diimine ligands constructing infinite chain structure. The assignments of intense emission bands of these oligo-copper compounds are complicate because weak interacted multi-copper centered (CC) charge transfer is often concurrent with common Cu(I) to ligand charge transfer. We have tried to observe direct geometrical distortion of the complex by photo excited state crystallographic technique in order to figure out this emission nature.

Single crystal X-ray diffraction experiments were performed by using the low-temperature vacuum X-ray camera at SPring-8 BL02B1 beamline. Full intensity data of both under light irradiated and non-irradiated conditions were collected by multiple-exposure method by using IP detector. Photo-difference Fourier syntheses show that a small portion of two I atoms in $\{Cu_2I_2\}$ unit move toward close to each other, while two Cu atoms tend to move apart from each other toward N atom of the bipyridine ligand.

[1] Henary M., Wootton J.L., Khan S.I., Zink J.I., *Inorg. Chem.*, 1997, **36**, 801. [2] Ozawa Y., Terashima M., Mitsumi M., Toriumi K., Yasuda N., Uekusa H., Ohashi Y., *Chem. Lett.*, 2003, **32**, 62.

Keywords: photochemistry coordination compound, accurate measurement, crystallography instrumentation synchrotron radiation

MS24.25.4

Acta Cryst. (2005). A**61**, C36

Multitemperature X-ray Diffraction Analysis in the Study of Phase Transitions, Molecular Dynamics and Crystal Disorder

Mikhail Yu. Antipin, *Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia.* E-mail: m_antipin@yahoo.com

Routine ability to analyze crystal structures of different compounds at many temperatures (including "low" temperatures - up to 100K, and "very low" ones - up to 20-30K or even less) is important in many cases for different applications in the study of phase transitions, the nature of crystal disorder, and the study of dynamics of molecular (atomic) motions in the solid state. In addition, low-temperature data collection allows one to increase dramatically real accuracy of diffraction data and to increase the field of its analytical applications (the study of low-melting and/or unstable compounds). In particular, several methods of low-temperature crystallization techniques were elaborated during last time to analyze crystal structures of compounds which are liquids or even gases at normal conditions. Some new examples of the low/multitemperature X-ray diffraction analysis of molecular crystals will be demonstrated. These examples include the study of strong H-bond dynamics in organic compounds, polymorphism, phase transitions in liquid-crystalline precursors, structural studies of high-energetic and non-linear optical materials.

Keywords: multitemperature X-ray diffraction analysis, phase transitions, crystal disorder

MS24.25.5

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Melting-point Variation in Isomeric Dibromobenzenes

Kamil F. Dziubek, Andrzej Katrusiak, *Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland.* E-mail: rumianek@amu.edu.pl

Single crystals of 1,2- and 1,3-dibromobenzenes have been *in situ* pressure crystallized in diamond anvil cells and studied by X-ray diffraction. Both structures are orthorhombic: 1,2-dibromobenzene (0.3 GPa), space group *Pbca*, $Z = 8$, $a = 7.831(1)$ Å, $b = 15.256(1)$ Å, $c = 11.701(2)$ Å; 1,3-dibromobenzene (0.2 GPa), space group $P2_12_12_1$, $Z = 8$, $a = 4.105(1)$ Å, $b = 12.899(5)$ Å, $c = 25.987(28)$ Å. The relationship between the molecular symmetry and the melting point of the dibromobenzene isomers has been discussed. According to the empirical Carnelley's rule high molecular symmetry is related with high melting point [1], [2]. This effect however can be justified in various ways. The melting points are: 278-280 K for 1,2-, 266 K for 1,3-, and 356-360 K for 1,4-dibromobenzene. The Br···Br intermolecular interactions are distinct in both these structures, and they can be considered to be the main factor responsible for the molecular rearrangements in these crystals.

[1] Carnelley T., *Philos Mag. 5th series*, 1985, **13**, 112-130. [2] Brown R. J. C., Brown R. F. C., *J. Chem. Educ.*, 2000, **77**, 724-731.

Keywords: high-pressure structure determination, halogens, structure-property relationships in solids

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MS25 STRUCTURE DETERMINATION FROM POWDER DIFFRACTION DATA (ORGANICS)

Chairpersons: Andrew Fitch, John Faber

MS25.25.1

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Solving Organic Structures from Powder Diffraction: News from the FOX

Vincent Favre-Nicolin[a,b], Radovan Černý[c], [a]*Commissariat à L'Energie Atomique, DRFMC/SP2M/NRS, 17 rue des martyrs, 38054 Grenoble Cedex 9, France.* [b]*Université Joseph Fourier, BP 53, 38041 Grenoble Cedex 9, France.* [c]*Laboratoire de Cristallographie, Université de Genève, 24, quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland.* E-mail: Vincent.Favre-Nicolin@cea.fr

FOX, "Free Objects for Xtallography" [1][2] is a program for *ab initio* crystal structure solution using direct-space methods. While it was first developped and used to solve inorganic structures (oxides, intermetallic, hydrides), the algorithms used were not dedicated to any type of compound and organic structures could also be solved.

