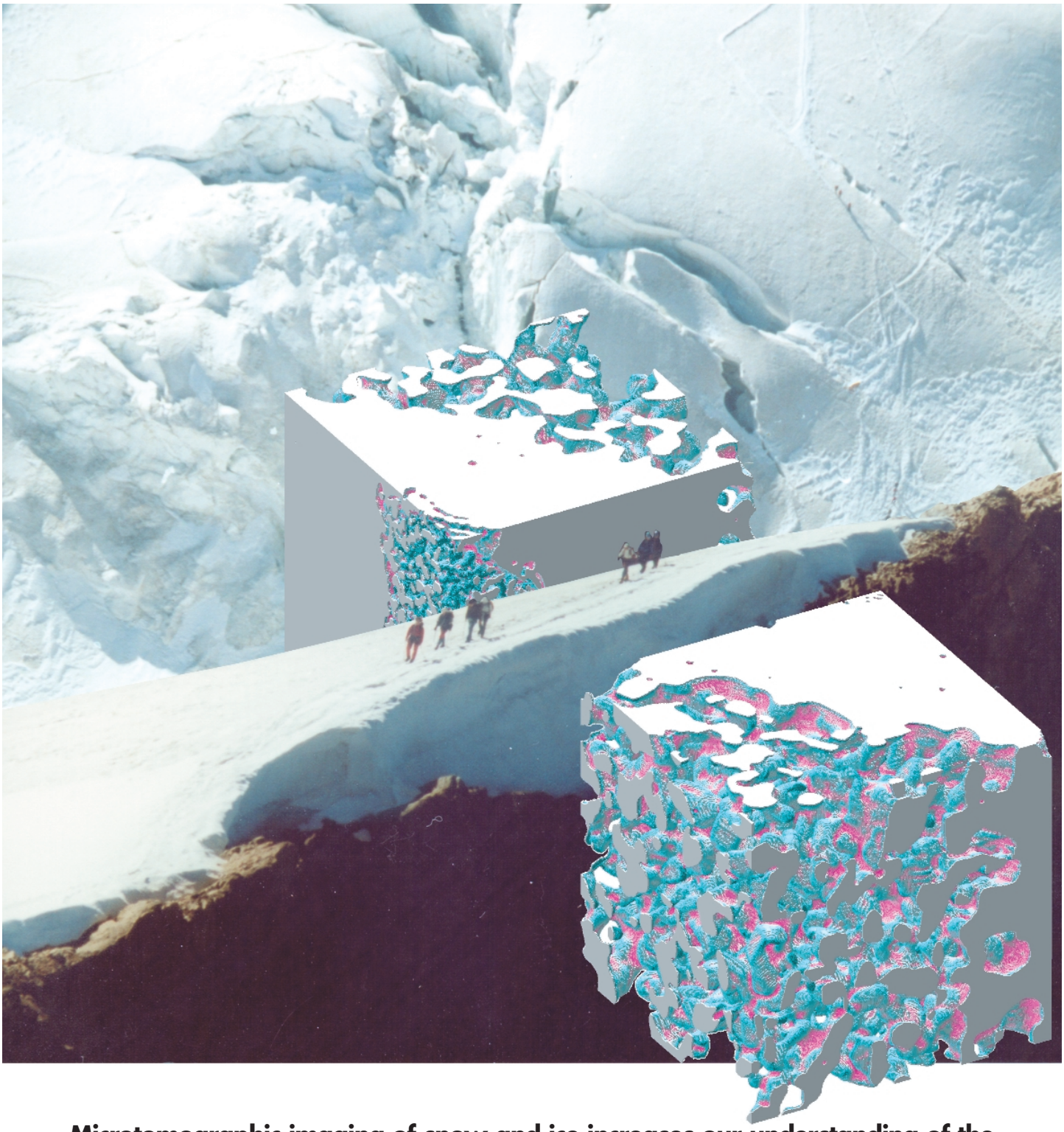
ESRF NEWSLETTER

JUNE 2001 EUROPEAN SYNCHROTRON RADIATION FACILITY N° 35



Microtomographic imaging of snow and ice increases our understanding of the environment: 3-D reconstructed views of snow taken from the site of an avalanche permit identification of the granular layers that contribute to their occurrence.

ISSN 1011-9310

COMMENT:

A PERSONAL VIEW BY THE DIRECTOR GENERAL

Yves Petroff and Bill Stirling.

My feelings on arriving at the ESRF in January as the new Director General were a mixture of apprehension and anticipation. I was aware that there were considerable gaps in my knowledge of the ESRF, but I looked forward with some excitement to the new colleagues and new challenges which awaited me. Despite several months of preparation – sitting in on meetings of the Direction and meetings of the Science Advisory Committee and Council, building on many years as a User and as a scientist in charge of a Collaborating Research Group – January was a tough month. As were February, March, April and May! Many hours of negotiation on the Collective Agreement with our colleagues from the unions have given me a profound insight into the workings of the ESRF as a human enterprise rather than just a wonderfully effective research institute. The preparation for our three major committees – the Administrative and Finance Committee, the Science Advisory Committee and the Council – have expanded my understanding of how the ESRF is organised with respect to its many member and associate countries (16 at the last count). My training is far from over, but I now feel that I am beginning to appreciate the major issues facing us.

For the ESRF is now in a process of profound change. The hectic activity of the construction period is giving way to a phase of scientific exploitation of all 30-plus beamlines. But this does not imply that our beamlines and instruments will become static, frozen into their current configurations. One of the pillars of the ESRF's success has been the continuous development of the machine and beamlines. This will continue as we make every effort to remain as international leaders in the use of synchrotron radiation.

This is also a period of major staff changes. We continue to benefit from the skill and experience of new young staff, predominantly in the scientific and technical areas. By the middle of 2002, all of the previous Directorate will have been replaced. Such a rapid turnover of senior management would not be possible without the conscientious support of the ESRF staff.

What are our major projects for the next few years? The Medium-Term Scientific Programme (MTSP), about to be updated, foresees exciting developments spanning the whole range of the ESRF's activities. New extensions of photoemission spectroscopy to higher energies will open up new research possibilities, while high magnetic field facilities could revolutionise the study of magnetic materials. The ESRF's advanced techniques in microscopy on the nanometre scale will have a major impact in the crucial areas of nanotechnology. In the life sciences, a "New Partnership for Structural Biology" will unite the ESRF with the EMBL and the ILL in an ambitious programme to create a major European centre for biological structure determination and genomics. We have already carried out extensive consultations with the ESRF's Users in the preparation of the MTSP. This partnership will be even more important during the implementation of the programme.

We will need to look carefully at our existing infrastructure and organisation in the light of these and other projects. The ESRF's buildings are already bursting at the seams – we must face the problem of our critical lack of office and laboratory space. Do we need a new building or buildings? Are our internal organisational structures appropriate to the current size of the ESRF and our role in the future? In some cases it is evident that we need to think about how to improve our organisation to face the new challenges ahead of us. Is our communication adequate, internally and towards the world outside? Once again, this is a question that requires careful consideration. Nevertheless, given the experience and expertise of our excellent staff, I have no doubt that we will succeed with the transformations required to prepare the ESRF for a long and successful future as the world's leading synchrotron radiation laboratory.

A final word of thanks to my predecessor, Yves Petroff: his effective and imaginative leadership has ensured that the ESRF and its staff are prepared to meet the challenges of future years. On behalf of all of us here, thank you Yves, and enjoy your time in Berkeley, once again carrying out experiments as a working physicist.

Bill Stirling

Contents

Photography by:
G. Admans, E.E. Alp, C. Argoud, S. Claisse, B. Denis, K. Fletcher.

HERCULES

Report from HERCULES 2001

The 11th session of the HERCULES (Higher European Research Course for Users of Large Experimental Systems) course was held from 4 March to 11 April 2001. This school was organised by the Universities in Grenoble (UJF and INPG), the University of Paris-Sud, and had the support of several large research facilities and laboratories (ESRF, ILL, CNRS, CEA, LURE, LLB, IBS, EMBL). It was dedicated to the use of "Neutron and Synchrotron Radiation" and offered two specialised sessions "Physics and Chemistry of Condensed Matter" and "Biomolecular Structure and Dynamics". This year the 72 selected PhD students and post-doctoral scientists came mainly from the EC, with a few from Eastern Europe (Bulgaria, Georgia, Rumania, Russia, Slovakia), America (Brazil, Canada, Mexico, US), and Israel.

Participants and organisers of the HERCULES 2001 Course on Neutron and Synchrotron Radiation for "Physics and Chemistry of Condensed Matter" and "Biomolecular Structure and Dynamics".

Participants were taught through lectures, tutorials and practicals. Lectures were given by 63 speakers, each an expert in the field concerned. The participants received 50 hours of personalised training, in groups of four, from the 100 research scientists and teachers who took charge of the practical and tutorial sessions. The scientists and teachers came from the local scientific community and represented a wide range of nationalities. Another specificity of the HERCULES course was its practical training organised at the neutron and synchrotron beamlines of the large-scale facilities, such as the ESRF, ILL, LURE and LLB. The participants gained "hands-on" practical experience of using neutron and synchrotron radiation for the study of materials, which aimed at demonstrating the importance of each method used. Furthermore they were able to establish contact with the scientists in charge in the large-scale facilities, and so they had the opportunity to discover the potential existing there.

The programme of the course was structured to highlight the impact of fundamental and technological breakthroughs in research using synchrotron radiation and neutrons centred at the large-scale facilities. As usual the scientific content included a variety of methods (diffraction, inelastic scattering, absorption imaging, etc.) which were applied to various materials. The programme of the Biomolecular session reflected the content of volume IV of the HERCULES series entitled "Structure and Dynamics of Biomolecules" (19 contributions) which was published in 2000 by Oxford University Press.

Although the schedule was as tight as usual, there was some time for participants to exchange scientific and non-scientific ideas, during the poster session and the skiing outing. They also joined in common musical and dancing experiments with the help of a jazz orchestra during a dinner party in the mountains, and, like last year, the course ended with a wine and cheese party preceded by a multi-disciplinary conference on Hercules, the Greek hero.

The HERCULES course will, of course, be organised again in 2002.

J-L. Hodeau

HERCULES 2002

HIGHER EUROPEAN RESEARCH COURSE FOR USERS OF LARGE EXPERIMENTAL SYSTEMS

Grenoble, 17 February - 28 March 2002

Session A:
"Neutron and synchrotron radiation for physics and chemistry of condensed matter"

Session B:
"Neutron and synchrotron radiation for biomolecular structure and dynamics"

Information:
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http://www.polycnrs-gre.fr/hercules.html

Deadline for application: 16 October 2001

ELEVENTH ESRF USERS' MEETING

19 February 2001

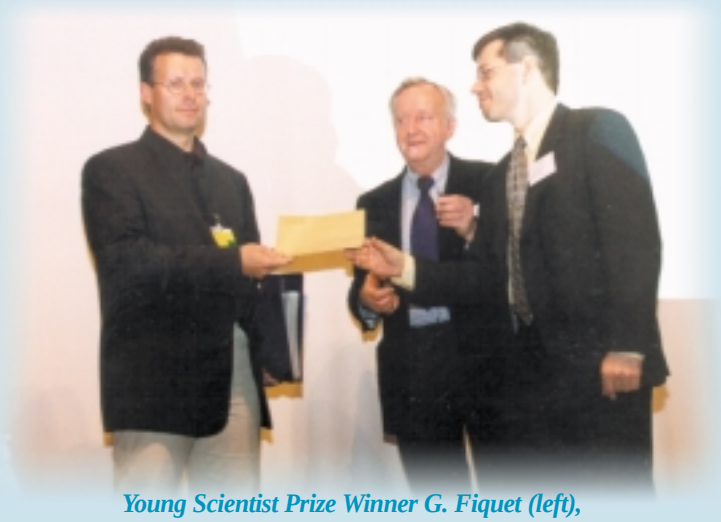
This year, the Users' Meeting was focussed on the ESRF's Medium Term Scientific Plan for most of the plenary session on Monday 19 February. This theme attracted just as many participants as the traditional format of reports and research highlights, with outside users constituting almost half of the ~ 400 registrations. Once again this healthy participation rate is due to the attraction of the accompanying workshop programme.

Bill Stirling opened the meeting with a historical view of developments at the ESRF, summarising the major advances to date. He stressed the importance of the Users' involvement to improve the Medium Term Scientific Plan (MTSP), and he invited their suggestions and criticism of the plan drafted beforehand by the ESRF's scientists and management. After a presentation about machine developments by Pascal Elleaume, there followed a succession of presentations by ESRF scientists engaged in crystal ball-gazing across the spectrum of experimental synchrotron radiation activities. They drew upon the discussions opened at the ESRF Local Scientists' Meeting, which took place at the end of May 2000 at Lac d'Annecy. Each speaker represented a group of beamlines and made predictions that covered a wide range of research areas. The presentations, by and large, took examples of recent research as exemplifying "The Way Forward", with progress coming from evolution rather than revolution. "Better, Faster and Smaller" was the recurrent theme with just a few specific suggestions for new ventures.

The experiment of holding lunchtime focus group discussions provided varied points for the afternoon feedback session and not too many complaints that talking should come a poor second to eating at that time of day. Some lack of focus in the feedback session perhaps reflected the absence of specific proposals in the current MTSP discussion document, but some recurrent themes did emerge. The Users' Organisation, through its new Chair, Keijo Hämäläinen (University of Helsinki) will be soliciting further feedback from attendees over the next few months.

The traditional meeting format was regained mid afternoon with Malcolm Cooper introducing the new members of the Users' Organisation. He then handed over to Keijo before the announcement of the winner of the Young Scientist prize. Keijo listed the previous winners of this award and pointed out that in 1995 the winner was Francesco Sette, who will soon become a research director of the ESRF. Keijo concluded by saying that as much is also expected of this year's winner. Jens Als-Nielsen, chairman of the award committee (the committee also included John Helliwell, Alan Leadbetter and Christian Vettier), gave a brief introduction to the scientific importance of the work done by the winner before inviting Guillaume Fiquet to collect his prize and to make a presentation. Guillaume described his work under the title "The Physics of the Earth's Interior".

The Users' Organisation Committee 2001: (from left to right) O. Figueiredo, P. Charlier, D. Nicholson, J.-Y. Buffière, M. Cooper, F. Bosherini (retiring member), F. D'Acapito, P. Fairclough and K. Hämäläinen. (absent: A. Kaprolat and R. Kahn).



Young Scientist Prize Winner G. Fiquet (left), with J. Als-Nielsen (centre) and K. Hämäläinen (right).

Keijo drew the plenary session to a close by presenting flowers to the Users' Office and CRG Office staff who had organised the meeting. To add a little humour, he even offered a bunch to Malcolm in thanks for his work as chairman of the Users' Organisation over the last two years. Later on there was a lively poster session, which ended with a reception hosted by Bill Stirling. Further lubrication was available to aid or hinder scientific discourse over a buffet dinner.

Our thanks go to the ESRF staff members who helped organise this meeting, particularly the CRG and Users' Office staff.

K. Hämäläinen and M. Cooper
on behalf of the Users' Organisation

… Eleventh ESRF Users' Meeting

WORKSHOPS ASSOCIATED WITH THE USERS' MEETING

There were three satellite workshops to the Users' Meeting: "High-Throughput Structural Biology", "Science at High Pressure" and "Environmental Studies using Neutron and Synchrotron Facilities". The workshops are introduced briefly here, and selected presentations from each workshop are included as articles in this edition of the Newsletter.

HIGH-THROUGHPUT STRUCTURAL BIOLOGY

Posters and aperitif.

The recent publication of the draft version of the Human Genome has highlighted the growing need for automation of the process of structure determination for biomolecules. Some of the issues around this problem were addressed in the High-Throughput Structural Biology Workshop, held at the ESRF on the 20 and 21 February 2001.

