner)

Possible real crystallites. Mode 1 – plates (irregular hexagonal prisms) with large size distribution c=0.94. Mode 2 - rods (regular hexagonal prisms) with sharp size distribution

Mode 1	Mode 2
$\bar{D}_{11} = 24.4\,(22)$ $\bar{D}_{12} = 102\,(9)$ $\bar{D}_{13} = 181\,(15)$ $c_1 = 0.94\,(8)$ $\xi_1 = 0.54\,(5)$	$\bar{D}_{21} = 207\,(20)$ $\bar{D}_{22} = \bar{D}_{21}$ $\bar{D}_{23} = 62.2\,(34)$ $c_2 = 0$
$R_p = 6.26\%$	$R_{wp} = 10.49\%$

12. **U_4O_9 : atoms in general sites giving *hkl* extinctions of special sites**. – N. C. Popa & B. T. M. Willis, *Acta Cryst.* (2004) **A60,** 318-321

See also the next one, Cooper & Willis, *Acta Cryst.* (2004) **A60,** 322-325 – the structure determination on the basis of **12** (both are “open access”).

A very dear paper for me as was able to explain in terms of classical crystallography this apparently impossible effect. Nevertheless the effect was systematically observed in the measured X-ray and neutron diffraction pattern of **U_4O_9** single crystal beginning with 1961 (one such pattern has been measured by neutron diffraction at ILL Grenoble in 1986 by Prof. Willis from Oxford – he given me this problem in 2002).

Moreover, I proved that the effect may appear in any space group. At the first attempt of publication the paper was brutally rejected.

At the second attempt one referee was rather confused, the second one very enthusiastic. Later Prof. Willis knew that the enthusiastic referee was Teo Hahn, the editor of International Tables for Crystallography, volume A.