Report on the To.Sca.Lat.-1.0 Summer School, total scattering analysis for nanoscience in Latin America

C. E. M. Campos,[1] K. F. Ulbrich,[1] M. Leoni,[2] N. Masciocchi,[3,a)] F. Bertolotti,[3] and A. Guagliardi[4]
[1]Departamento de Física, Universidade Federal de Santa Catarina, Campus Trindade s/n, 88040-900 Florianópolis, Brazil
[2]Department of Civil, Environmental and Mechanical Engineering, University of Trento, via Mesiano 77, 38123 Trento, Italy
[3]Dipartimento di Scienza e Alta Tecnologia and To.Sca.Lab, Università dell'Insubria, via Valleggio 11, 22100 Como, Italy
[4]Istituto di Cristallografia and To.Sca.Lab, Consiglio Nazionale delle Ricerche, via Valleggio 11, 22100 Como, Italy
[a)]Author to whom correspondence should be addressed. Electronic mail: norberto.masciocchi@uninsubria.it

(Received 15 January 2019; accepted 7 February 2019)

Advanced courses in Applied Crystallography for Nanosciences are not often delivered in Academia and, consequently, require the organization of events specifically tailored to PhD students, postdocs, and young researchers at the very beginning of their scientific careers. © *2019 International Centre for Diffraction Data*. [doi:10.1017/S0885715619000113]

Key words: Nanoscience, To.Sca.Lat.-1.0 Summer School

Advanced courses in Applied Crystallography for Nanosciences are not often delivered in Academia and, consequently, require the organization of events specifically tailored to PhD students, postdocs, and young researchers at the very beginning of their scientific careers. The efforts of Brazilian scientists (from the Federal University of Santa Catarina) and Italian ones (from To.Sca.Lab in Como and University of Trento) made it possible to organize, in December 2018, a successful Summer School in Florianópolis, in the beautiful location of the Casa de Retiros Vila Fátima (see Figure 1). The event, titled "To.Sca.Lat.-1.0: Total Scattering Analysis for Nanoscience in Latin America," took inspiration from the previous editions of To.Sca.Lake (Masciocchi *et al*., 2015; 2017, taking place in Italy) and ECRISLA summer schools (ecrisla2015.paginas.ufsc.br, taking place in Brazil) and merged advanced topics and tutorial sessions of popular software programs for the youngest Latin American scientific community. Nearly 40 participants from six countries (Brazil, Colombia, Costa Rica, Cuba, Peru, and Uruguay) attended the School. Regrettably, additional registered students from Argentina, Chile, and Venezuela, though granted full accommodation and food during the entire School duration, could not attend the School, because of shortage of funds in their own countries. Figure 2 portrays the group photo.

The organization of the To.Sca.Lat.-1.0 falls well within the educational activities of Prof. Carlos Eduardo Maduro de Campos (see pcemc.paginas.ufsc.br) and of the To.Sca.Lab project (see also toscalab.uninsubria.it). Indeed, as a result of intense international collaboration, an official agreement was signed between UFSC and the Insubria University. All these actions put Latin American institutions in the route of the founders of To.Sca.Lab (a Total Scattering Laboratory co-founded in 2013 by the University of Insubria and the Institute of Crystallography of the Italian CNR), who share theoretical and experimental expertise in chemistry, crystallography, materials science, and physics, merged within an amalgamated project based on (X-rays to visible light) scattering techniques.

Accordingly, diffuse total scattering methods, in the form of direct- and reciprocal-space analyses [one-dimensional Pair Distribution Function method – PDF; and Debye Scattering Equation approach – DSE (Debye, 1915), respectively], were thoroughly presented, together with "conventional" structure solution processes from powder diffraction data. Extra sessions were also dedicated to answer questions originating from the daily scientific activities of the young participants.

To widen the range of scientific topics relevant to the Latin American scientific community, To.Sca.Lat.-1.0 "engaged" Prof. Matteo Leoni from the University of Trento (Italy), Chairman of the International Centre for Diffraction Data – ICDD, in the list of co-organizers. Prof. Leoni delivered several vivid talks on microstructural analysis by powder diffraction, grounded on his huge experience in the field of crystal defectiveness (stacking faults, vacancies, microstrain, etc.) at the nanoscale.