The scientific programme addressed the concerns of those involved in structural biology, whether they are affiliated to proprietary or academic groups or to synchrotron radiation sources. The meeting was set in the context of the availability of the human genome with opening lectures by I. Mattaj (EMBL Heidelberg, Germany), and T. Hubbard (Sanger Centre, Cambridge, UK). The challenges of high-throughput protein production, purification and crystallisation were addressed from an academic and commercial perspective. Plans to adapt synchrotron radiation beamlines to allow for a very high degree of automation were presented by P. Kuhn (SSRL), B-C. Wang (Univ. Georgia), and E. Mitchell (ESRF). Following on from this the techniques for automatic data collection, analysis, structure solution and refinement were discussed.

The use of bioinformatics as both an aid for target selection, protein structure evaluation, as well as a tool for genome annotation and analysis were discussed in another session. The meeting was brought to a conclusion by M. van der Rest (IBS, Grenoble, France) who asked the question "Where do we go from here ?" This address then led into a lively discussion session.

A number of talks made the point that proteins and enzymes do not work in isolation but are normally components in more complex processes and thus the "structural genomics approach" may not always be the answer to the scientific question being asked. However, given that, in the USA, the National Institute of Medical Sciences has predicted the need for around 10,000 structures to be solved in the next ten years, "high throughput" is likely to be one of the key phrases in structural biology for a number of years to come.

A. Leslie, speaking about automated data processing.

Our intention in drawing up the programme was that the meeting should address both the practical difficulties and the scientific opportunities brought by the massive increase in genomic information.

The three presentations reported here focus on various areas of the programme. In the first article "Structural Genomics:- Pitfalls and Prospects", on page 35, A. Bridges describes how the genome sequence is used for drug design, and the need for scale-up and automation. The next two articles concern automation of the process of protein structure determination: in "Automated Data Collection and Processing for Macromolecular Crystallography", on page 36, A. Leslie discusses some of the ideas for complete automation of data collection and demonstrates that this goal may well be feasible within a relatively short time. Finally, E. Mitchell discusses the practical implementation of automation processes at synchrotron radiation sources, in the article "Automation of the Macromolecular Crystallography Beamlines at the ESRF", on page 39.

S. McSweeney

Science at High Pressure

The workshop entitled "Science at High Pressure: Latest Trends from Third-Generation Sources" was held at the ESRF on the 16 and 17 February 2001, accompanying the traditional Users' Meeting. The workshop attracted about 100 participants. Twenty-one scientists, representing the main research groups active in the field across the globe, gave some very interesting presentations on the latest contributions of third-generation synchrotron sources to high-pressure science. The programme was divided into three sessions reflecting the most relevant activities in the field: i.e. earth sciences, chemistry and hard-condensed matter. The presentations focussed on the hottest scientific questions relating to these fields and were followed by dynamic discussions. A variety of techniques such as X-ray diffraction, Mössbauer spectroscopy, inelastic X-ray scattering, Compton scattering and EXAFS were presented. Two of the presentations were selected for articles: High-pressure syntheses of superhard materials "*In situ* Synchrotron X-ray Diffraction Studies of HP-HT Synthesis of Superhard Phases in the B–C–N System" are presented by V. Solozhenko, on page 30. Unusual structures found in metals at high-pressures are described by M. McMahon in the article "Weird Metals – Modulations within Guests within Hosts" on page 33.

M. Mezouar and M. Hanfland

F. Guyot (centre) gave a plenary lecture entitled "New Opportunities for High-pressure Geophysics at Third-Generation Synchrotrons". He is pictured here with G. Fiquet (left) and M. Krisch (right).

Environmental Studies Using Neutron and Synchrotron Facilities

The ESRF and the ILL jointly organised a two-day workshop on environmental studies on the 20 and 21 February 2001. The workshop attracted more than one hundred scientists in the field and featured 19 invited speakers.

The workshop was closed by an animated discussion of the future need of the ILL and the ESRF in environmental research. Topics like time-resolved studies, microfocussing, *in situ* studies, neutron activation and combinations of methods were of great interest. The management was also encouraged to provide means of rapid access to the facilities for urgent studies.

Visiting the ILL research facilities: A. Hewat, ILL, showing the ILL D19 diffractometer to participants of the workshop.

The first session addressed nuclear and chemical pollution. It included talks about nuclear waste transmutation, characterisation of particles, and heavy-metal speciation. The analytical techniques discussed were neutron reflectometry, synchrotron-based X-ray microbeam techniques, and EXAFS studies. The second session was about general pollution detection and waste disposal, and included talks on neutron activation analysis, probing natural material with microspectroscopy using synchrotron radiation, the environmental relevance of gas hydrates, and recent advances in analysis of heavy metals in plant tissues. The session was concluded with three talks on snow and ice. A poster session and a press conference rounded off the day.

The theme for the second day was energy and efficient energy storage. Topics included: the tracking of metals in geofluids; use of SANS and SAXS in petroleum geology; attempts to produce efficient hydrogen storage in metals; new environmentally-friendly battery materials; and a study of hydrocarbons in zeolites. Following lunch, participants were invited to take a tour of the ESRF and ILL facilities.

Three talks have been selected for inclusion in this edition of the Newsletter, and demonstrate well the variety of topics covered. The first, which was also the introductory talk of the workshop, is entitled "X-ray and Neutron Studies of the Optimised Synthesis, the Structure and the Transformations Involving Novel Ion Exchangers" by J. Parise (State University of New York, USA), on page 22. The second "3-D Snow and Ice Images by X-ray Microtomography", on page 24, is by C. Coléou and J.-M. Barnola (Météo-France, Centre d'Etudes de la Neige and Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS, Grenoble). Finally, "Investigation of Positive Electrode Materials for Lithium Batteries by Means of X-ray and Neutron Diffraction", page 27, by C. Masquelier (Laboratoire de Réactivité et de Chimie des Solides, CNRS, Amiens).

Å. Kvick

MEDICAL APPLICATIONS OF SYNCHROTRON RADIATION WORKSHOP

1/3 March 2001

A scientific meeting of elder statesmen and young scientists is a good way to summarise the Medical Applications of Synchrotron Radiation Workshop, held at the ESRF between 1 and 3 March 2001. The workshop was jointly funded by the ESRF, the Centre Hospitalier Universitaire de Grenoble (CHU), and the Université Joseph Fourier. The programme was comprehensive in its breadth of synchrotron radiation research in the medical field. Over 100 participants from 12 countries celebrated the extraordinary growth of the field during the 15 years since the first human angiograms were obtained at SSRL.

The workshop opened with historical overviews by the organisers W. Thomlinson, F. Estève and JF. Le Bas. E. Rubenstein then initiated the scientific sessions with a lecture describing a new potential application of our technology to neurodegenerative disorders of the brain. This talk by the director of the first medical applications programme – human coronary angiography at SSRL – a high point of the workshop as he tied together the older mature programmes and new and exciting prospective research.

The growth of the field has been made possible because of the existence of dedicated medical research facilities. This was the theme developed in a talk by E. Castelli who highlighted the facilities at ELETTRA, NSLS, HASYLAB, Photon Factory, and our new one at ESRF. Several new facilities are being constructed or planned in Korea, Canada and Japan, giving evidence for the healthy growth of the field over the coming years.

The first session on imaging was devoted to the bronchography project that is a collaboration between the ESRF, the CHU, and the University of Helsinki Hospital and Physics Department. An overview of the present status and future needs in the field of lung functional and structural imaging was presented by C-G. Standertskjöld-Nordenstam, followed by an overview of the local project by S. Bayat.

Radiation therapy took centre stage for two sessions. The first of three major areas of research presented was photon activation therapy. J. Balosso presented results on the use of platinum to increase the response to radiation doses by cells in an *in vitro* cell model. A second talk on this topic was given by B. Laster who highlighted the use of incorporated target atoms for overcoming the small cross-section for dose delivery. H. Blattmann presented the microbeam radiation therapy project that is being pursued on the ESRF ID17 beamline by a team from the Univ. of Bern, Switzerland. He presented the very exciting results obtained so far on small and large animals. If the programme continues to show success, it may be possible to advance it to the stage of human research for treatment of some brain tumours in infants and small children. A. Norman presented the concept of using mono-energetic X-rays to improve the therapeutic ratio in X-ray tomography therapy of brain tumours. At the ESRF, a team of researchers from the CHU is developing the necessary synchrotron-based protocol for potential extension to human research. H. Elleaume presented the status of this programme.

The workshop highlighted human coronary angiography, the only programmes involving in vivo human studies. W R. Dix described the results of the extensive programme at HASYLAB on 370 patients. His summary described

the strengths and problems associated with the synchrotron imaging compared with MRI. S. Ohtsuka discussed the results at the Photon Factory. B. Bertrand described the results obtained during the first protocol on 32 patients at the ESRF.

F. Berger presented a critical analysis of the importance of angiogenesis with emphasis on therapeutic applications. Recent experiments have been carried out at the ESRF to develop the technology of measuring cerebral blood volume. JF Adam and I. Troprès presented their results and showed a good correlation between MRI and synchrotron CT measurements.

Medical imaging at synchrotrons is now utilising phase information. P. Cloetens presented an overview of the various methods being developed for phase contrast imaging. M. Ando discussed a novel use of asymmetric reflection optics to simultaneously obtain images of a sample that contain absorption, phase contrast, and refraction information. S. Fiedler described the fundamental concepts of diffraction enhanced imaging being pursued at the ESRF.

The two previous workshops of this series, held in Japan, featured outstanding hospitality in wonderful mountain settings. Hot springs and karaoke brought the participants together in happy, interactive gatherings. In Grenoble, we have not only mountains but also genuine French châteaux! It is fair to say that the evening at the Château du Mollard will never be forgotten. Starting with aperitifs and music provided by a joint ESRF-CHU group, the evening rapidly warmed up! During the early course of dinner, the young Italian participants started singing. From that point on we were rewarded with songs by our colleagues from around the world in French, Japanese, English, Finnish, Italian, and Swedish.

The workshop had three sessions devoted to research on cell/tissue imaging and the analysis of tissues. The role of X-ray scattering in medicine was critically reviewed by J. Doucet. He ranked the contributions of scattering to medical research as important, but its importance to diagnosis and screening is far from being demonstrated. Talks by M. Fernandez and A. Evans discussed the analysis of cancerous tissues using scattered radiation. F. Peyrin discussed the application of synchrotron radiation microtomography to the evaluation of bone quality.

The development of the diffraction enhanced imaging (DEI) technique has renewed interest in synchrotron radiation mammography. E. Pisano motivated the mammography studies with an overview of the current status of diagnosis in the clinic and the need for better imaging. She and A. Dilmanian summarised the results obtained by the DEI group in the United States. Recent experiments at the ESRF were presented by A. Bravin and F. Arfelli discussed the images recorded at the SYRMEP beamline at ELETTRA.

In his conference summary, P. Suortti highlighted the many new directions of research, built upon 25 years of instrumentation and science. A challenge was given to the participants to find a solution to the serious problem of the lack of a compact source technology. Without such a source, many of the promising technologies will never be applicable in the clinic. The next workshop of this series will be in Trieste, Italy, in September 2003.

W. Thomlinson

Bill Thomlinson, beamline scientist at the Medical Beamline, ID17.

Frank Kreith Distinguished Lecturer Award

Bill Thomlinson has been selected to receive the Frank Kreith Distinguished Lecturer Award from the Faculty of Engineering Sciences of the Ben Gurion University of the Negev in Beer-Sheva, Israel.

This award recognises and acknowledges Bill's capabilities in conducting experimental research for the application of synchrotron radiation to medicine, and for his ability to bring forth to the scientific community a better understanding of the potential benefits of this important instrument for medical research.

Future Applications of Science with Synchrotron Radiation and Free-Electron Lasers in Europe

16/17 March 2001

The workshop took place at the ESRF on 16 and 17 March 2001. It was organised following several suggestions emerging from the 2000 meeting of the European Round Table for Synchrotron Radiation and Free Electron Lasers (FEL's) held in Karlsruhe in September 2000. The main purpose was to initiate an open and broad discussion on the development of new sources in Europe over the next 10-20 years. The objectives were a clarification of the possible development of lines after the recent approval of the Soleil and Diamond projects, and –if possible– a consensus on priorities. The discussions encompassed large storage rings, linac-driven self-amplified spontaneous emission (SASE) devices and energy recovery linac (ERL) based systems. The participants included experts on accelerators and X-ray sources from Europe and the USA, and a limited number of X-ray users. A school on the same theme at Les Houches preceded the workshop in Grenoble.

Two days of presentations and discussions were extremely helpful in clarifying the foreseeable avenues of technical development. They also revealed several important points of broad consensus that could provide the basis for a realistic and effective long-term strategy in Europe. A report to be presented to the European Commission by the chairman of the Round Table (G. Margaritondo) is in preparation.

P. Lindley

Workshop on Nuclear Inelastic Scattering

23/24 April 2001

After the preceding workshop four years ago at APS (Argonne, USA) the Nuclear Resonance groups organised a two-day workshop on Nuclear Inelastic Scattering at the ESRF on 23 and 24 April 2001. The aim was to bring together the developers of the method, the experimentalists and the theoreticians in order to discuss this new field. About forty participants from North America, Japan and Europe listened to sixteen talks on the development, prospects and highlights from the three third generation synchrotron radiation sources (APS, ESRF and SPring-8) and on applications specially devoted to high pressure, biology/chemistry and surfaces/interfaces. They were accompanied by talks on the theoretical understanding and treatment of the data with ample time for discussions. The participants look forward to continuing this successful series of workshops and suggested that the next one be held at SPring-8 (Japan).

R. Rüffer and E.E. Alp

Attendees at the NIS Workshop.

History of the Production of a CD-ROM: Synchrotron Light… to Explore Matter

When I arrived at the ESRF at the beginning of 1993, as Information Officer, I was in charge both of information to the scientific community (Newsletter, Annual Report) and of communication with the public, particularly through guided tours, open days, and events such as the French Science Week. My PhD in physics helped for the first part of my work, but I felt that I had few resources for the second part. The most basic book that could be found about the subject was "Introduction to Synchrotron Radiation" by Giorgio Margaritondo, but even this was intended for potential users of synchrotron radiation. Communicating to the public in terms that can be easily understood is quite a difficult task and I still consider it the main challenge of my job today.

The "Synchrotron Light" CD-ROM may be ordered from Springer's web site at http://www.springer.de/synchro

Most of the visitors coming to the ESRF – about 3000 every year – are students and scientists. However, there are also secondary school children and retired people, as well as professionals of all sorts (engineers, doctors of medicine, computer specialists, businessmen, journalists and politicians…). The feature common to all these visitors is their curiosity about science, even when they do not have scientific backgrounds. They are generally enthusiastic about synchrotron technology and science and they sometimes asked so many questions that it was difficult for me to end the visit.

A problem became evident: On one hand, due to lack of personnel, we were unable to accept all the demands for visits and, on the other hand, not all of the school children and university students from European countries would be able to afford to make a trip to the ESRF. It was obvious that something was needed to replace the traditional visit and that a brochure was not sufficient.

The idea of producing a CD-ROM emerged quite naturally and, as soon as 1994, with the very fruitful collaboration of the Daresbury Laboratory and some financial help from the European Commission through the European Science Week, we produced a pilot CD-ROM entitled "Materials for the future". This was a first step but going further needed more resources.

In 1996, the launching of the European "Info 2000" programme offered us the opportunity to present an ambitious CD-ROM project to Bruxelles, associating various partners. Our proposal was not retained and, again, we had the problem of how to finance the project. Finally, in 1998, a solution was found, involving three partners: the ESRF as the producer of the CD-ROM contents, iMediaSoft as the multimedia developer and Springer-Verlag as the worldwide distributor.

Subsequently followed many years of hard work involving many scientific colleagues, which culminated in the release of the CD-ROM "Synchrotron Light… to explore matter", in February 2001. I must say that the reception of the CD-ROM has been extremely positive, particularly among teachers. At a time when fewer and fewer young people are interested in science and scientific careers, the multimedia approach offers the possibility to mix texts, images, sound and animation - a revolution in scientific teaching. Virtual representations, interactivity and computer-generated films offer great possibilities to stimulate the young.

