MS12.24.4

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Diffuse Scattering Study of 2D Superstructure in a T' Electron-Doped Cuprate Superconductor

Branton J. Campbell[a], Stephan Rosenkranz[b], Peter J. Chupas[b], Hye Jung Kang[c], Pengcheng Dai[c], Yasuaki Kurita[d], Seiki Komiya[d], Yoichi Ando[d], [a]*Dept. of Physics & Astronomy, Brigham Young University, Provo, UT 84602.* [b]*Materials Science Division, Argonne National Laboratory, Argonne, IL 60439.* [c]*Dept. of Physics & Astronomy, University of Tennessee, Knoxville, TN 37996.* [d]*Central Research Institute of the Electric Power Industry, Komae, Tokyo 201-8511, Japan.* E-mail: branton_campbell@byu.edu

It is well-known that electron-doped superconductor $Nd_{0.85}Ce_{0.15}CuO_4$ can be reversibly rendered a superconductor or non-superconductor by appropriate high-temperature treatments in reducing or oxidizing environments, respectively. We find that superconducting samples exhibit diffuse (0, 0, L) rods of scattering at superlattice positions in the (H, K, 0) plane corresponding to a larger $2\sqrt{2} \times 2\sqrt{2}$ unit cell. We present a synchrotron x-ray diffuse scattering analysis of this rod scattering in related compound $Pr_{0.88}LaCe_{0.12}CuO_4$ (PLCCO) and demonstrate that it arises from a two-dimensional superstructural distortion of the CuO_2 sheets rather than from cubic Nd_2O_3 (bixbyite) impurities.

Keywords: diffuse scattering, superconducting oxides, superstructures

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Cooperative Evolution - a New Algorithm for Refining Disordered Structures

Thomas Weber, *Laboratory of Crystallography, ETH Zurich. Zurich, Switzerland.* E-mail: thomas.weber@mat.ethz.ch

The combination of evolutionary algorithms and Monte Carlo simulation is a powerful tool for the investigation of disordered crystals [1]. In analogy to natural evolution, Monte Carlo parameters are optimized by selection, mutation and recombination of previous, suboptimal solutions ("individuals"). In contrast to the technique used in [1] the method proposed in this contribution is not based on competition, but takes advantage of cooperation between individuals. Each of the individuals is allowed to live as long as it is capable of improving the structure. It is shown that this technique leads to a better performance than the algorithm described in [1]. The principle of Cooperative Evolution and its application to disordered structures will be presented.

[1] Weber T., Bürgi H. B., *Acta Cryst.*, 2002, A**58**, 526.

Keywords: diffuse scattering, optimization algorithms, disorder

MS13 Advances in Computational Methods for Powder Diffraction

Chairpersons: Brian H. Toby, Lachlan M. D. Cranswick

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Application of Symmetry to Magnetism and its Consequences for Crystallography

Andrew S. Wills[a,b], [a]*Department of Chemistry, University College London, UK.* [b]*Davy-Faraday Research Laboratory,The Royal Institution of Great Britain, 21 Albermarle Street,London, UK.* E-mail: a.s.wills@ucl.ac.uk

The microscopic picture of magnetism developed by Néel required extensions to be made to the description of symmetry in crystalline solids. Historically, the first of these was the application of the so-called "coloured" groups or Shubnikov groups, created by the addition to the conventional symmetry elements of crystallography of an operation that reverses magnetic moments. Whilst these are conventionally tabulated for simple commensurate periodicities defined by the Lifshits condition they can be used to describe both commensurate and incommensurate symmetries. There are, however, fundamental restrictions to the types of symmetry that can be effectively characterized using the coloured groups which limits greatly their usefulness. The most general description of symmetry in crystalline solids is that developed by Wigner and is based on the use of irreducible corepresentations.

This presentation will explain the fundamentals behind Shubnikov's space groups and Wigner's theory, and will detail how unspecialized researchers can use corepresentation theory to determine magnetic structures from neutron diffraction data using the computer program SARA*h* (ftp://ftp.ill.fr/pub/dif/sarah/) in combination with the refinement programs GSAS or Fullprof [1,2].

[1] Wills A.S., *Physica B*, 2000, **276**, 680. [2] Wills A.S., Lappas A., *J. Phys. Chem. Solids*, 2004, **65**, 65.