Kindly endorsed by the LNLS scientific Director (Dr. Harry Westfahl Jr.), Dr. Alexandre Magnus Gomes Carvalho, beamline scientist at the XRD1 of the Brazilian synchrotron facility (Sirius/LNLS/CNPEM), delivered a topical presentation on the present applications and future perspectives of Latin American synchrotron facilities.

Monday, Dec 10th

Norberto Masciocchi opened the School giving a very educational Introduction to Single Crystal and Powder Diffraction techniques and their applications to Structural Analysis of crystalline phases. Several methods for indexing, volume prediction, and structure determination were presented. The influence of instrumental effects and many tips for identifying and correcting them were discussed. During his lectures, he also highlighted the importance of using synchrotron sources, especially in the case of moderately complex materials (as better figures of merit and more accurate

Figure 1. (Colour online) The conference venue, "Casa de Retiros Vila Fátima", facing Armação beach.

structural models can be obtained – at the expenses of much longer beam-access times).

Matteo Leoni illustrated the fundamental physics behind diffraction and reviewed the "crystallographic" phase problem. He also brilliantly presented powerful computational tools for Microstructural Analysis of many classes of materials (metals, intermetallics, oxides, and clays) developed in Trento, Italy, jointly with Paolo Scardi (Scardi *et al.*, 2002; Leoni *et al.*, 2006; Scardi and Leoni, 2006).

Finally, remote and local Software Installation sessions were gently organized by all teachers of the School, even by extending installation late in the night to overcome some technical problems offered by the variety of operating systems. Wi-fi-driven TOPAS-6 licenses were provided to all participants for the hands-on sessions.

Tuesday, Dec 11th

Before the Hands-on Session on Structure Solution, Norberto Masciocchi illustrated very important crystallographic concepts behind all the computational procedures presented in the following hours using the TOPAS-6 program.

Figure 2. (Colour online) The group photo of the To.Sca.Lat.-1.0 Summer School.

https://doi.org/10.1017/S0885715619000113 Published online by Cambridge University Press

Starting from a simple inorganic structure ($CaSiF_6 \cdot 2H_2O$), and ending with organics ones (salicylic acid, triphenylphosphine, and a widely marketed antismoke drug), an extensive tutorial session provided hints on how to solve the indexing step, the space-group selection, the Le-Bail/Pawley refinement, and the structure solution processes (by real space modeling and global optimization procedures). Some relevant information, such as fast estimates of crystal densities, unit cell rational transformations, and rigid body formalisms, were presented. Data which could not be analyzed locally were supplied to all participants for further use. A glance on the Fundamental Parameters Approach and to Rietveld-based Quantitative Phase Analysis terminated the session.

In the afternoon, before entering the hands-on session, Matteo Leoni highlighted the philosophy of the Whole Pattern Powder Modeling, starting from a historical context and the meaning of the very popular (seldom misused) equations (Scherrer, Williamson–Hall). The use of phenomenological peak profile functions (Gaussian, Lorentzian, or mixture thereof), widely used in a number of programs, was criticized, in favor of a physically-based approach, like the one implemented in WPPM to describe shapes and widths of the Bragg peaks. Hands-on tutorials were initially based on a simple X-ray diffraction pattern of defective nanocrystalline ceria, used to show evidence all different contributions (including instrumental ones) to peak broadening to extract the shape and size distribution of the domains and the content of dislocation and faults. The case was proposed in a very didactic manner, by including a step-by-step procedure to embrace several microstructural parameters. Subsequently, all attendees were asked to perform on their laptops the full analysis of diffraction data from a ball-milled Fe-Mo alloy. Using PM2K, under the continuous supervision by Matteo, participants learned about the difficult steps which are inherent in such an intricate modeling, particularly if a conventional lab source is employed. This was significantly illustrated by the difficult modeling on a simple NIST standard, such as LaB_6.