The "Synchrotron Light" CD-ROM is only a beginning. I am already thinking about a second edition (maybe a DVD) with developments in two directions: a fun discovery of a synchrotron for secondary school children (with a quiz?) and more about science for high-level students and scientists. For this new venture, I need the help of all interested people. Please contact me if you have found any errors in the CD-ROM and/or you have any ideas about how to improve it.

To know more about the contents of the CD-ROM itself, please refer to the one-page review written by Michael Hart in the Journal of Synchrotron Radiation (April 2001).

D. Cornuéjols
ESRF Information Officer
Editorial director of the CD-ROM

34TH AND 35TH MEETINGS OF THE COUNCIL

27/28 November 2000 and 5/6 June 2001

Scientific and infrastructure matters

The Council approved the Medium-Term Scientific Programme for the period 2001 to 2005, as presented by Management, as a basis for the financial planning for the medium-term period (see also www.esrf.fr/conferences/usersmeeting01/MTSP/index.htm). The Council agreed that the ESRF Management should continue discussions with the EMBL, the ILL and other relevant agencies with a view to forming a "Partnership for Structural Biology", which would provide the basis for a long-term European strategic initiative in the post-genomic era.

Legal, procedural and financial matters

The Council approved the budget for 2001, providing for an expenditure of 68 777.2 kEuro in payments, and requiring Members' contributions of 62 513.2 kEuro. It confirmed 63 451 kEuro as the planning figure for new contributions from Members to the budget of 2002. It agreed that the contributions received from Portugal towards the initial construction costs of the ESRF shall be incorporated directly into the budgets of the ESRF and no longer assigned to the Members' accounts, with retroactive effect from 2000.

The Council noted Management's intention to extend the arrangement between the Institute of Physics of the Academy of Sciences of the Czech Republic (FZU) and the ESRF concerning the medium-term scientific use of synchrotron radiation for non-proprietary research (with the extension by a further two years, the contribution level has been increased from 0.26 to 0.35% of that of the Members).

The Council also authorised the Director General to sign 5-year extensions of the contracts with INFN concerning the GRAAL experiment and with the Grenoble University Hospital on scientific collaboration especially on the Medical Beamline (ID17).

With regard to corrective measures to improve the balance between scientific use and financial contributions, the Council adopted a resolution (cf. side panel), noted that, in accordance with this resolution, the Members from Nordsync and France will make additional contributions to the 2002 budget of 430 302 Euros and 44 416 Euros, respectively, and noted that for any future allocation of beam time, the French Contracting Party accepts a limitation of its scientific use – keeping it within the acceptable margin as set out in the Council's guidelines.

The Council amended the ESRF's Statutes in order to permit the Scientific Associates to nominate together one member of the Science Advisory Committee (in addition to the previously foreseen 22 members). Another amendment of the Statutes and also of Annex 4 to the Financial Rules was implemented in order to adapt these texts to the new European currency (Euro).

Appointment of Directors, Committees and Chairpersons

The Council appointed

- P. Elleaume as Machine Director for the period from 1 March 2001 to 28 February 2006 (J.M. Filhol having resigned from the post in February 2001);
- A new Science Advisory Committee (see extra box) with J. Bordas as Chairman and L. Braicovich as Vice-Chairman;
- R. Comès as Council Chairman for the period 1 January 2002 to 31 December 2003,

and re-appointed H. Weijma as Chairman of the Administrative and Finance Committee for a further year (1 July 2001 to 30 June 2002).

K. Witte

RESOLUTION ON CORRECTIVE MEASURES

(as adopted by the ESRF Council at its 35th meeting on 5 and 6 June 2001)

1. Having regard to

- the principle of allocation of beam time in accordance with scientific excellence and
- the concern with respect to a possible lasting and significant imbalance between the scientific use of the facility and the contributions to its operation, as expressed in § 6.4 of the ESRF Convention,

the Council decides that any such imbalance shall, in the first instance, be redressed by pragmatic measures of a temporary nature, i.e. without amendments of Convention or Statutes, but rather based on a consensual interpretation of these texts.

2. To this end, at each summer meeting of the Council, the scientific juste retour situation shall be assessed

MEMBERS OF THE SCIENCE ADVISORY COMMITTEE FOR THE YEARS 2001/2002

G. Artioli (Università degli Studi di Milano),
J. Bordas (Universitat Autonoma de Barcelona),
L. Braicovich (Politecnico di Milano),
H. Dosch (Max-Planck-Institut für Metallforschung, Stuttgart),
R. Fourme (LURE),
J.P. Gaspard (Université de Liège),
R. Hilgenfeld (Institut für Molekulare Biotechnologie, Jena),
K. Hodgson (SSRL, Stanford),
D. Juul-Jensen (Risoe National Laboratory, Roskilde), **G.H. Lander** (Institute for Transuranium Elements, Karlsruhe),
L.B. McCusker (ETH Zürich),
P. Monceau (CNRS, Grenoble),
H. Reynaers (Katholieke Universiteit Leuven),
G. Rossi (TASC Laboratori, Trieste),
G.C. Ruocco (Universita dell'Aquila),
D. Shechtmann (Technion, Haifa),
G. Schneider (Karolinska Institutet, Stockholm),
D. Stuart (Wellcome Trust Centre for Human Genetics, Oxford),
S. Suga (University of Osaka),
D.P. Woodruff (University of Warwick),
G. Wortmann (Universität GH Paderborn),
T. Zemb (CEA Saclay).

based on a three-year gliding period, in accordance with the "Guidelines for a Re-adjustment of Contribution Rates" adopted by the Council at its 29th meeting on 9 and 10 June 1998.

3. Those Contracting Parties that, according to these figures, are significantly overbalanced (return coefficient > 1.25 or absolute difference > 3%) shall be requested by the Council

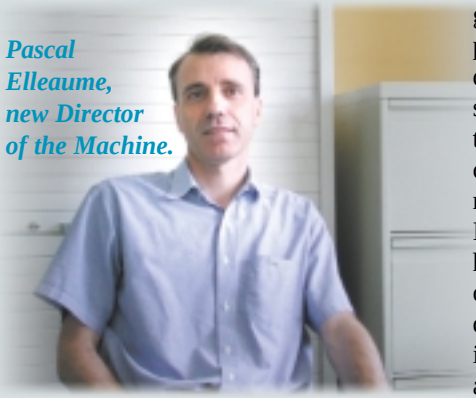
- to make an additional contribution to the next year's budget to such extent that, had it been made for each of the previous three years, it would have kept the return coefficient within the acceptable margin, or
- to accept a limitation of their scientific use during the following year, keeping it within the acceptable margin.

Any additional income created by such a measure should be used by the Management to increase the available beam time or experimental capacity.

4. More permanent measures shall be considered in preparation of the renewal of the Convention or in the event of the accession of new Contracting Parties.

CHANGE OF DIRECTOR IN THE MACHINE DIVISION

Jean-Marc Filhol, Machine Director since January 1997, resigned from his functions on 14 February 2001 to take up a leading role in the construction of the French synchrotron SOLEIL. In his new position as deputy project director, he is more particularly in charge of the construction of the Machine and of the infrastructure.



Pascal Elleaume, new Director of the Machine.

Pascal Elleaume was appointed as Director of the ESRF Machine Division and began his term of office on 1 March 2000, following the earlier-than-expected departure of J.M. Filhol. Pascal graduated in physics at the Ecole Normale Superieure in Paris and obtained the "Agrégation de Physique" in 1978. After a one-year stay at the University of California, Berkeley, he joined the CEA (Saclay) in 1980, where he carried out PhD and postdoctoral studies on the development of the first storage ring based free electron laser operating in the visible range of the spectrum. P. Elleaume joined the ESRF in 1986, in the early days of the project. He was given the task of defining the expected performances from the insertion devices and has contributed significantly to the "Red Book", i.e. the foundation phase report. During the construction phase, he was given the responsibility of setting up the Insertion Devices group which, under his leadership, has designed, built and optimised all the ESRF's insertion devices (more than 60 segments are installed on the ring today). The quality and variety of the ESRF's insertion devices are unique in the world and their innovative concepts have had a strong impact on insertion device technology. Since 1991, he has also been involved in the development of various machine diagnostics based on X-rays (ID6 beamline, pinhole cameras) and scientific software (Xray, Radia, SRW).

OPERATION WITH USERS DURING 2000

During the year 2000, the full complement of 30 ESRF beamlines, together with 8 Collaborating Research Group beamlines (CRGs), were open for user experiments, the CRGs making 1/3 of their beam time available for general ESRF Users. For the purposes of scheduling experiments, the year was divided into two periods, February to July 2000, and August 2000 to mid-February 2001, with run periods of six to seven weeks, broken by shutdown periods for installation, commissioning and maintenance.

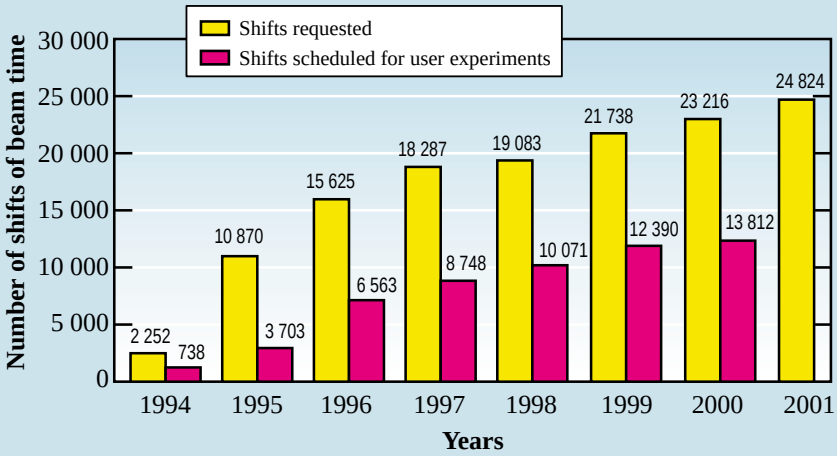


Fig. 1: Details of shifts of beam time requested and scheduled for user experiments per year, 1994 to 2000.

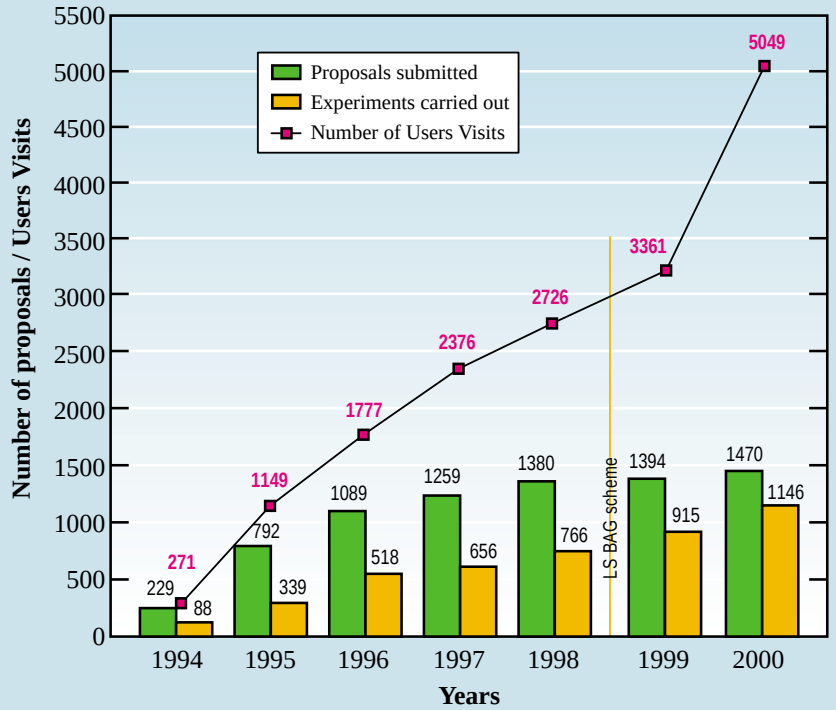


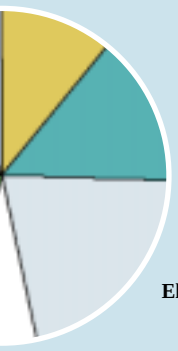
Fig. 2: Numbers of applications for beam time submitted, experiments carried out, and user visits, 1994 to 2000.

Scientists requesting beam time submit applications for two deadlines – 1 March and 1 September – each year. For the proposal round in September 2000, users were able to submit proposals electronically, and some 67% chose to use this new method. For the March 2001 deadline all 837 proposals were successfully submitted electronically.

The increase in requests for beam time since 1994 is shown in **Figure 1**. It is to be noted that although the main beamline construction effort was complete by 1999, requests for beam time continue to rise, and totalled 24 824 shifts in 2001. In the past, such requests have outweighed the beam time available for allocation by roughly a factor of two. This pattern continued during 2000, which saw beam time allocated to 53% or 12 309 of the 23 216 shifts initially requested. **Figure 1** also shows the shifts that have been scheduled for experiments since the beginning of user operation.

The total number of proposals submitted and experiments carried out over the scheduling periods to date is shown in **Figure 2**, which also shows the increase in the number of users since 1994. The most recent proposal rounds have seen a marked increase in the number of applications arriving in the area of Materials Science, both for the Structures review committee and the new committee Materials, Engineering and Environmental Matters, which was created in September 1999. In the Life Sciences, the number of applications from Block Allocation Groups (BAGs) also continues to rise, from 23 groups in 1999 to 34 late in 2000.

Also seen in **Figure 2** is the sharp increase - some 50% in the past 12 months - in the number of user visits, from 3361 user visits in 1999, to 5049 in 2000. This reflects a rise of more than 9% in projects allocated beam



Surfaces and Interfaces	**6 %**
Chemistry	**11 %**
Hard Condensed Matter:	
Elect. & Magn. Properties	**15 %**
Hard Condensed Matter:	
Structures	**21 %**
Materials Eng. & Environmental Matters	**7 %**
Life Sciences	**21 %**
Methods and Instrumentation	**7 %**
Soft Condensed Matter	**8 %**
Other :	
Training, feasibility tests, proprietary research	**4 %**

Fig. 3: Shifts of beam time scheduled and experiments carried out in 2000, by scientific area.

time overall, an increase in the number of Users in each experimental team, and the success of the Life Sciences Block Allocation (BAG) scheme; the latter user teams make multiple visits to groups of beamlines, and are thus able to make maximum use of the facilities for macromolecular crystallography.

The breakdown of shifts scheduled in 2000, per scientific area, is shown in **Figure 3**: some 43% of the shifts scheduled on beamlines were devoted to hard condensed matter and materials research, whilst 21% were devoted to life sciences projects. Further, in order to cater to different types of experimental requirements, beam delivered to the stations was made in a variety of modes: multibunch (2 * 1/3 filling) – 65%; "hybrid" mode - 5%; 16-bunch fill - 24%, and single-bunch fill - 6%, in support of a very diverse scientific programme.

Finally, interested readers are reminded that the next deadline for proposals, for beam time between February and July 2002, is 1st September 2001. Further details can be consulted on the Web at http://www.esrf.fr.

R. Mason

DIAGNOSTICS AND INSTRUMENTATION FOR PARTICLE ACCELERATORS - DIPAC 2001 WORKSHOP

The workshop serves as a forum for the exchange of the latest experiences, results and development in the field of accelerator beam instrumentation worldwide. It takes place at a biennial rhythm, with DIPAC-2001 being the fifth edition.

A total of 150 people attended the workshop on 13-15 May 2001. They represented 42 different institutes or organisations from 14 countries. Among them, 18 came from the USA, 4 from Japan, 1 from Taiwan and 1 from Brazil.