Keywords: magnetic structures, symmetry theory, neutron scattering

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CrysFML: a Library to Develop Crystallographic Programs in Fortran 95. Powder diffraction examples

Juan Rodríguez-Carvajal[a], Javier González-Platas[b], [a]*Laboratoire Léon Brillouin (CEA-CNRS), CEA/Saclay France.* [b]*Depto. Física Fundamental, Universidad de La Laguna, Tenerife, Spain.* E-mail: Juan.Rodriguez-Carvajal@cea.fr

CrysFML is a set of Fortran 95 modules to be *used* in crystallographic and diffraction computing programs [1]. Modern array syntax and new features of Fortran 95 are used through the modules. We take advantage of all object oriented programming techniques already available in Fortran (user-defined types, encapsulation, overload of procedures and functions). The lacking features (e.g. inheritance and class methods) will be easily implemented as soon as compilers of the new standard become available. We aim to preserve the efficiency, the simplicity and the adequacy of modern Fortran for numerical calculations. All aspects of symmetry and handling of reflections and structure factor calculations are treated in dedicated modules. Main programs using the adequate modules may perform more or less complicated calculations with only few lines of code. The documentation is written in the source code. A document, in HTML format can be generated using a program.

We shall present an overview of the present status of the library and a series of examples useful for powder diffraction: simple crystallographic calculations, bond-valence sums, aids to space group determination, profile fitting, powder diffraction simulations, kernel of the Rietveld method, etc.

[1] Rodríguez-Carvajal J., González-Platas J., *Compcomm Newsletter* 2003, **1**, 50.

Keywords: computational crystallography, algorithms, modelling

MS13.24.3

Acta Cryst. (2005). A**61**, C22-C23

Peter Piper Picked a Problem Trickier than most. Can Computer Science Solve the Problem Peter Piper Picked?

Simon J. L. Billinge, *Department of Physics and Astronomy, Michigan State University.* E-mail: billinge@pa.msu.edu

Modern materials of scientific and technological interest are notoriously complex. This is exemplified by efforts to control the atomic organization of materials on the nanoscale to give them directed functionality. Clearly it is necessary to be able to characterize the structure of these materials. This is a difficult problem. In a crystal there is a good match between the information required to solve the problem (atomic positions, symmetry and unit cell metrics) and the information in the data (Bragg peak positions and intensities). We are all aware of the power of crystallography. In a nanostructured material the peaks broaden and become overlapped resulting in diffuse scattering which contains much less information. On the other hand the number of degrees of freedom needed to specify the model increases (in principle of order the number of atoms in the

nanoparticle). This is the pesky problem Peter Piper picked.

In this talk I will illustrate the problem and discuss some efforts we are taking to overcome these difficulties. I will describe some developments inspired by computer science that could be brought to bear on problems like this. We are not currently able to answer the question posed in the title, but even thinking about it is proving to be a lot of fun.

Keywords: nanocrystallography, software, local structure

MS13.24.4

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Single Crystal Quality Structures from Polycrystalline Samples

Gavin B.M. Vaughan[a], Henning O. Sorensen[b], Soeren Schmidt[b], Henning F. Poulsen[b], [a]*European Synchrotron Radiation Facility, Grenoble, France.* [b]*Risoe National Lab., Roskilde Denmark.* E-mail: vaughan@esrf.fr

We have recently demonstrated [1,2] a method whereby single crystal quality data can be extracted from polycrystalline samples comprising up to 1000 crystals. The method works by focusing the X-ray beam on the sample such that a sufficiently small active area is illuminated such that the diffraction from the individual crystallites is sufficiently distinct that some individual spots may be extracted. With these data we simultaneously determine, via a novel algorithm [3], the orientation matrices of the crystallites which constitute the powder specimen.

Given these orientation matrices, the intensities of the contributions from the different crystallites may then be deconvoluted, scaled, and filtered/reweighted by a variety of methods. In this way we determine not only the average structure of a powder specimen, with single crystal precision, but also the distribution of structural properties within the sample.

We have now attempted to apply this technique to progressively more complicated systems; the latest results will be presented.

[1] Schmidt S., Poulsen H.F., Vaughan G.B.M., *J. Appl. Cryst.*, 2003, **36**, 326. [2] Vaughan G.B.M., Schmidt S., Poulsen H.F., *Z. Kristallogr.*, 2004, **219**, 813. [3] Lauridsen E.M., Schmidt S., Suter R.M., Poulsen. H.F., *J. Appl. Cryst.*, 2001, **34**, 744.

Keywords: structure determination methods, algorithmic methods, computer algorithm development

MS13.24.5

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'Pushing the Boundaries' of Differential Evolution in SDPD

Samantha Y. Chong, Maryjane Tremayne, *School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT.* E-mail: spc715@bham.ac.uk

The development of direct space structure solution techniques is an important factor in the increasing number of crystal structures determined using PXRD [1]. Direct space methods involve assigning *R* factors to trial structures by comparison of the calculated powder profile to the experimental pattern. A global optimisation algorithm, such as Monte Carlo or evolutionary algorithms is applied to locate the correct crystal structure.