Wednesday, Dec 12th

After 2 days of activities stressing the importance of using diffraction data from synchrotron sources to perform high level analyses of defective and nanomaterials, Alexandre M.G. Carvalho (beamline scientist at XRD1 of LNLS/CNPEM) delivered a very informative lecture, entitled "LNLS/Sirius Past and Future of the Brazilian Light Sources". Beyond summarizing the status of the actual XRD beamlines of LNLS (UVX machine), he also presented the features of the new hard X-rays beamlines present at Sirius, the recently inaugurated Synchrotron in the Campinas Area (first photons delivered in November 2018), where faster and more flexible experiments can be planned. Details on the HARPIA (High angular resolution powder X-ray diffraction), PAINEIRA (Powder Diffraction), HERA, and EMA (Extreme condition X-ray Methods of Analysis) beamlines were provided. Participants of To.Sca.Lat.-1.0 also learned about the opportunities to apply for beamtime, and how to participate in CNPEM Summer Schools, PhD, and Post-doctoral Programs.

In the following presentation, Antonella Guagliardi introduced Total Scattering methods, comparing them with conventional Rietveld analyses. The main focus of her presentation was the Debye Scattering Equation analysis for nanomaterials, a topic mastered also in the form of computational tools developed by her Group (specifically, the DebUsSy suite, Cervellino *et al*., 2010, 2015). By treating Bragg and non-Bragg (diffuse) scattering on the same footing and including inelastic Compton effects, DebUsSy uses a physically-based modeling to retrieve important structural and microstructural information of nanosized materials, ranging from lattice relaxation and sample stoichiometry, to size and shape (and their distribution) of nanocrystals and, finally, to more complex defectiveness in the core (stacking faults, localized strain) and on the surface (e.g. in homo- or hetero-core-shell systems).

The Atomic Pair Distribution Function method was later introduced by Federica Bertolotti, who brilliantly showed the main differences between the conventional approaches that assume an ideal infinite crystal periodicity. Federica showed that the quality of a meaningful PDF, particularly targeted toward defective or nanosized materials, depends on experimental parameters ($Q_{max} > 20$ Å^{-1}) and on data reduction and modeling processing (following the so-called *small* or *large* box modeling approaches). Some frontier applications of the method were finally presented (e.g. PDF computed tomography and *in-situ* studies of nanoparticles growth).

The last lecture of the day was delivered by Matteo Leoni who introduced a probabilistic, physically-based formulation to interpret general stacking defects in a variety of materials, including intermetallics, clays and, of course, nanostructured species. A demonstration of the power of the DIFFaX+ code for the refinement of faulted and <3D periodic structures was also presented.

Thursday, Dec 13th

The hands-on session using DebUsSy started from a general overview of the philosophy of the database construction (as integrated within DebUsSy) from available structural information (loading CIF files or manually introduced by the user). At this point, simulation of XRPD patterns from selected clusters (e.g. with different sizes) was performed and used to visually compare the effects of the physical parameters used to build the database. The second part of the tutorial session on DebUsSy was performed jointly with all participants using scattering data from nanometric magnetite and TiO_2, the last sample containing two polymorphic phases and data from synchrotron and lab sources, respectively. Step-by-step settings of all parameters were presented by Antonella, who also taught the participants how to interpret the results given by the refinement using DebUsSy. A nice discussion followed, focused on the meaning of the mass and number distribution and on their validity when compared by imaging analysis.

In the afternoon, a hands-on session with PDFGui (Farrow *et al*., 2007) was organized by Federica Bertolotti, who showed how to calibrate the instrumental parameters from the analysis of PDF data of a standard material (here, microcrystalline nickel powder). One case of a PDF analysis

https://doi.org/10.1017/S0885715619000113 Published online by Cambridge University Press