The intensive programme consisted of 12 invited talks, 11 contributed talks, 42 posters and 6 discussion sessions. A guided visit to the ESRF storage ring, an industrial exhibition with 8 participating companies and an exhibition of 'BPM blocks' were also organised. With a large part of the workshop dedicated to oral presentations, the more informal and direct exchange of contacts and information between the participants took place during the discussion sessions and the poster sessions.

The workshop covered a large variety of accelerators (electron, proton, heavy-particles, free-electron lasers, linacs, specific projects) that are operated to serve very different types of objectives. This means that many different types of parameters can be measured, under very different conditions, implementing very different technical methods and technology. The part represented by synchrotron light sources was about 40%.

Proceedings of the workshop will be published.

K. Scheidt

Structural Determination of Catalytically-Active Ag^+ Sites in an Ag-Y Zeolite: a Combined Anomalous XRPD and EXAFS Study

C. Lamberti[1,2], M. Milanesio[1], C. Prestipino[1], S. Bordiga[1], A.N. Fitch[3] and G.L. Marra[4]

1 Department of Inorganic, Physical and Material Chemistry, University of Turin (Italy)
2 INFM Unità di Torino Università (Italy)
3 ESRF
4 EniChem S.p.A., Istituto "G. Donegani" (Italy)

Catalytically-active centres within the complex structure of a silver-exchanged zeolite were located using a combination of X-ray techniques.

Zeolites [1] are nanoporous crystalline aluminosilicates formed by a framework of corner-sharing [TO_4] tetrahedra, where T represents a silicon or an aluminum atom. The chemical composition can be described by the general formula: $X^{n+}_{x/n}[(AlO_2)_x(SiO_2)_y]^{x-}$. Formally, the introduction of trivalent Al(III) into [TO_4] units (substituting tetravalent Si(IV) atoms) induces a net negative charge on the framework (x-) which must be compensated by the presence of charge-balancing extra-framework cations ($X^{n+}_{x/n}$). Such cations act as Lewis acid centres, being electron acceptors.

Starting from the basic [TO_4] constituent, the framework of any zeolite is constructed by progressively connecting two adjacent [TO_4] units by sharing an oxygen atom, which becomes a bridge between the two T atoms (T-O-T). Using the [TO_4] unit as the sole building block, the remarkable flexibility of the T-O-T angle (from ≈ 100° up to 180°) allows the realisation of an impressive number of different zeolites, characterised by a regular system of intercrystalline voids and channels of well-defined size, (in the nanometre and sub-nm range), accessible through apertures of well-defined dimensions. The regularity in channel dimensions controls accessibility and makes zeolites much more selective in the adsorption of specific molecules as compared to amorphous carbon or silica gel, which have irregular pore systems. This is the reason for their widespread use as molecular sieves. The same characteristics explain the ever-increasing role that zeolites and related zeotypes have in heterogeneous catalysis (*e.g.* for the petrochemical industry, pollution control and fine chemistry). Moreover, their ability to encapsulate organised molecules, crystalline nano-phases and supramolecular entities inside their channels and pores makes zeolites promising materials in the field of low-dimensional physics, where the quantum effects due to the spatial confinement become observable. Semiconductor quantum wires and quantum dots can thus potentially be obtained by hosting semiconductor crystalline nano-phases inside the channels or cages, so obtaining interesting applications in the fields of optoelectronic, non linear optics, photochemistry, and chemical sensors [2]. The same idea applies for metal and bimetallic dots: the incorporation of such nano-particles inside the pores or channels of zeotype materials opens a new frontier in the chemistry of metal-supported catalysts.

In this article we report on the structural determination of an Ag-Y zeolite (Si/Al = 2.63) obtained by a combined anomalous X-ray powder diffraction, (XRPD), and EXAFS study performed on beamlines BM16 and BM29, respectively. Silver-exchanged zeolites are used in several catalytic and photocatalytic processes, which take advantage of the presence of both isolated Ag^+ ions and aggregated Ag_n clusters. Examples include the photochemical dissociation of H_2O into H_2 and O_2, the disproportionation of ethylbenzene, the oxidation of ethanol to acetaldehyde, the aromatisation of alkanes and alkenes, the selective reduction of NO by ethylene, and the photocatalytic decomposition of NO [3].

The first step in the characterisation of a zeolite involves a thermal treatment to remove all the molecules coming from the ambient atmosphere already adsorbed on the catalytically-active centres. This activation process is essential to guarantee the study of a well-defined system [4]. Once this step has been achieved, measurements can be performed *in situ*, either on the activated sample (*i.e.* the zeolite under vacuum conditions) or after adsorption of a well-defined amount of high-purity gas onto the sample. The conditions of the activation process are critical for silver-exchanged zeolites because an increase in the activation temperature, suitable to remove the most strongly bonded molecules, has the disadvantage of promoting the aggregation of Ag^+ ions into Ag_n clusters [5]. Such clusters, needed for some catalytic application (*vide supra*), are undesired if the aim of the study is the location of isolated Ag^+ ions. Based on our previous study of the zeolite Ag-ZSM-5 [6,7], an activation temperature of 120° was adopted.

XRPD experiments were carried out on an Ag-Y zeolite activated in a borosilicate glass capillary at the Ag-K edge [λ = 0.486093(2) Å], just before [λ = 0.486103(2) Å] and far away [λ = 0.491153(2) Å], in order to single

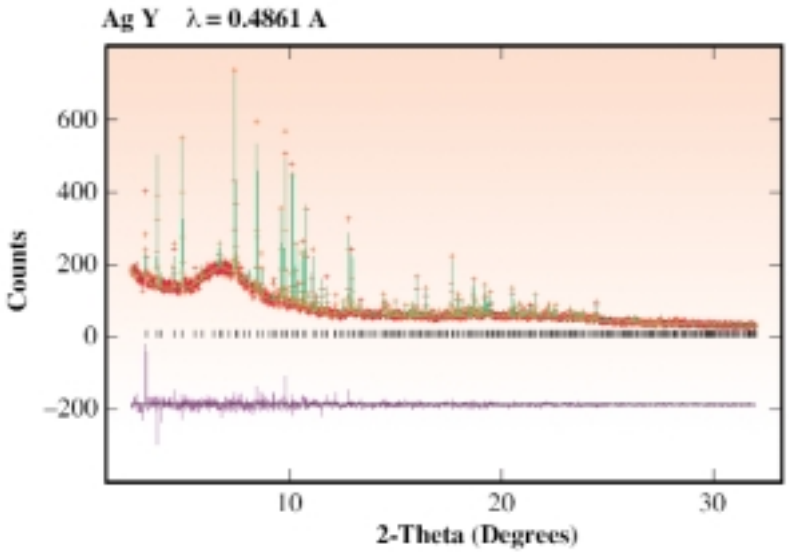


Fig. 1: Observed, calculated and difference profiles and reflection positions of the Ag^{I}-Y zeolite.

out, as much as possible, the contribution coming from the silver cations. Figure 1 shows the high resolution XRPD pattern collected at [λ = 0.486103(2) Å]. A Rietveld refinement was performed simultaneously on the three data sets. This made it possible to obtain the zeolite framework and to locate the near totality of the expected (on the basis of the Si/Al ratio) Ag^{+} counterions: 52.0(4) out of 52.9 per unit cell. The result is quite remarkable when compared with that obtained in the cases of Cu^{+}-Y [8] and of Rb^{+}-Na^{+}-Y [9] (also BM16 data), systems where we were able to locate only 41.0(5) and 48(1) cations, respectively. This noticeable improvement is ascribed to the following factors: (i) the higher scattering power of Ag; (ii) the simultaneous use of three separate data sets; (iii) the extra information in the patterns arising from the anomalous-scattering effect.

Figure 2 illustrates the structure of zeolite Y, which is generated by connecting sodalite units with hexagonal prisms to give a framework containing large cavities (supercages) with a diameter of about 13 Å. Figure 2 also shows the position of the five different extraframework Ag^{+} sites obtained from the Rietveld refinement, labelled as sites I (8.2), I'(17.4), IIa (6.6), IIb (15.2) and I'_m(4.6) (the occupancy per unit cell is given in parenthesis). Four of the sites are positions typical of dehydrated cations. In contrast, I'_m is in the middle of the sodalite cage: implying that such ions

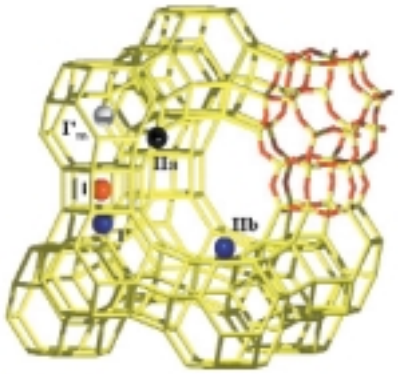


Fig. 2: Representation of the Y zeolite framework and cation location. In the fraction of the framework located in the upper right part of the figure O atoms are represented in red and the T atoms (Si or Al) in yellow. For clarity, in the remaining part of the framework, only yellow sticks have been adopted. Ag^{I} cations are represented as spheres and are labelled with I, I', IIa, IIb and I'_m. The supercage cavity, where guest molecules can be hosted, can be seen in the centre of the figure.

must be coordinated to residual water molecules. In anhydrous conditions, the positively-charged cations are actually in contact with the walls of the cavities, where they interact with the negatively-charged oxygen atoms of the framework. The fact that so few cations, less than 5 out of 52, are coordinated by water molecules indicates that the temperature for the activation procedure was appropriately selected.

We have used the output of the Rietveld refinement to simulate the EXAFS data (collected at BM29) and shown in Figure 3. In theory we have to simulate five EXAFS signals representing the contribution to the overall signal coming from the Ag absorbers located in the 5 different sites found by XRPD. The contribution coming from the hydrated I'_m site has been ignored because: (i) less than 10 % of the absorbers occupy this site and (ii) a rather high Ag-OH_2 Debye-Waller factor is expected. Moreover, since sites I' and IIb show a similar local environment, (three oxygen atoms at the close distance of 2.46 or 2.47 Å), the corresponding contributions were merged. As a result, 3 different contributions have been used to simulate the experimental EXAFS signal. For each contribution, the Ag-O distance was fixed at the crystallographic value (2.31 Å for IIa, 2.61 Å for I and 2.465 Å for I' and IIb), while the coordination number was obtained from the theoretical number of first-shell O neighbours multiplied by a weighting factor obtained from the relative occupancies obtained from the Rietveld refinement. Ref. [8] describes the procedure for the Cu^{+}-Y case in great detail. The two superimposed spectra at the bottom of Figure 3 represent the experimental EXAFS signal, filtered on the Ag-O peak, and the best fit obtained by adding the three contributions described above, where the refined parameters were one common ΔE and three different Debye-Waller factors. The quality of the EXAFS fit, obtained with only four independent variables on such a complex sample, represents a conclusive proof of the quality of the Rietveld refinement from the XRPD data.

We conclude that the use of anomalous diffraction data collected at the high resolution powder diffraction beamline (BM16) has allowed us to locate nearly all extraframework Ag^{+} ions hosted in a Y zeolite, *i.e.* 52.0(4) out of 52.9. The XRPD data have been of fundamental help in the understanding of the complex Ag-K edge EXAFS signal generated by Ag^{+} ions probing different local environments (BM29 data). These studies enhance our understanding of the structure of cation-exchanged zeolites and in particular of the extraframework cations which are known to determine the catalytic properties of such zeolites. ■

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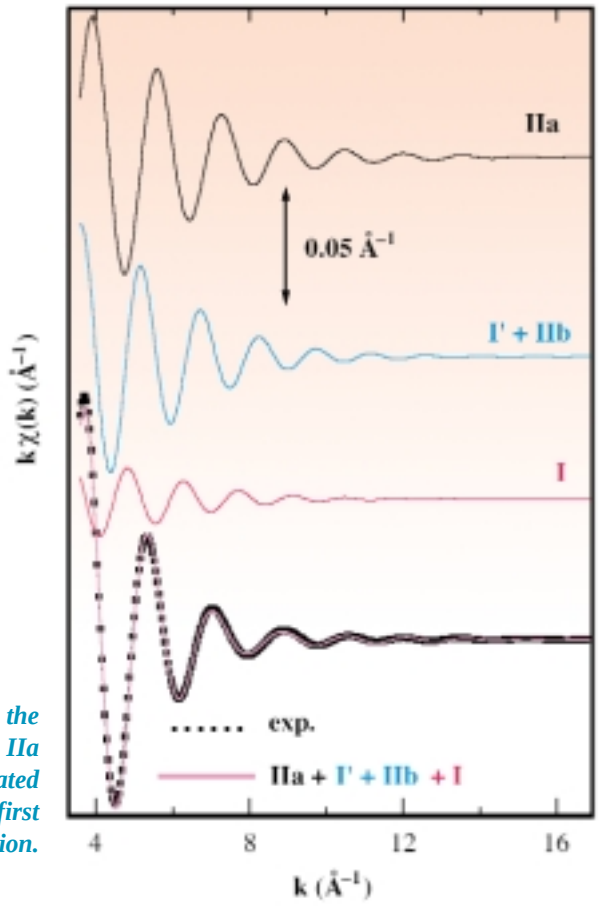

Best fit and simulated EXAFS spectra of the contribution to the overall signal of silver cations located in, from top to bottom: site IIa (I' and IIb merged) and I and sum of the three simulated contributions (full line) superimposed with the experimental first shell filtered kχ(k) function.

If you are interested, please send us a fax (+33 (0) 4 76 88 24 60) or an e-mail (recruitm@esrf.fr) with your address, and we will provide you with an application form. You can also print out an application form on the World Wide Web http://www.esrf.fr

VACANCIES AT THE ESRF ON 14 JUNE 2001

	Ref	Subject	Deadline
SCIENTIST	2228	Beamline Operation Managers on ID21 and ID22	15/06/01
Previous post-doctoral experience with synchrotron radiation is essential.			
POST-DOC	PDID01-3	For the Anomalous Scattering beamline ID01	15/06/01
	PDID03-1	For the Surface Science Diffraction beamline ID03	15/06/01
	PDID10A-3	For the TROIKA beamline ID10A	22/06/01
	PDID26	In XAS and related spectroscopies on the X-ray Absorption Spectroscopy beamline ID26	30/06/01
	PDID15B-2	For the High Energy beamlines ID15A+B	24/08/01
PhD STUDENT	CFR260	Growth, structure and magnetic properties of ultrathin magnetic films	30/07/01
	CFR255	Microscopic deformation in rubber	24/08/01
	CFR278	Micro-imaging investigation of the wetting of metallic grain boundaries by a liquid metal	24/08/01
	CFR275	Time-resolved and *in situ* diffraction on metals and thin layer compounds	24/08/01
	CFR271	Diffuse X-ray scattering at grazing incidence on Si after ionimplantation at ultra-low energy	15/09/01

All applications received after the deadline will be considered for the selected vacancy if not filled or for future similar positions

GLANCING-INCIDENCE DIFFRACTION ANOMALOUS FINE STRUCTURE OF INAS/INP SELF-ASSEMBLED QUANTUM WIRES

S. GRENIER[1], M.G. PROIETTI[1,2], H. RENEVIER[1], L. GONZALEZ[3], J.M. GARCÍA[3] AND J. GARCÍA[2]

1 LABORATOIRE DE CRISTALLOGRAPHIE, CNRS, GRENOBLE (FRANCE)
2 INSTITUTO DE CIENCIA DE MATERIALES DE ARAGÓN, C.S.I.C.-UNIVERSIDAD DE ZARAGOZA (SPAIN)
3 INSTITUTO DE MICROELECTRÓNICA DE MADRID, C.S.I.C., MADRID (SPAIN)

Anomalous X-ray diffraction at glancing angles is shown to be an appropriate technique to study the inner part of nanostructures self-assembled in a very thin epilayer. The site and chemical specificity of anomalous diffraction has permitted us to probe atoms of the quantum wires only and not those belonging to the oxide layer or to the substrate.