Over the last two years many modifications have been brought to the algorithm (mostly through a restraint-based description rather than a z-matrix one), to allow a better, more flexible description of molecular compounds.

We will present how the evolution of the algorithm has improved the ability to solve organic structures, along with new Fox features (multiple solutions, maximum likelihood,...).

[1] Favre-Nicolin V., Černý, R., *J. Appl. Cryst.*, 2002, **35**, 734. [2]Favre-Nicolin V.,Černý R., *Z. Kristallogr.*, 2004, **219**, 847.

Keywords: powder structures, ab initio structure determination, algorithms

MS25.25.2

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Molecular Crystal Structures from Low-Resolution Powder Diffraction Data: Reliability and Validation of the Results Obtained

Vladimir V. Chernyshev, *Department of Chemistry, Moscow State University, 199992 Moscow, Russia.* E-mail: vladimir@struct.chem.msu.ru

In recent years, an obvious progress has occurred in the determination of molecular crystal structures *ab initio* from powder diffraction data. There are no doubts now, the molecular crystal structures with the known connectivity set in the molecule(s) can be routinely solved even from the data measured at the laboratory powder diffractometer. However, there are the questions still waiting for an exhaustive answering. One of them is a question on how to estimate the reliability of the solution obtained. Another one concerns the accuracy of structural parameters extracted. These questions are exceptionally important for the results obtained at laboratory commonly used devices. There are problems, which can not be clarified with the use of laboratory data only. So the problem of positioning of the selected hydrogens is beyond the facilities of many laboratory X-ray powder diffractometers, which are virtually "insensitive" to the position of H atoms. In this particular case, the neutron diffraction often helps to find a correct position, especially when some, or even all, of the hydrogens are replaced by the deuteriums.

For the new crystal structure solved from laboratory powder data we have a good chance to validate its correctness by the comparison of the results with those, obtained either from high-resolution synchrotron data or, in some cases, from neutron powder diffraction data. The aforementioned comparison allows us to estimate the real accuracy of the results derived from the laboratory powder pattern.

This will be demonstrated on a number of molecular structures solved from laboratory data and validated later with the use of synchrotron and/or neutron data.

Keywords: crystal structure determination X-ray powder data, synchrotron powder diffraction, neutron powder diffraction

MS25.25.3

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Close Contact Penalty Functions in Direct Space Methods and Energetic Considerations in Structure Refinement

Cikui Liang, *Accelrys Software Inc. 10188 Telesis Court, Suite 100, San Diego, CA 92121, USA*. E-mail: cliang@accelrys.com

When solving crystal structures from powder diffraction data using direct space methods, all available information such as molecular structures and space group symmetry is used to limit the number of degrees of freedom. When limited quantity of information is available from a powder diffraction pattern (e.g., broad peaks, preferred orientation, positions of weak scatters) and/or the number of degrees of freedom is large, it may be necessary to add extra chemical information in order to obtain a solution. This chemical information can be that the generated structures should be energetically stable, where the potential energy contributes to a combined figure of merit alongside the powder pattern similarity, R_{wp}.

Considering the fact that viable solutions should not contain overlapping atoms, adding a simple close contact penalty that prevents solutions with non-viable intermolecular interactions from being generated is adequate for the global optimization process, which aims at locating a rough, refinenable solution.

During Rietveld refinement an accurate description of the potential energy should be used in combination with the R_{wp} in a weighted optimization process. The a priori determination of the weighting factor might not be intuitive; in such cases a Pareto optimization (a posteriori preference articulation) can be used to obtain an appropriate value so as to ensure that structures that are both chemically viable and in close agreement with the experimental powder pattern.