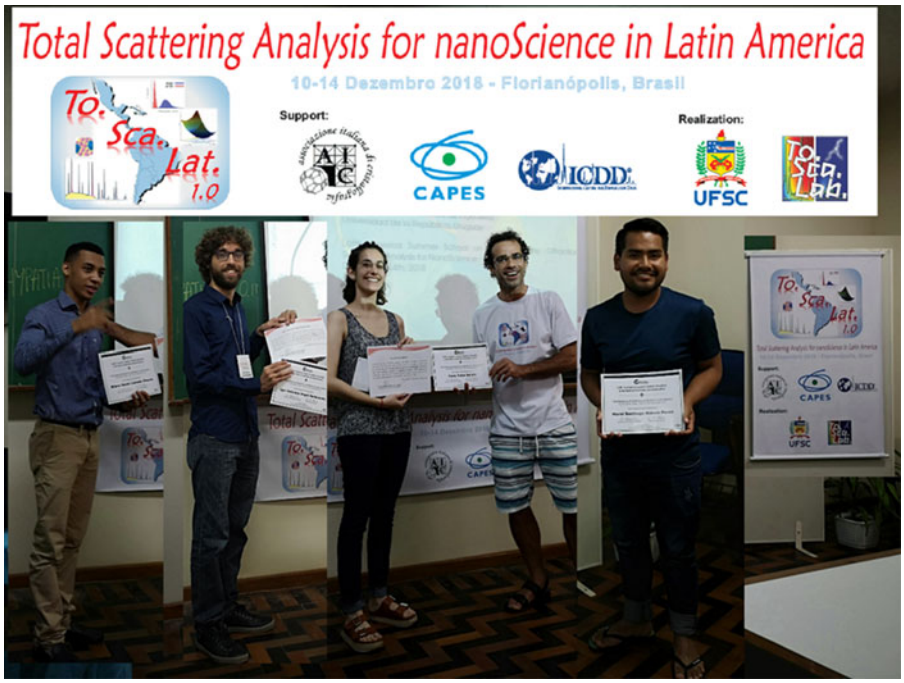

Figure 3. (Colour online) Four attendees receiving the ICDD prize from School Director Carlos Eduardo Maduro de Campos. Left to right: Wilson Daniel Calcedo Chacón (Colombia), Igon Antunes Vogel Maldonado (Brazil), Carla Yelpo Galán (Uruguay), Prof. Carlos Eduardo Maduro de Campos (School Director, Brazil), Harol Santiago Álvarez Pérez (Peru).

of a biphasic sample was presented and generated a deep discussion on the data reduction procedure (which assumes the *a-priori* knowledge of the sample stoichiometry when averaging atomic scattering factors of each element in the scaling procedure). Finally, the correct relation between the PDF-derived scale factors and the phase composition was analytically derived. All the experimental data and input files for the PDFGui tutorial were kindly provided by Prof. Simon J.L. Billinge (Columbia University).

At the end of this day, all participants were encouraged to explore the neighborhood of the location where the To.Sca. Lat.-1.0 was held. In the natural preservation area next to beautiful Armação beach and Peri lagoon, teachers and attendees shared sport activities such as football, tracking, swimming, and contemplating nature.

Friday, Dec 14th

In the final day, a scientific presentation titled "An Overview of Total Scattering Analysis for NanoScience" was delivered by Antonella Guagliardi, who illustrated forefront examples of the Debye scattering equation applied to explore the structural defectiveness of nanomaterials and, particularly, quantum dots. These included the case of crystal symmetry breaking and vacancies in colloidal lead chalcogenides quantum dots (Bertolotti *et al.*, 2016a), stacking faults modeling in zincblende cadmium selenide nanocrystals (Moscheni *et al.*, 2018), twin boundaries in fully inorganic lead halide perovskite nanocrystals (Bertolotti *et al.*, 2017), and strain in metals and alloys (Bertolotti *et al.*, 2016b; Ulbrich *et al.*, 2018).

To.Sca.Lat.-1.0 participants were invited to present their scientific projects during the School. A total of 10 oral communications were presented by young students, most of them supported by grants generously offered by ICDD, AIC, and Bruker.

During the Closing Session all teachers, attendees, and organization members were warmly acknowledged by Prof. Campos, the local Chairman of To.Sca.Lat.-1.0. Prof. Leopoldo Suescun (Uruguay), one of the most active Latin America crystallographers, encouraged to start thinking about a second edition of the school and the proposal was greatly embraced by the attendees. Future locations (and local Chairmen) for a potential second edition of To.Sca.Lat. were also proposed: Costa Rica (Prof. José Javier Saavedra Arias) or Uruguay (Prof. Leopoldo Suescun) are awaiting you!