InAs quantum dots or quantum wires provide attractive quantum properties for optoelectronic devices like micro-laser sources [1]. They are grown by molecular beam epitaxy and formed during the first steps of growth by a "spontaneous" self-ordering process driven by the strain due to the lattice mismatch between the substrate and the epilayer. The resulting objects are on the nanometre scale. They are characterised mainly in terms of optical (luminescence, photoreflectance) and vibrational properties (Raman), while AFM (atomic force microscopy) and TEM (transmission electron microscopy) give an image of the shape and an idea of the spatial homogeneity. However, the inner composition is still not well known, as mixing with the substrate atoms and segregation mechanisms of the impinging species could occur during the epitaxial growth.

We have studied InAs/InP(001) quantum wires by Diffraction Anomalous Fine Structure (DAFS). This spectroscopic method offers the advantage of providing the local information of the chemical selective Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy with the spatial and site selectivity of X-ray diffraction. In such a way, we are able to obtain local information about the atoms that belong to the nanostructures.

Our sample consists of an array of quantum wires (Figure 1) aligned along the [1-10] direction with a typical length above 5 μm, a height between 0.6 and 2 nm, a period of 20 nm with an equivalent InAs coverage of about 2.5 monolayers. The DAFS measurements were carried out at the French Collaborative Research Group beamline BM2 (D2AM). We measured the intensity at the maximum of two Bragg reflections of the quantum wire array, near the 420 and 440 InP substrate Bragg peaks, as a function of energy, around the As K-edge (11.867 keV) (Figure 2). The measurements were performed in glancing-angle geometry, with an incidence angle kept constant close to the critical angle of InP (about 0.2°). This lets us collect the diffracted photons from an extremely thin quasi-surface layer enhancing its contribution to the diffracted intensity in comparison with the substrate contribution.

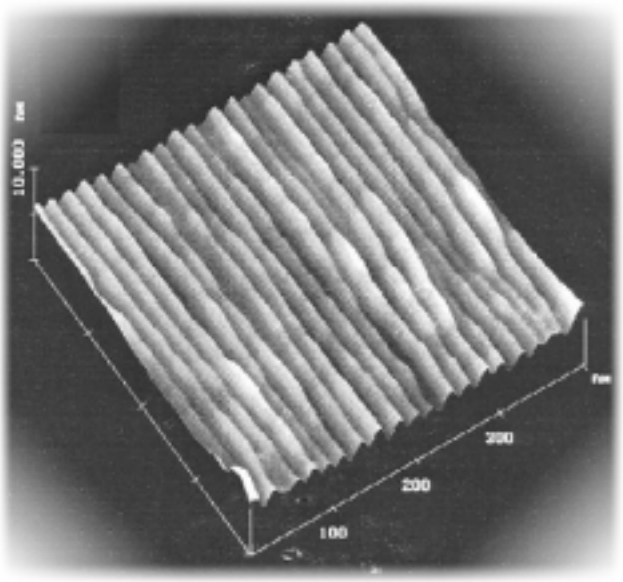

Fig. 1: AFM tridimensional view of InAs quantum wires on InP buffer [7].

The data analysis is a two-step process. First, we performed a simultaneous crystallographic fit to the lineshape of the smooth part of the two DAFS spectra (Figure 2) refining the P concentration, 1-x, for $InAs_xP_{1-x}$, Debye-Waller factors and experimental factors. We introduced corrections to the calculated diffraction intensity in the framework of the Distorted Born Wave Approximation (DBWA) [2] such that, in the total reflection regime, the thin epilayer is a small perturbation for the evanescent X-ray wave that penetrates a few nanometres into the refracting medium. Another fit parameter was the

thickness of an oxided dead layer that was found 15 ± 5 Å thick. To reproduce the shape of the anomaly at the edge, we had to include P atoms, 1-x = 0.5 ± 0.1: a considerable amount of P atoms is contributing to the satellite diffraction peaks, showing the same periodicity of the wires. However, at this stage of the analysis, we are not yet able to discern whether the P atoms belong to the wires or to the InP substrate which could show a periodic modulation as well as periodic strain spots due to the strain with the InAs wires.

In a second step, we extracted the Extended DAFS oscillations that appear after the edge (Figure 3) and we analysed them according to an EXAFS data processing scheme to get local parameters such as distances and populations [3]. Theoretical multiple-scattering EXAFS signals were calculated by the FEFF code [4] simulating the fine structure signal from an As atom inside a cluster containing In atoms, As (x) and P (1-x) atoms. The polarisation of the incoming photons was perpendicular to the surface, so the As and P next nearest neighbour atoms contribution to EDAFS is due only to the out-of-plane atoms. Refinement of the data was completed by the least-square fit procedure of the FEFFIT program [5] (Figure 3a and 4a). The relevant results are the P concentration, (1-x) = 0.4, and the As-P distance, found at 4.17 Å. While the As-As distance was fixed at 4.29 Å, the P content is, within the error, equal to the value found by the crystallographic fit of the anomalous diffraction lineshape.

The two independent analyses detected a consistent amount of P atoms: (1-x) = 0.4-0.5. In a previous study of $InAs_{0.5}P_{0.5}$/InP superlattices samples [6], the out-of-plane As-As and As-P distances were found much closer to each other, about 4.28 Å and 4.25 Å respectively. In our analysis, the As-P distance is 4.17 Å, close to the P-P distance in bulk InP (4.15 Å), therefore, we could exclude the hypothesis of a fully relaxed InAsP epilayer. The P atoms contributing to EDAFS have to belong to the interface region, 0.5-2 monolayers, and the core of the quantum wire is essentially strained InAs. Two types of interface or a combination of both can explain the results: a) an abrupt InAs/InP interface with periodical strain strips generated in the InP buffer layer due to the interface mismatch strain; b) a corrugated InAs/InP interface with the same wire's periodicity.

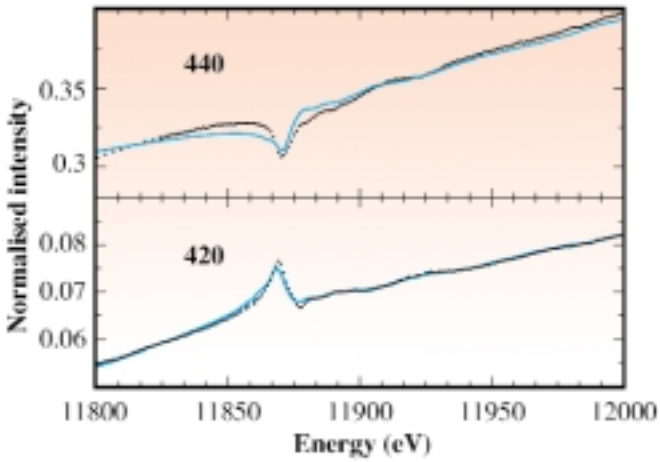

Fig. 2: Glancing-angle DAFS spectra of quantum wires, for (440) and (420) Bragg peaks, at the As K-edge (dotted curves) and crystalloghraphic fits (continuous curves).

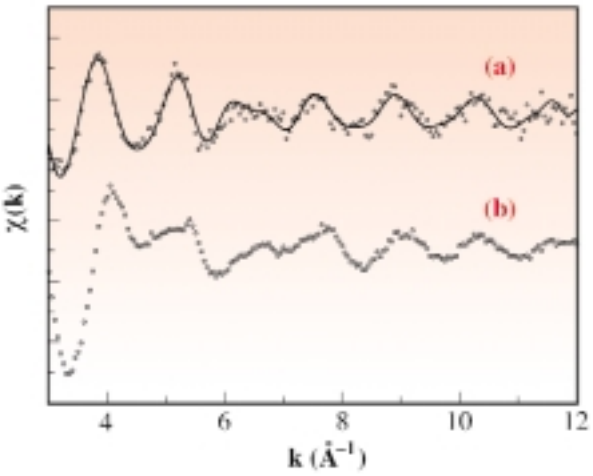

Fig. 3: (a) InAs quantum wire Glancing-angle EDAFS oscillations, after background subtraction, with best fit (continuous line), (b) EXAFS of the quantum wires. The curves have been rescaled for clarity.

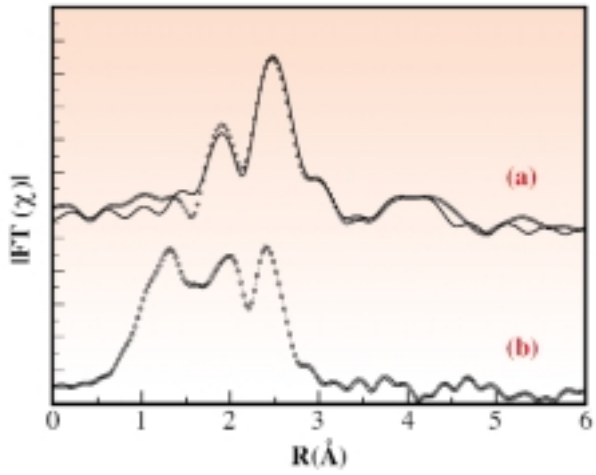

Fig. 4: (a) FT of quantum wire EDAFS, with best fit (continuous curve), (b) FT of quantum wire EXAFS. The curves have been rescaled for clarity.

We have also measured a glancing-angle EXAFS spectrum at the As K-edge (Figure 3b) at beamline BM8 (GILDA). The spectrum shows a clear As oxide shape with a strong low-frequency component that corresponds to a huge peak at 1.2 Å in its Fourier Transform (FT) (Figure 4b). The oxide layer causes a significant loss of information in particular for shells beyond the first one, whereas, for a DAFS spectrum, it lowers the overall diffracted intensity and the jump at the edge but it does not perturb the fine structure signal of the interesting atoms.

In conclusion, we have shown for the first time that DAFS can been applied in the glancing-angle regime to the study of

auto-organised nanostructured materials with an extremely low equivalent coverage. As the interface effects on the EDAFS spectrum are remarkable due to the low epilayer thickness and to the X-ray beam polarisation, we were able to show, as a preliminary result, that the inner composition of the quantum wires is not a relaxed InAsP structure. Furthermore, we have detected a P-rich region at the interface with the same periodicity as the quantum wires.

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X-RAY AND NEUTRON STUDIES OF THE OPTIMISED SYNTHESIS, THE STRUCTURE AND THE TRANSFORMATIONS INVOLVING NOVEL ION EXCHANGERS

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Presentation given at the ESRF-ILL Workshop "Environmental Studies Using Neutron and Synchrotron Facilities", 20-21 February 2001.

A combination of X-ray and neutron techniques can be used to elucidate the often rather complex structures of ion-exchangers - materials designed to trap and remove certain chemicals from an aqueous environment.

The shear number of sites worldwide contaminated by industrial and military waste represents a major environmental and public health concern. For example, approximately 40,000 uncontrolled waste sites have been reported to U.S. federal agencies. About 1,300 of these have made it to the National Priorities List of sites for remediation. The US experience is not unique.

In those cases where the toxic materials are transported in anionic or cationic forms, inorganic ion exchangers can be used to replace benign ions in the crystalline lattice for contaminant ions, thereby limiting availability of these toxins to the biosphere [1]. In favourable instances the inorganic ion exchanger occurs naturally, can be mined and applied directly. For example the zeolites, naturally occurring aluminosilicate minerals possessing pores and channels of molecular dimensions, are well known ion exchangers. One of the most abundant, and therefore cheap, naturally occurring zeolites is the mineral clinoptilolite, which is commonly used for ammonia control and sorption in animal feed, fish tanks and kitty litter. It also happens to have a strong affinity for ^{90}Sr and ^{137}Cs, and is used routinely to treat radioactive effluent [2]. Unlike ion exchange resins, which are susceptible to radiation damage, the zeolites sequester the strontium and caesium over long periods. Clays, layered aluminosilicates, are also commonly used to treat contaminated soils and to sequester contaminants [1].

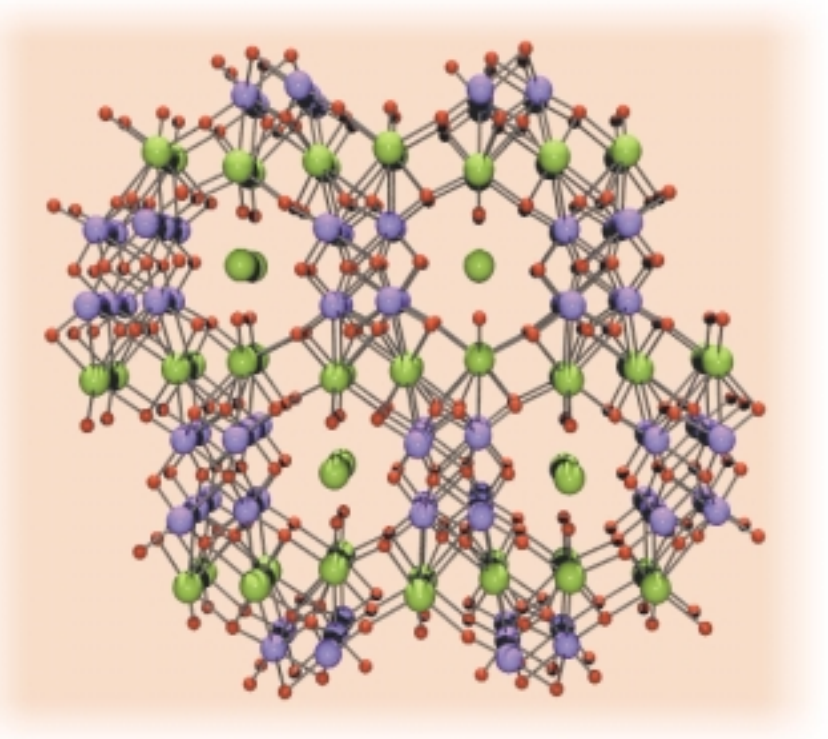

Fig. 1: Structure of $Na_{16}Nb_{12.8}Ti_{3.2}O_{44.8}(OH)_{3.2}\cdot 8H_2O$ (SOMS-1) determined from a 5x5x8 μm^3 twined crystal. Large green balls are octahedral framework sodium cations, purple spheres are Nb/Ti sites and red spheres are oxygen.

The naturally occurring materials suffer from some disadvantages, including low capacity and a tendency to release contaminants if environmental circumstances such as pH are altered. The zeolites, and indeed the other mineral ion exchangers, are inspirational however when we seek fertile synthetic territory to explore for materials with these desirable ion exchange properties. The general formula $A^{x+}z[Si_{1-y}T_y^{w+}O_2]\bullet mH_2O$ with $z = (4-w)y/x$, summarises the composition for most silicate zeolites. The framework cation sites substituting for silicon in the formula for quartz (SiO_2) are designated T; these cations, with typical valence w = 3 (Al^{3+}), are tetrahedrally coordinated by oxygen. The symbol A is used for possible charge balancing cations occluded in the regularly spaced pores and channels. Conventionally the ion-exchange capacity, determined by the Si/T ratio, has been maximised in aluminosilicate zeolites by producing materials with low Si/Al ($xSiO_2 + 1\text{-}xAl_2O_3) + 1\text{-}x(A_2O) \rightarrow (Si_2xAl_{2-2x}O_4)^{(2-x)-}.(2\text{-}x)A$. Unfortunately this limit is 1.0 and so the capacity for the aluminosilicates is limited.

Strategies designed to increase the ion exchange capacity include lowering the valence of the substituting "T-atom" in the formula above, increasing the number of anions in the framework by introducing octahedrally coordinated cations, and combinations of these two. Both strategies lead to new materials with increased capacity and selectivity [3,4]. In the first instance the substitution of Li^+ for Si^{4+} increases capacity and leads to other unusual properties including ion conductivity [3,5]. In the second instance, our collaborators T. Nenoff and M. Nyman at Sandia National Laboratory found inclusion of Ti^{4+}, although it does not decrease cation charge in the framework, does boost the anion content because of its octahedral coordination, and this requires extra charge-balancing cations in the pores and channels. Crystal structures, determined from the combined use of synchrotron X-ray diffraction from microcrystals (2 – 10 μm on edge) and neutron diffraction from powders, reveal that both strategies come together in the SOMS crystalline inorganic molecular sieves (Figure 1) developed at Sandia. In this instance a framework of octahedrally coordinated Nb^{5+}/Ti^{4+} and Na^+ is formed, which is selective for removal of strontium from acidified solutions and in the presence of such benign cations as Na^+, Mg^{2+} and Ca^{2+}. Part of the sodium in the structure is exchangeable, and it also serves to decrease the total cation charge in this anion-rich framework. This results in increased cation exchange capacity, in a manner analogous to the principles observed in the Li-silicates [3].

