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A NEW METHOD FOR COMPLETING A POLYHEDRALLY COORDINATED STRUCTURE IN EXpo2002

A. Altomare[1] C. Cuocci[2] C. Giacovazzo[1,2] A.G.G. Moliterni[1] R. Rizzi[1]
[1]Institute of Crystallography - CNR, c/o Dipartimento Geomineralogico, Campus Universitario, Bari, Italy, [2]Dipartimento Geomineralogico, Universita' di Bari, Campus Universitario, Italy

The structural model provided by Direct Methods when powder diffraction data are used is often partial. The recently developed POLPO procedure [Altomare et al., (2000). J. Appl. Cryst. 33] aims at locating the missing atoms in a partial structure model where all the cations are positioned. The procedure exploits the prior knowledge of the expected cation coordination and their connectivity. The POLPO procedure has been extended to more general cases in which not all the cations are located [Altomare et al., (2002). J. Appl. Cryst. Submitted]. It uses the prior information on the polyhedral coordination of both the located and the missing cations and is able to recover the missing cations and all the coordination anions. The main points of the extended procedure are: 1) a suitable atomic chain is selected (its corresponding Z-matrix is considered) and described by using internal coordinates [Andreev et al., (1997). Phys. Rev. B55; Arnott et al., (1966). Polymer. 7]; 2) the stereochemical parameters of the chain not restrained by the geometrical rules about the polyhedral coordination are randomly varied. Different feasible solutions are generated and ranked according to the Rp profile reliability parameter. The procedure has been successfully tested by some test structures providing models whose atomic positions slightly differ from the true ones. POLPO has been introduced in EXPO2002, the new version of EXPO [Altomare et al.,(1999). J. Appl. Cryst. 32]. The method may be adopted for completing partial models of organic or metallorganic compounds whose molecular geometry is usually known.

Keywords: AB-INITIO CRYSTAL STRUCTURE SOLUTION POWDER DIFFRACTION POLYHEDRAL COORDINATION

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MAXIMUM LIKELIHOOD APPLIED TO STRUCTURE SOLUTION FROM POWDER DIFFRACTION DATA

A.J. Markvardsen
Isis Rutherford Appleton Laboratory ISIS Facility CHILTON OX11 0QX UK

The maximum likelihood method has become a frequently used tool in both macromolecular crystallography and fiber diffraction. In this talk, we show that it is also of considerable use in the context of structure solution from powder diffraction data using the global optimization approach [1]. The method offers a statistically consistent way to leave out fragments of a molecular model used in a global optimization search for the crystal structure. A maximum-likelihood figure-of-merit is introduced which is shown to have the same properties as a least-squares figure-of-merit when no parts of the molecular model are left out in the global optimization search, but otherwise shows improved properties. The later is illustrated practically, with two pharmaceutical salts where only the position, orientation and conformation of the molecule is optimized while the counter ion is treated as an unknown blur. Results will also be presented where errors in the included fragment are also considered; this corresponds to introducing a Luzzati D-parameter [2] smaller than one.

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DIFFUSE SCATTERING STUDIES OF PHONON DISPERSION RELATIONS AND PHASE TRANSITIONS

T. C. Chiang[1,2]
[1]University of Illinois at Urbana-Champaign Department of Physics 1110 W. Green Street URBANA IL 61801 USA [2]Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign

Analysis of x-ray thermal diffuse scattering (TDS) is among the oldest experimental methods that deal with the dispersion of phonons in crystals. This method was first proposed by Laval in 1938 but remained largely impractical, in part due to poor data collection rates and difficult procedures for quantitative data analysis. As a result, the TDS method was almost immediately abandoned with the advent of neutron diffraction. The situation has changed recently due to advances in synchrotron radiation instrumentation. The vast improvement in photon flux at synchrotron radiation sources combined with modern computational capabilities has made it possible to carry out detailed quantitative phonon studies via x-ray TDS measurements. In this talk, results from Si and Nb will be used to illustrate the method. TDS patterns of Si and Nb obtained in a transmission Laue geometry, displayed on a logarithmic intensity scale, reveal rich features. Theoretical patterns based on a lattice dynamics calculation are generated, and a least-squares fit of the patterns yields the phonon dispersion relations over the entire reciprocal space. The method has several advantages: a simple experimental setup, a high efficiency, and a minimal requirement on sample size. Perhaps the most promising application of this method is for studies of phase transitions. An investigation of the charge-density-wave transition in $TiSe_2$ shows phonon softening with characteristics in good accord with the predictions of a Landau theory.

Keywords: DIFFUSE SCATTERING, PHONON DISPERSION, PHASE TRANSITION

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SYNCHROTRON X-RAY DIFFUSE SCATTERING REVEALS MOSAIC STACKING-FAULT PATTERN IN ZEOLITE MORDENITE

B. J. Campbell[1] T. R. Welberry[2] R. W. Broach[3] A. K. Cheetham[4]
[1]Argonne National Laboratory Materials Science Division 9700 So. Cass Ave., MSD/223 ARGONNE IL 60440 USA [2]Research School of Chemistry, Australian National University [3]UOP, Des Plaines, IL, USA [4]Materials Research Laboratory, University of California at Santa Barbara

Single-crystal x-ray diffuse scattering data from a natural mordenite sample reveal an unusual block-mosaic pattern of framework stacking faults that has implications for the functional properties of this widely-used industrial zeolite catalyst. High-intensity synchrotron x-rays enabled the observation of an intricate pattern of weak scattering features which were reconstructed over a large contiguous volume of reciprocal space using a CCD area detector. Supercomputer simulations of the diffuse scattering were then applied to determine the structure and distribution of the fault-plane interfaces. Both structural detail and methodology will be presented.

Keywords: DIFFUSE SCATTERING AREA DETECTOR ZEOLITE