Of course, this event could not have existed without the help of several public bodies and private companies, here collectively gathered in a non-ordered list: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES grant PAEP no. 88881.192068/2018-01), To.Sca.Lab. (University of Insubria & IC-CNR), the Italian Crystallographic Association, the University of Trento and, as generous commercial sponsor, Bruker (who also provided a shared wi-fi access to the TOPAS-6 license). The International Center for Diffraction Data (ICDD) generously sponsored the attendance of a few participants, by assigning them a special award (see Figure 3). We are heartily indebted to all of them for their financial support.

Bertolotti, F., Dirin, D. N., Ibáñez, M., Krumeich, F., Cervellino, A., Frison, R., Voznyy, O., Sargent, E. H., Kovalenko, M. V., Guagliardi, A., and Masciocchi, N. (**2016a**). "Crystal symmetry breaking and vacancies in colloidal lead chalcogenide quantum dots," Nat. Mater. **15**, 987–994.

Bertolotti, F., Moscheni, D., Migliori, A., Zacchini, S., Cervellino, A., Guagliardi, A., and Masciocchi, N. (**2016b**). "Unravelling the growth of Pt nanorods inside a

https://doi.org/10.1017/S0885715619000113 Published online by Cambridge University Press

porous matrix by total scattering Debye function analysis," Acta Crystallogr. **A72**, 632–644.

Bertolotti, F., Protesescu, L., Kovalenko, M. V., Yakunin, S., Cervellino, A., Billinge, S. J. L., Terban, M. W., Pedersen, J. S., Masciocchi, N., and Guagliardi, A. (**2017**). "Coherent nanotwins and dynamic disorder in cesium lead halide perovskite nanocrystals," ACS Nano **11**, 3819–3831.

Cervellino, A., Giannini, C., and Guagliardi, A. (**2010**). "DEBUSSY: a Debye user system for nanocrystalline materials," J. Appl. Crystallogr. **43**, 1543–1547.

Cervellino, A., Frison, R., Bertolotti, F., and Guagliardi, A. (**2015**). "DEBUSSY 2.0 – the new release of a Debye user system for nanocrystalline and/or disordered materials," J. Appl. Crystallogr. **48**, 2026–2032.

Debye, P. (**1915**). "Zerstreuung von Röntgenstrahlen," Ann. Phys. **351**, 809–823.

Farrow, C. L., Juhás, P., Liu, J., Bryndin, D., Božin, E. S., Bloch, J., Proffen, T., and Billinge, S. J. L. (**2007**). "PDFfit2 and PDFgui: computer programs for studying nanostructure in crystals," J. Phys.: Condens. Matter. **19**, 335219.

Leoni, M., Confente, T., and Scardi, P. (**2006**). "PM2K: a flexible program implementing Whole Powder Pattern Modelling," Z. Kristallogr. Suppl. **23**, 249–254.

Masciocchi, N., Bertolotti, F., and Guagliardi, A. (**2015**). "Report on the To.Sca.Lake workshop: total scattering for nanotechnology held at Como lake," Powder Diffr. **30**, 320–322.

Masciocchi, N., Ferri, F., Bertolotti, F., and Guagliardi, A. (**2017**). "Report on the To.Sca.Lake 2.0 workshop: total scattering for nanotechnology held at Como lake," Powder Diffr. **32**, 213–216.

Moscheni, D., Bertolotti, F., Piveteau, L., Protesescu, L., Dirin, D. N., Kovalenko, M. V., Cervellino, A., Pedersen, J. S., Masciocchi, N., and Guagliardi, A. (**2018**). "Size-dependent fault-driven relaxation and faceting in zincblende CdSe colloidal quantum dots," ACS Nano **12**, 12558–12570.

Scardi, P., and Leoni, M. (**2002**). "Whole powder Pattern Modelling," Acta Crystallogr. **A58**, 190–200.

Scardi, P., and Leoni, M. (**2006**). "Line profile analysis: pattern modelling versus profile fitting," J. Appl. Crystallogr. **39**, 24–31.

Ulbrich, K. F., Bertolotti, F., Masciocchi, N., Cervellino, A., Guagliardi, A., and Campos, C. E. M. (**2018**). "A comprehensive structural and microstructural investigation of a new iron–telluride nano phase," J. Mater. Chem. C. **6**, 3047–3057.

https://doi.org/10.1017/S0885715619000113 Published online by Cambridge University Press