It is important to determine accurate crystal structures for the materials resulting from the syntheses inspired by the strategies outlined above. This completes a feedback loop involving synthesis, ion exchange properties and structure and provides a basis for rationalising the functionality of the exchangers and for the development of new ones. Many of the structures of interest involve atoms of widely varying X-ray scattering powers, Li and Cs in the case of the Li-silicates for example [3]. They also crystallise from gels at low temperatures and so are often kinetically stabilised phases. This leads to samples that are mixtures of phases crystallising in fine hair-like crystal bundles. Structural studies have therefore relied heavily on synchrotron radiation, to both screen and collect useful diffraction data on microcrystals for determination of framework connectivity, and on neutron diffraction to provide the positions of light atoms either in the channels (Figure 1) or in the framework [3]. Time-resolved synchrotron X-ray powder diffraction is invaluable also since it allows us to observe directly the phases crystallising during a hydrothermal synthesis. Information from these studies can immediately be implemented in larger batch processes to prepare the single phases samples required for meaningful neutron diffraction, property and spectroscopic measurements.

The pressure to make the search for selective ion-exchangers more rational and efficient requires further development of time-resolved techniques. Along with wide-angle diffraction, this includes interrogating the crystallising gels with both SAXS and SANS to determine the incipient behaviour that leads to the formation of open materials rather than dense phases. Subtle changes in the starting materials chosen for synthesis often lead to quite different products. Some experiments in this area have begun (see for example [6]) and the joint use of X-ray and neutron diffraction on the same sample is clearly a priority in the future. ■

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3-D Snow and Ice Images by X-ray Microtomography

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Evolution of snow in temperate as well as in polar regions is strongly dependent on its structural properties. We present 3-D imaging results obtained by X-ray absorption tomography, a technique that will allow the extraction of quantitative information about the structural parameters of snow and ice.

Snow is a porous medium. At negative temperatures it consists of ice and air with water vapour. Snow is constantly moving and its porosity decreases with time. It is slowly compacted into firn and then ice. A very wide range of porosity can be found: from more than 95% for fresh snow to around 40% for firn and then to less than 10% for ice. Changes in dry snow are caused by vapour diffusion among the grains - they are driven by temperature gradients and grain curvatures [1]. On polar ice caps, below a depth of 10 metres, the medium becomes isothermal although its porosity is still open. Then the porosity decreases more slowly, firn evolves into ice by a process similar to sintering under load. The transition from an open to a closed porosity is called close off and it occurs when firn becomes ice. During the transition, air is trapped in bubbles between the ice crystals.

Three-dimensional images of snow and ice with a spatial resolution of 10 μm were obtained using X-ray absorption tomography, an established technique used on the ID19 beamline [2]. 900 two-dimensional X-ray absorption images

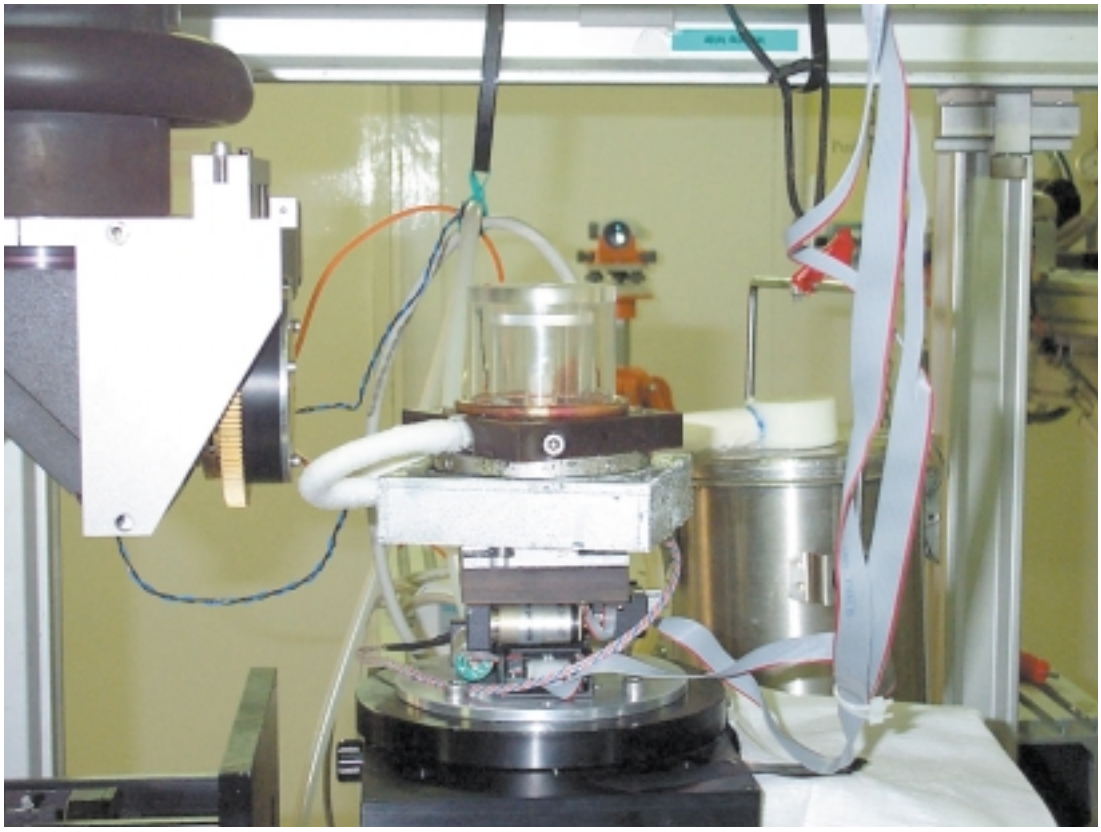

Fig. 1: View of the experimental setup used for snow and ice samples. The cryostat was mounted on a high-accuracy rotation and translation stage. Images were recorded with a Frelon CCD camera.

were recorded at angular positions of the object around an axis spanning 180°. An appropriate algorithm was then used to reconstruct a 3-D image from the data.

SAMPLE PREPARATION

Specificities of snow and ice need special requirements for sample preparation. Since firn and ice is rather hard, it was possible to carve out a cubic sample (edge about 15 mm). Ice and air offer a good level of contrast and so the images could be obtained by local absorption tomography at an energy of 18 keV. Snow needed strengthening prior to being machined into the shape of a cylinder (9 mm high, 9 mm diameter). Dense snow was cohesive enough to allow removal of the filling medium before imaging. X-ray absorption tomography at 10 keV was used. Snow with low density was too fragile to stand up to the rinsing stage. A selection of pure chemicals have been tested, examples being trans-1,2-dibromocyclohexane and cycloheptane. They fulfilled the required conditions regarding their melting point, reaction with ice, hardness and their attenuation coefficient which has to be different from that of ice. In all cases, a special device (a liquid-nitrogen cooled cell at about –50°C) was used to prevent both melting and metamorphism of the samples during the experiments (Figure 1).

RESULTS ON SNOW

From the grey level data files produced at the ESRF, a 3-D binary image was obtained by morphological processing on each image plane. The first 3-D images [3] have shown the feasibility of this technique which provides us with good quality images of the snow structure or grain assembly.

What is the interest of such images? Most physical properties and physical processes occurring inside snow are strictly linked to its microstructure. The aim was then to extract relevant information from these images. The two first geometrical parameters studied were porosity, which is the simplest descriptive parameter but often the most important for many of snows physical properties, and local curvature, which is a governing parameter of snow metamorphism. We have shown that the size of the sample studied is statistically representative for these parameters [4]. Another important geometrical parameter is surface area, which denotes the ability of a given snow to evolve. 3-D images will be used as a reference for the development of a snow metamorphism model at uniform temperature. Under such conditions, snow tends to minimise its specific area and should lead to a symmetric histogram of curvature peaked at zero.

A large area of interest where snow images could improve our knowledge is the study of avalanches and mechanical properties of snow. Snow stability on a slope is linked to the superposition of the different snow types. For instance, a cohesive layer above a weak layer is typical of most of the slab avalanches triggered by skiers. Figure 2 shows views from a snow sample collected at the failure of a slab avalanche. Classical observations describe the layering of the snow pack. X-ray microtomography is an interesting tool for visualising the bonding between different snow layers.

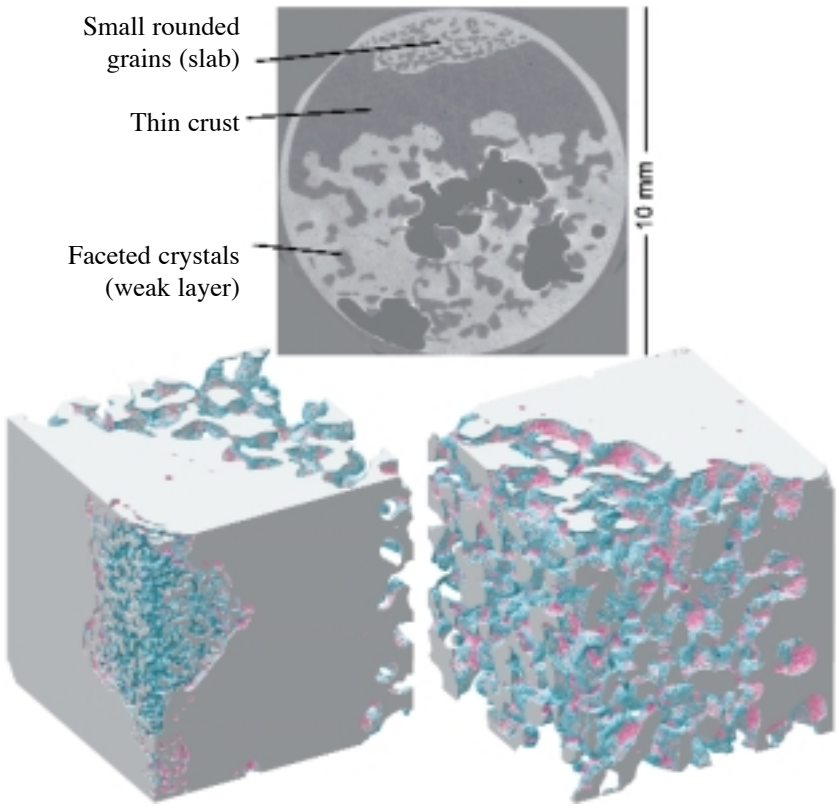

Fig. 2: Plane and 3-D reconstructed views from a snow sample collected at the failure of a slab avalanche.

RESULTS ON FIRN AND ICE

The transformation of the snow into ice can be very slow in polar regions (up to 3000 years) and it is very important to know precisely when and how the gas was trapped in order to interpret the air archive (atmospheric information) compared to the ice archive (climatic information) [5]. Thus the aim of the firn and ice part of the project was to study the evolution of both open and closed porosity of the material and in a first step to test the feasibility of the method. Twelve samples have been analysed. They were taken at depths between 62 and 120 m on a Vostok (Antarctic) core, thus covering the entire range of the pore closure. The results were excellent: in Figure 3, two examples are shown and compared with the 2-D technique also used at the LGGE to study the firn structure [6]. This last method presents the advantage of revealing both pores and grain boundaries. However, it is obvious

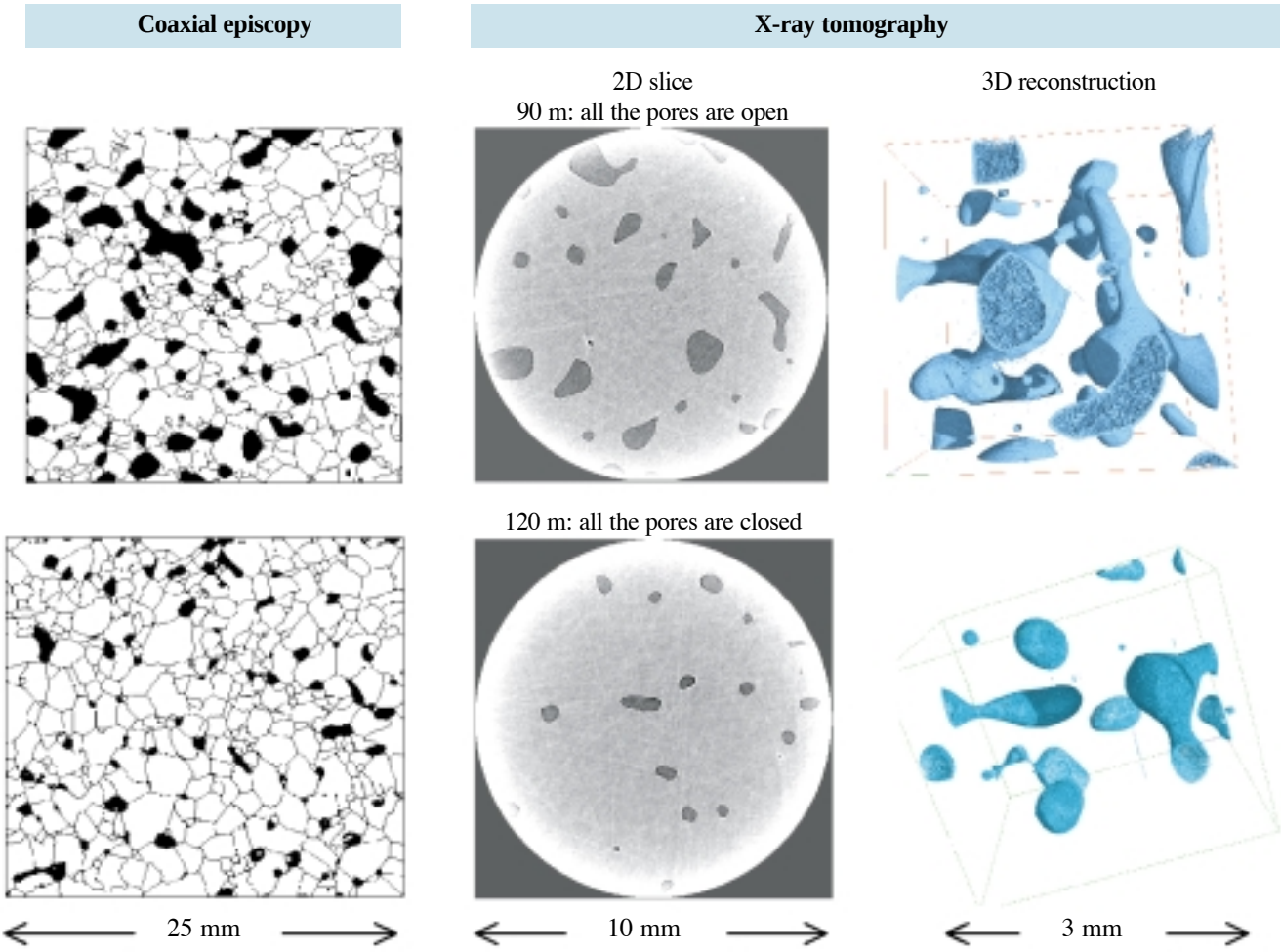

Fig. 3: 2- and 3-dimensional images of ice around the firn-ice transition: porosities appear in black in the 2-D images. The episcopy technique reveals that the pores are located at crystal boundaries. 3-D reconstructions from the 2-D slices give access to the real shape of the porosities.

from Figure 3 that the 2-D information alone is unable to give precise information on the open to closed porosity ratio. The detailed images of the shape of the pore phase near their closure show some particularities: at 90 m all the main pores are open, however very small bubbles, which are certainly formed well before the "close off", are visible. At 120 m, even if all the pores seem to be well isolated, some very small channels still exist and the gases can be fractionated when they diffuse through them.