Differential Evolution (DE) is an evolutionary algorithm, which is simple to implement and offers robust searching of minima [2,3]. A population of trial structures is generated, characterised by parameters describing position, orientation of the molecule and any variable torsion angles. Associated with each parameter is a minimum and maximum boundary. The population is mated and mutated in a single step to produce successive generations until the structure with the lowest *R* factor is found.

This presentation describes a modification of the DE algorithm which enables the boundaries to be updated during a structure solution calculation, using information previously gained within the search. We examine the effect of restricting the search to regions where low *R* factor has been found on the efficiency of the DE optimisation.

[1] Tremayne M., *Phil. Trans. R. Soc. Lond. A*, 2004, **362**, 2691. [2] Price K.V. in *New Ideas in Optimization*, ed: Corne D., Dorigo M., Glover F., McGraw-Hill, London. 1999. [3] Tremayne M., Seaton C.C., Glidewell C., *Acta. Cryst.*, 2002, **B58**, 823.

Keywords: powder structure determination, structure solution methods, computer algorithms

MS14 Modularity and Modulation in Inorganic and Mineral Structures

Chairpersons: Emil Makovicky, Stefano Merlino

MS14.24.1

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Layered Compounds: from Modular Description to Rational Design

Laurent Cario, *Institut des Matériaux Jean Rouxel, CNRS - University of Nantes, France.* E-mail: laurent.cario@cnrs-imn.fr

As a reliable *ab-initio* theory for crystal structure is still lacking, the rational design of new compounds remains a major challenge in solid state sciences. In that quest, the modular description of 2D structures could provide an interesting alternative pathway, as exemplified by the family of 2D-misfit layered chalcogenides $[(MX)_m]_{1+x}[TX_2]_n$ (M = rare earth, Sn, Pb, Sb or Bi ; T = Ti, V, Cr, Nb, or Ta ; X = S, Se) [1]. These compounds have incommensurate layered composite structures which are built from an alternated stacking of $[MX]$ module of the rock salt type and $[TX_2]$ module of the CdI_2 or NbS_2 types. Combinations of divalent or trivalent metals M and transition metals T led to the recognition of numerous new compounds with different alternated stacking sequences as defined by the m/n ratio. A careful analysis of structure databases proves that similar 2D modules (rock salt or CdI_2 types) are encountered in many structures and in many different chemical environments. This observation led to consider these modules as 2D building blocks and suggests a novel way to predict the structures and the compositions of some new inorganic compounds [2]. Starting from the modular description of misfit layered compounds this presentation aims to give an insight of the concept of 2D building blocks and to present its first application to the design of commensurate or incommensurate 2D layered compounds.

[1] *Materials Science Forum*, Trans. Tech. Publications, ed. by Meerschaut A., 1992, 100-101. [2] Cario L., Kabbour H., Meerschaut A., *Chem. Mater.*, 2005, **17**, 234.

Keywords: incommensurate modulated structures, layered materials, design

MS14.24.2

Acta Cryst. (2005). A**61**, C23-C24

Recurrent Modules in Modular Structures

Giovanni Ferraris, *Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino – Istituto di Geoscienze e Georisorse, CNR, Italy.* E-mail: giovanni.ferraris@unito.it

Modular structures are based on complex structural fragments (modules) that occur in different crystal structures. Let A and B be bidimensional and crystal-chemically different modules; A_mB_n represents a polysomatic series formed by members based on different m/n ratios. The cell parameters and chemical composition of the members linearly depend from those of the building modules.

A survey of polysomatic structures recently reported in [1] shows a large variety of recurrent modules. In oxygenated compounds, among others, the following modules recur: bafertisite, brucite, corundum, epidote, gibbsite, mica, nasonite, nolanite, palmierite, perovskite, pyrochlore, pyroxene, rutile, schafarzikite, spinel, talc, and topaz. Tetrahedral (T) and octahedral (O) modules are widespread in nature both as TOT and TO slices; slices of perovskite with various thickness and orientation are present in hundreds of synthetic inorganic materials, including superconductors, and are the basis of several series of inorganic-organic hybrids.

The concept of modularity is a powerful tool increasingly used to handle various crystal-chemical aspects of the structures: (i) modelling the unknown structure of new members of a series; (ii) interpreting topotactic reactions and defects in real structures; (iii) tuning the properties of synthetic materials; (iv) inspiring the synthesis of mesoporous (e.g., pillared clays) and intercalation materials.