Keywords: ab-initio structure determination, Rietveld structure refinement, potential energy

MS25.25.4

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Differential Thermal Expansion and Laboratory Capillary X-ray Powder Diffraction: Progress, Practicalities and Performance

Philippe Fernandes[a], Alastair J. Florence[a], Norman Shankland[a], Alan R. Kennedy[b], Bill David[c], Kenneth Shankland[c], [a]*Dept. of Pharmaceutical Sciences, University of Strathclyde, 27 Taylor Street Glasgow, G4 0NR, U.K.* . [b] *Dept. of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL.* [c]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon., U.K.* E-mail: Philipe.fernandes@strath.ac.uk

The challenge for experimental XRPD applied to crystal structure determination, is to obtain the best possible estimates of diffracted intensities. The chance of achieving this is enhanced by using (i) low-***T*** data collections to decrease thermal vibration and therefore boost the intensities seen at higher diffraction angles and (ii) new PSD detector technologies yielding improved signal-to-noise and count-rates. Importantly, significant improvements to the extracted intensity information available from overlapping peaks may be gained by using multiple low-***T*** data collections, thereby exploiting differential thermal expansion (DTE) [1,2]. Here we present the exploitation of DTE to retrieve an immense amount of accurate intensity data from a series of laboratory capillary X-ray powder diffraction data sets collected at several temperatures. We describe a validated method for intensity extraction and include details on the impact of improved PSD detectors and high intensity laboratory X-ray sources on this approach.

[1] David W. I. F., Shankland K., McCusker L. B., Baerlocher Ch. in Structure Determination from Powder Diffraction Data, Ch. 1, David et al. (Eds), Oxford University Press, Oxford, 2002. [2] Zachariasen W. H., Ellinger F. H., *Acta Crystallogr.*, 1963, **16**, 369.

Keywords: X-ray powder diffraction, differential thermal expansion, crystal structure determination

MS25.25.5

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Rapid Structure Solution using Global Optimisation and Distributed Computing

Kenneth Shankland[a], Tom Griffin[a], Anders J. Markvardsen[a], Bill David[a], Jacco van de Streek[b], [a]*ISIS Facility, Rutherford Appleton Laboratory UK.* . [b] *CCCD, 12 Union Road, Cambridge.* E-mail: k.shankland@rl.ac.uk

The use of global optimisation methods has helped to increase the size and complexity of molecular organic structures that can be solved directly from powder diffraction data. These methods require many repeat runs to be performed in order to confirm the location of the global minimum in parameter space; this is particularly true for very complex structures, where success rates in locating the minimum may fall to only a few percent. Fortunately, these multiple runs can be performed independently of each other and as such, they are ideally suited to the notion of grid-type computing. We have recently adapted the DASH [1] program to run under the GridMP [2] distributed computing system; the current setup allows up to eighty DASH simulated annealing runs to be executed in parallel on *existing* desktop resources. Initial results show not only impressive performance gains but also indicate that new computational routes that were previously closed to us (due to their compute-intensive requirements) are now open. For example, full characterisation of a hybrid Monte Carlo (HMC) method of structure determination from powder diffraction data required many months of CPU time; the work was performed in a matter of days using a grid-adapted version of the HMC code [3].

[1] David W.I.F., Shankland K., Shankland N., *Chem. Commun.*, 1998, 931-932. [2] http://www.ud.com [3] Markvardsen A.J., Shankland K., David W.I.F., Didlick G., *J. Appl. Cryst.*, 2005, **38**, 107-111.

Keywords: powder diffraction, structure determination, parallel computing

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MS26 RECENT ADVANCES IN QUASICRYSTAL RESEARCH

Chairpersons: Koh Saitoh, Ron Lifshitz

MS26.25.1

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Fabricating Novel Symmetry Nanoscale Systems using Quasicrystal Surfaces

Rónán McGrath, *Department of Physics and Surface Science Research Centre, University of Liverpool, Liverpool L69 3BX, UK.* . E-mail: mcgrath@liv.ac.uk

Quasicrystals are metallic alloys which have unusual structural properties: they are aperiodic and may display symmetries not observed in periodic materials. The surfaces of these materials offer opportunities for the fabrication of nanostructures and thin films which themselves have unusual symmetries and structures. In turn, measurements of such nanostructured systems may offer insights into the larger question of the relationship between physical properties and aperiodicity. Several such systems have been fabricated and are under investigation in our laboratory, and some examples will be shown.

One spectacular case is that of an ultrathin film grown by the deposition of copper atoms on the five-fold surface of the icosahedral $Al_{70}Pd_{21}Mn_9$ quasicrystal [1]. STM images show that the in-plane structure comprises rows having separations of S=4.5±0.2 Å and L=7.3±0.3 Å, whose ratio is the Golden mean τ=1.618... within experimental error. The sequences of such row separations form segments of terms of the Fibonacci sequence, indicative of the formation of a pseudomorphic Cu film. We have recently demonstrated that such films can also be grown using magnetic elements such as Co, Fe and Ni. Characterisation of their magnetic properties has also been undertaken and will be discussed.

[1] Ledieu J., Hoeft J.T., Reid D.E., Smerdon J.A., Diehl R.D., Lograsso T.A., Ross A.R., McGrath R., *Phys. Rev. Lett.*, 2004, **92**, 135507.

Keywords: quasicrystals, nanostructures, scanning tunnelling microscopy