Quantitative studies are in progress to look in particular at the influence of the sample size on the quality of the information given by such reconstructions.

CONCLUSION

X-ray microtomography appears as a very powerful tool for the study of snow microstructure and firn-ice porosities. Furthermore, 3-D imaging is gaining momentum in several domains dealing with the structure of materials. New ways to provide relevant information from the images and model development will certainly benefit from exchanges between the different research areas. ■

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Investigation of Positive Electrode Materials for Lithium Batteries by Means of X-ray and Neutron Diffraction

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In situ X-ray diffraction studies allow the following of the structural changes associated with lithium extraction from positive electrode materials for Li batteries. Two recent examples are presented here.

The "layered" rock salts compositions $LiCoO_2$ and $LiNiO_2$ as well as the spinel $Li[Mn_2]O_4$ have been extensively studied for use as positive electrodes for rechargeable lithium batteries. Their interest lies in the delivery of voltages close to 4V vs Li^+/Li when lithium is extracted reversibly. Other families of compounds, *i.e.* polyanionic structures built up from MO_6 octahedra (M = Fe, V, Ti) and PO_4^{3-} or $P_2O_7^{4-}$ polyanions have also been identified as alternative electrodes, among which are $LiFePO_4$, $LiMP_2O_7$ and the NASICON family $Li_xM_1M_2(PO_4)_3$ [1]. A review of electrode materials for lithium batteries is given in ref [2].

Besides the need to identify new materials for electrochemical devices, it is also a challenge to understand the topotactic lithium insertion/de-insertion mechanisms (associated with reduction or oxidation of the transition element at the positive electrode) that occur within these materials. Lithium batteries have ever increasing industrial and technological importance. Additionally, they do indeed offer a rather nice tool for solid state electrochemists because the redox processes involved often lead to subtle phase transitions and to metastable new forms of materials with "exotic" oxidation states or compositions [3]. These processes may also lead to structural instabilities that are penalising for the integrity of the host material over extensive charge/discharge cycles. In this regard, X-ray and neutron diffraction are powerful – and complementary – techniques for the investigation of positive electrode materials for lithium batteries as they benefit from the crystalline nature of the material used. Powder neutron diffraction is used for highly reliable crystal structure determinations of *pristine* materials containing lithium into which local disorders, local distortions, phase purity etc… play a major role for their effective use in a battery system. On the other hand, *in situ* X-ray diffraction that use either standard equipment in the laboratory or high-resolution synchrotron radiation, has been used by several groups for the investigation of structural changes during cell operation. For this purpose, specially-designed cells for diffraction in either reflection or transmission geometry, were developed following J. Dahn's pioneer concept [4].

The intent of this communication is to demonstrate the use of neutron and/or X-ray diffraction for the investigation of positive electrode materials in lithium batteries. For this purpose we have chosen to present two typical examples that have recently been addressed: $Li_xMn_2O_4$ and Li_xCoO_2.

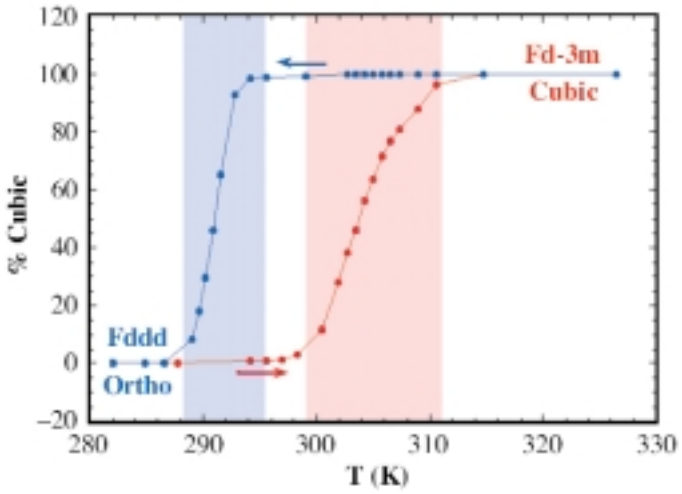

***Fig. 1: Ratio between cubic and orthorhombic forms of $LiMn_2O_4$ as a function of temperature, determined by synchrotron diffraction (LURE, WD4C). From* [6].**

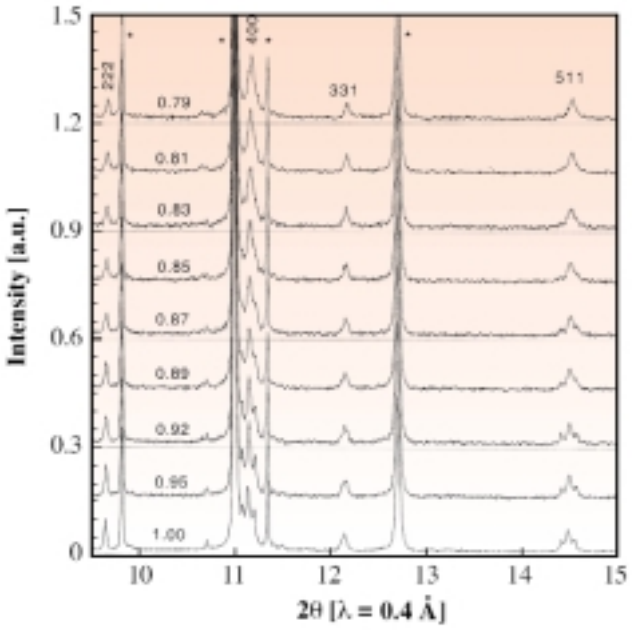

Fig. 2: Parts of in situ synchrotron diffraction patterns (ESRF, BM16) as a function of x during electrochemical extraction of lithium from $Li_xMn_2(O_{3.74}F_{0.26})$. From [5].

$Li_XMn_2O_4$

Palacin *et al.* [5] reported an *in situ* synchrotron study carried out at the ESRF (Beamline BM16, transmission geometry through a Bellcore Plion "plastic" cell) on the structural phenomena that occur during lithium extraction out of a fluorine-substituted spinel $LiMn_2(O_{3.74}F_{0.26})$. Besides the "classical" features previously observed in the 4.1 V – 4.2 V region for $Li_xMn_2O_4$, two extra phenomena of interest were observed at the beginning and then at the end of the charge process:

i) The pristine material, with average oxidation state for manganese equal to +3.4, is indeed a mixture of two phases: a minor cubic spinel phase and a major orthorhombic form that had just been discovered from combined electronic, X-ray (at LURE, Orsay) and neutron (at LLB, Saclay) diffraction. The orthorhombic distortion of the spinel results from a charge-ordering transition on Mn^{3+} and Mn^{4+} sites that occurs very close to room temperature when the concentration of Mn^{3+} present in the spinel phase is above the critical level of 50% [6] (Figure 1). The *in situ* data presented in Figure 2 (beginning of charge) nicely revealed that this distortion disappears exactly for 0.18 lithium extracted from $LiMn_2(O_{3.74}F_{0.26})$, *i.e.* when the average valence of manganese reaches 3.5+.

ii) On charging above 4.4 V, Palacin *et al.* also observed an apparent irreversible capacity of $\Delta x = 0.08$, associated with extra electrochemical phenomena at 4.5 V (on oxidation) and at 3.3 V (on reduction). A complementary study [7] was undertaken that allowed, with the help of high-resolution transmission electron microscopy, to identify the formation of a new $Li_{1-x}Mn_2O_4$ double hexagonal (DH) structure isotypic with $LiFeSnO_4$ (Figure 3). The transition between spinel $Li_xMn_2O_4$ (ABCABC… stacking) and DH-LixMn2O4 (ABACABAC… stacking) was explained in detail [6] through a translation mechanism of Kagome (OC_3) and Te_2OC type blocks that are common to both structures (Figure 3).

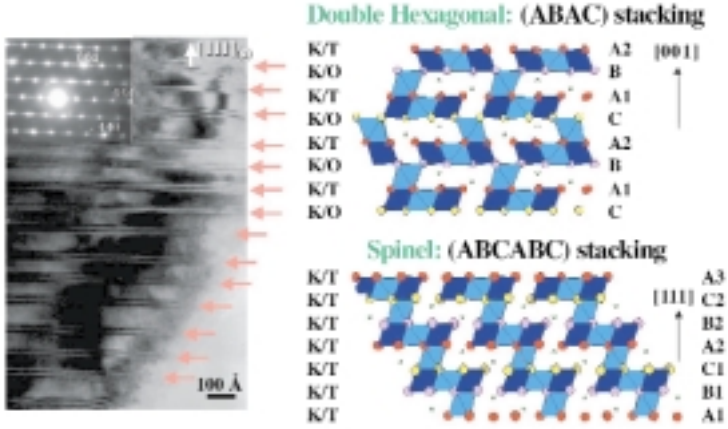

Fig. 3: TEM image of stacking faults along $[111]_{spinel}$ due to the intergrowth of the double hexagonal structure. The structural relationships between Spinel and DH arrangements are drawn. From [6] and [7].

Li_XCoO_2

Another interesting *in situ* experiment was carried out at the ESRF, to understand the structural behaviour of $Li_{1-x}CoO_2$ when charged (lithium extracted) to high values of x, *i.e.* up to a voltage close to 5V vs Li^+/Li. This was the subject of a recent communication [8] whose main outlines are recalled here. The originality of the experiment was the use of the microdiffraction beam line ID11, where the 0.2 x 0.2 mm beam was small enough to pass through the grids of the Al and Cu current collectors of a PLion plastic cell. The diffracted beam was collected on a 2-D image plate detector that permitted very short acquisition times (~ 10 seconds per pattern !).

Several processes of de-intercalation of lithium can be distinguished in Figure 4: the incremental capacity peaks at 3.92 V, 4.05 V, 4.18 V and 4.55 V are the signature of transitions between phases at various stages of charge. A very large number of diffraction patterns were collected between 8° and 20° for a wavelength of 0.3757 Å (Figure 5). Besides the interesting evolution of lattice parameters vs x in Li_xCoO_2 (Figure 6), successful Rietveld Refinements allowed the determination of the atomic positions in each of the phases formed [8]. Of particular importance for the cycling behaviour of Li_xCoO_2 is the region close to x = 0.5 / V = 4.18 V where a monoclinic phase, M1, extends from x = 0.55 to 0.47. This region corresponds to the maximum of the c equivalent lattice parameter, i.e. to the maximum distance between CoO_2 close packed layers. At deeper extents of charge, i.e. at potentials higher than 4.28 V vs Li^+/Li, irreversible

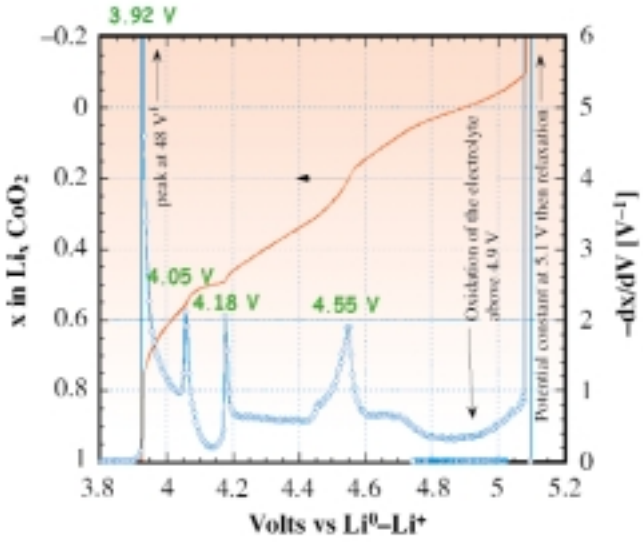

Fig. 4: Potentiostatic intermittent extraction of lithium from $LiCoO_2$ at an equivalent rate of C/20. From [8].

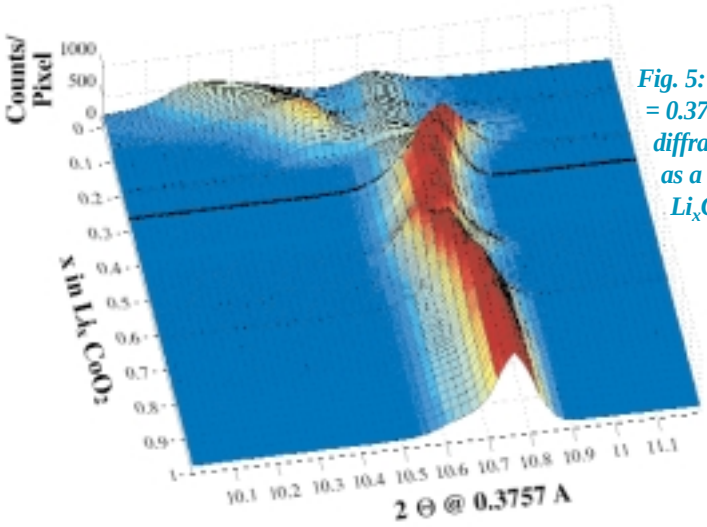

Fig. 5: Synchrotron (λ = 0.3757 Å) diffraction patterns as a function of x in Li_xCoO_2. From [8].

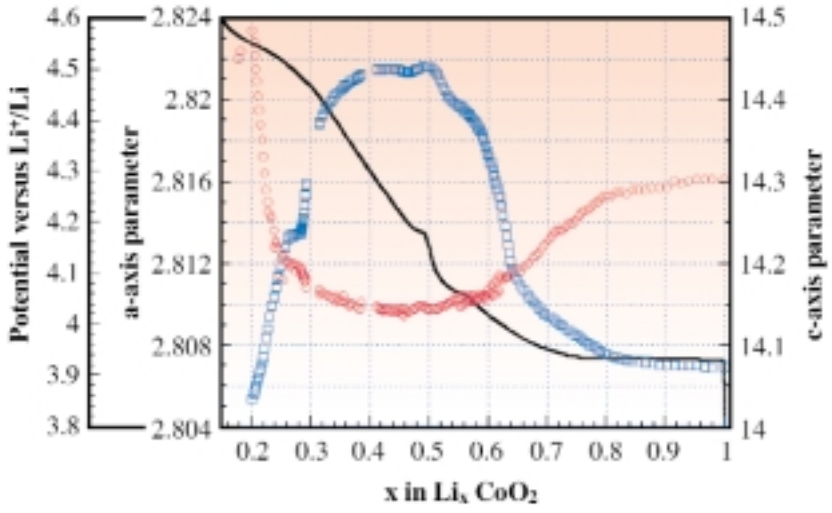

Fig. 6: Evolution of cell parameters (rhombohedral description) as a function of x in Li_xCoO_2. From [8].

transformations occur and hence, the practical composition range for cycling Li_xCoO_2 in a real battery system when x is between 0.5 and 1.

CONCLUSION

The two examples developed in this paper show the effective use of *in situ* synchrotron X-ray diffraction to help understand and solve problems associated with structural changes that occur upon lithium extraction from positive electrode materials. Despite its great potential use for Li-containing materials, neutron diffraction is still limited for *in situ* studies due to the small quantity of active material and to the large amount of hydrogen-containing components within the battery. Both techniques are complementary and should be used more systematically alongside the essential *in situ* and/or *ex situ* experiments on "in-house" X-ray diffractometers. ■

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In situ Synchrotron X-ray Diffraction Studies of HP-HT Synthesis of Superhard Phases in the B–C–N System

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The present paper briefly reviews results of our very recent studies of high-pressure high-temperature synthesis of superhard phases in the B-C-N system using powder X-ray diffraction with synchrotron radiation.

Materials Science under extreme conditions is one of the most important lines of research using the third-generation synchrotron radiation sources. The high resolution and improved sensitivity resulting from the use of high-intensity synchrotron-derived X-ray radiation from these sources are indispensable for *in situ* studies of phase formation and reaction kinetics of compounds of low-Z elements at high pressures and temperatures.

Here we report the results of *in situ* studies of synthesis of superhard phases in the B-C-N system that have recently been performed at the high-pressure beamline ID30.

SYNTHESIS OF NEW SUPERHARD PHASE, CUBIC BC_2N

Phase transitions of graphite-like BN-C solid solutions (g-BC_xN) were studied up to 32 GPa and 3000 K using a laser heated diamond anvil cell and angle-dispersive X-ray diffraction [1]. At room temperature an increase in pressure is accompanied by a pronounced decrease in the line intensities of the turbostratic g-BC_2N (Figure 1). Upon compression to 19.9 GPa, the intensity of the strongest 002 line decreases by a factor of 6, and at 25.8 GPa this line almost disappears. Also, with increasing pressure, a variation in the 10 asymmetric line of the turbostratic structure is observed. The intensity of scattering in this region increases, the profile of the line becomes increasingly symmetric and its peak shifts towards a value of 2.07 Å which is close to those observed for the 111 reflections of diamond-like phases. These effects point to the reconstruction of the graphite-like sp^2-structure into the diamond-like sp^3-structure, which starts at about 5 GPa and ends at about 25 GPa.

At 25.8 GPa, the heating of g-BC_2N up to 1600 K is not accompanied by any change in the diffraction patterns which exhibit only a broad line in the region of 111 reflections of diamond-like phases. At higher temperatures, the profile of this broad line changes to a rather complicated fine structure, and two new weak lines with d_{hkl} = 1.26 and 1.09 Å (at ambient temperature) also appear. Finally, above 2200 K a drastic change in the spectrum is observed (Figure 1, top pattern) which clearly points to the formation of a new phase. The diffraction pattern of the quenched sample exhibits only 111, 220, and 311 lines of the cubic lattice, which indicates that the sample is single-phase.

Laser heating experiments at different pressures have shown that the formation of c-BC_2N is observed only at pressures

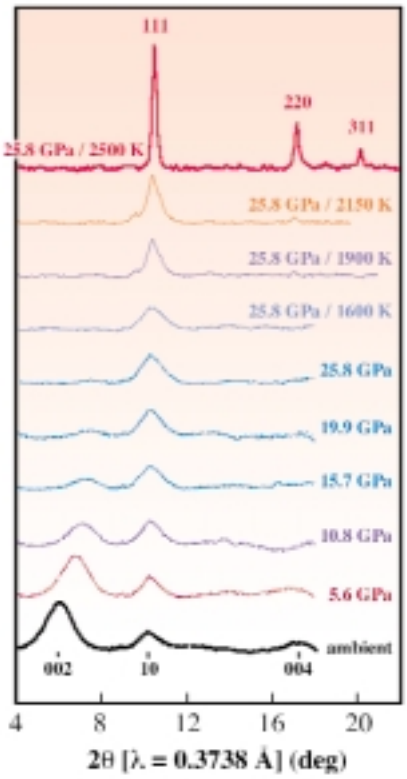

Fig. 1: Laser-heating sequence of diffraction patterns taken at several pressures and temperatures. Bottom and top patterns correspond to g-BC_2N and c-BC_2N, respectively.

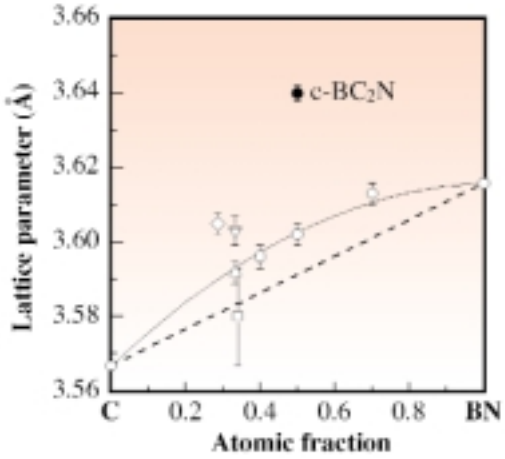

Fig. 2: Lattice parameters of c-BC_2N (solid circle) and "cubic BN-C solid solutions" reported by Kakudate et al. [3] (open down triangle), Knittle et al. [4] (open circles), Nakano [5] (open up triangle), Kagi et al. [6] (open square) and Komatsu et al. [7] (open diamond). The dashed line represents ideal mixing between cBN and diamond, while solid curve shows the deviation from ideality for the data reported by Knittle et al. [4].

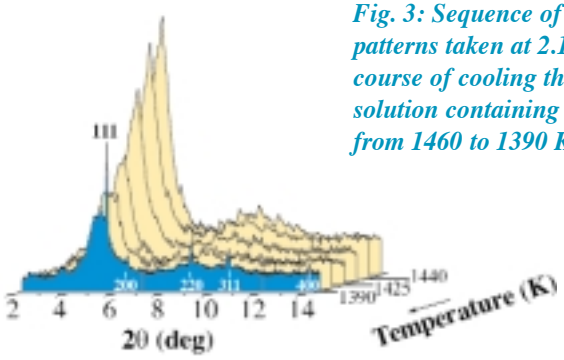

Fig. 3: Sequence of ADX diffraction patterns taken at 2.1 GPa in the course of cooling the supercritical solution containing 74.5 mol.% BN from 1460 to 1390 K.

above 18 GPa. At 14.5 GPa and temperatures above 2000 K g-BC_2N decomposes to form a mixture of cubic boron nitride (cBN) and diamond. On further decrease in pressure down to 11.0 GPa, thermal decomposition of g-BC_2N proceeds to form cBN and disordered graphite, as reported previously [2].

The lattice parameter of c-BC_2N at ambient conditions is a = 3.642(2) Å, which is larger than those of both diamond and cBN. The large deviation of the lattice parameter of cubic BC_2N from the value expected from ideal mixing between diamond and cBN testifies that the synthesised phase differs from the so-called "diamond-cBN solid solutions" reported earlier [3-7] (Figure 2).

The bulk modulus of c-BC_2N is 282(15) GPa which is exceeded only by the bulk moduli of diamond and cBN [8,9]. The Vickers hardness of c-BC_2N is 76 GPa, which makes it the hardest known solid after diamond.

CBN CRYSTALLISATION FROM BN SOLUTIONS IN SUPERCRITICAL FLUIDS

In situ studies of the BN-N_2H_4 system at pressures to 5 GPa and temperatures to 1500 K using a Paris-Edinburgh press and X-ray diffraction (energy- and angle-dispersive) provided us the ability to investigate the local structure of boron nitride solutions in supercritical fluid, and BN crystallisation from these solutions on cooling.

At 4.1 GPa, cooling the solution containing 81 mol.% BN is accompanied by spontaneous crystallisation of cubic boron nitride. The emergence of cBN lines is accompanied by a change in the shape of the solution spectrum, in particular by the appearance of a broad halo with a maximum at d_{hkl} = 1.1 Å. A similar change in the shape of the solution spectrum was also observed at 4 GPa and 1350 K by cooling the solution containing 33 mol.% BN. In this case, however, no formation of any crystalline phase was recorded even on cooling the solution down to room temperature. This fact should be attributable to the formation of an unknown amorphous phase of the BN-N-H system (phase X). A subsequent heating up to 1600 K in both cases gave rise to a recovery of the characteristic shape of the solution spectrum due to dissolution of solid phase(s) which is unambiguous evidence for the reversibility of the observed precipitation/dissolution processes.

Our findings show that spontaneous crystallisation of cBN is observed down to 2.1 GPa (Figure 3). This is the lowest pressure of cBN crystallisation ever reported before, though the process occurs without any catalyst. At 1.7 GPa, cooling of the solution containing 73 mol.% BN is accompanied by crystallisation of graphite-like hexagonal boron nitride (hBN) with a simultaneous formation of the phase X. This fact points to the predominant nucleation of metastable hBN in the region of cBN thermodynamical stability. The broad halo of phase X disappears upon quenching down to ambient conditions. This fact allows the suggestion that phase X is metastable at low pressures.

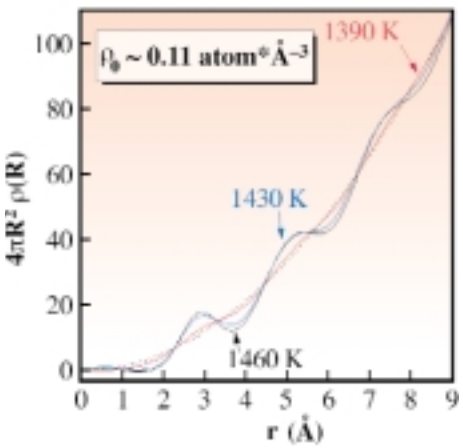

Fig. 4: The radial distribution functions for the supercritical solution containing 74.5 mol.% BN at 2.1 GPa. Dash line is the 4 $\pi r^2 \rho_0$ curve. The average atomic density ρ_0 was estimated from the linear fit to the reduced RDF G(r) in the range of r = 0-1 Å.

The radial distribution function $4\pi r^2\rho(r)$ (RDF) was used to characterise BN solutions in supercritical fluid at different pressures and temperatures. Our findings have shown that above 1450 K between 2.1 and 4.8 GPa in the concentration range from 74.5 to 82.5 mol.% BN, interference function i(s) for BN solutions exhibits a sharp first maximum (s = 2.84 $Å^{-1}$) with a small shoulder on its high-s side, a second maximum at 5.1 $Å^{-1}$ and a third maximum at about 7 $Å^{-1}$.

RDFs for the solution containing 74.5 mol.% BN at 2.1 GPa and different temperatures are presented in Figure 4. In cooling the solution, the intensities of the maxima in the RDFs decrease, and at 1390 K the maxima nearly disappear while the most prominent 111 line of cBN becomes visible in the corresponding X-ray pattern (Figure 3), *i.e.* this temperature can be considered as the temperature of cBN liquidus at the above pressure and concentration of the solution. Thus, the cBN crystallisation is accompanied (or even preceded) by disappearance of short-range order in the solution.

Similar changes of RDFs of solutions close to BN liquidus are observed over the whole ranges of concentrations and pressures being studied. Therefore, it can be suggested that crystallisation of boron nitride is preceded by decomposition of the BN associated solutions in the supercritical fluid of the N-H system.

KINETICS OF DIAMOND CRYSTALLISATION FROM METAL-CARBON MELTS

In situ studies of diamond crystallisation from the Fe-Ni-C melt at pressures up to 6 GPa and temperatures up to 1700 K were performed using a Paris-Edinburgh press and energy-dispersive X-ray diffraction. At 5.2 GPa and the heating rate of 25 K/min, spontaneous crystallisation of diamond starts at 1510 K immediately after the halo of the liquid phase appears, and is fully completed at 1605 K (Figure 5). We note that despite the presence of a liquid in the system over the whole temperature range of diamond crystallisation, all diffraction patterns exhibit lines of the solid phase that can be ascribed to the fcc Fe-Ni-C solid solution (γ-phase).

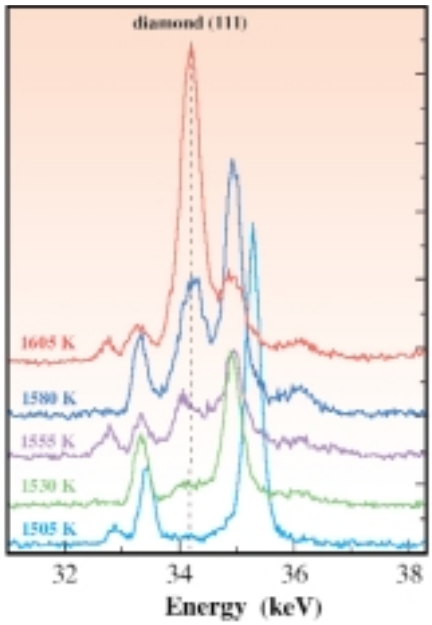

Fig. 5: Diffraction patterns of the Fe-Ni-C system taken at 5.2 GPa in the course of a linear heating at a rate of 25 K/min.

This fact indicates that in accordance with the p,T-phase diagram of the Fe-Ni-C system [10], under experimental conditions the L = C + γ monovariant eutectic reaction takes place. In this case, the melt is in equilibrium with both diamond and γ-phase.

Diamond crystallisation in the system under study is very fast and proceeds in a narrow temperature range that plagues essentially isothermal kinetics studies. Because of this, the present work describes a non-isothermal approach. As all the diffraction patterns exhibited diffraction lines of graphite, we state that diamond crystallisation from the Fe-Ni-C melt occurs at the constant carbon supersaturation with respect to diamond, which is ensured by dissolution of the initial graphite. Based on this, the degrees of the graphite-to-diamond conversion proceeding via melt has been calculated by normalising integral intensities of the (111) reflection of diamond at various temperatures to the appropriate value at 1605 K (α = 1).

From the non-isothermal kinetic data it follows that at 5.2 GPa diamond crystallisation is controlled by carbon diffusion in the melt to the surface of a growing crystal. Kinetic data might be best fit by the model that assumes a constant nucleation rate and three-dimensional growth of the resulting nuclei. From the temperature dependence of the rate constant in the 1505-1605 K range, the activation energy of diamond crystallisation from the Fe-Ni-C melt at 5.2 GPa was calculated to be 148(64) kJ/mole.

These studies firmly establish synchrotron radiation experiments at the third-generation sources as a powerful tool for studies of materials synthesis in the B-C-N system at high pressures and temperatures on a real timescale. ■

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WEIRD METALS – MODULATIONS WITHIN GUESTS WITHIN HOSTS

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High-pressure studies on certain elemental metals have unravelled unusual structures such as host-guest complexes. The characteristics of these structures cannot easily be explained and pose quite a challenge for theoretical studies.

It is now more than 40 years since the first high-pressure structures were determined using diamond anvil pressure cells. In that time, great advances have been made in the pressure range accessible with such devices, and in the quality of diffraction data obtainable from them. It is then somewhat surprising that so many significant uncertainties have remained, even in the structures of elements – at quite modest pressures in some cases.

Among the most persistent of the unsolved problems have been those in groups II and V of the periodic table, where the high-pressure phases Ba-IV, Sr-V, Bi-III, Sb-II and As-III have been shown to be complex, but have resisted all previous attempts at full solutions. Recently, using a combination of single-crystal and powder diffraction data collected at the SRS (Daresbury, UK), in-house, and at the ESRF, we have found that in all these cases, the high-pressure structure is very similar and of an entirely new type – described as the 'weirdest known atomic structure of … any pure element' [1].

Figure 1 shows a diffraction pattern collected from a single-crystal of Ba-IV at 12 GPa at the SRS. The diffraction pattern comprises layers of diffuse scattering (seen edge-on in this image), Bragg reflections that lie on the planes of diffuse scattering, "satellite" reflections around these reflections (enlarged in the inset), and Bragg reflections not on the diffuse planes are marked by arrows.

The structure explaining all these features is shown in Figure 2. It is a composite arrangement comprising a tetragonal 'host' structure (which gives rise to the Bragg reflections not on the diffuse planes), and chains of 'guest' atoms lying in channels that run along the c-axis of the host. These chains form C-centred tetragonal and C-centred monoclinic guest structures [2] which give rise, respectively, to the Bragg reflections on the diffuse planes and to the satellite reflections. The diffuse scattering itself can be attributed to a lack of inter-chain ordering in some fraction of the chains. The most surprising thing about this composite structure is that the host and guest structures are *incommensurate* with each other along the c-axis: the ratio of their c-axis lattice parameters, c_H/c_G, is 1.388 at 12 GPa, and varies continuously with pressure.

Further studies of Ba-IV have revealed that at 12.5 GPa, the monoclinic guest structure undergoes a structural phase transition, without any accompanying change in the host [2]. We have termed this an intra-phase transition. Another intriguing aspect of the structure is that the number of atoms in the host unit cell – which is non-integer and equal to $8 + 2x(c_H/c_G) = 10.776$ at 12 GPa – is pressure dependent, through the pressure dependence of c_H/c_G. Some of the chain atoms must then be 'squeezed out' of the channels with increasing pressure.

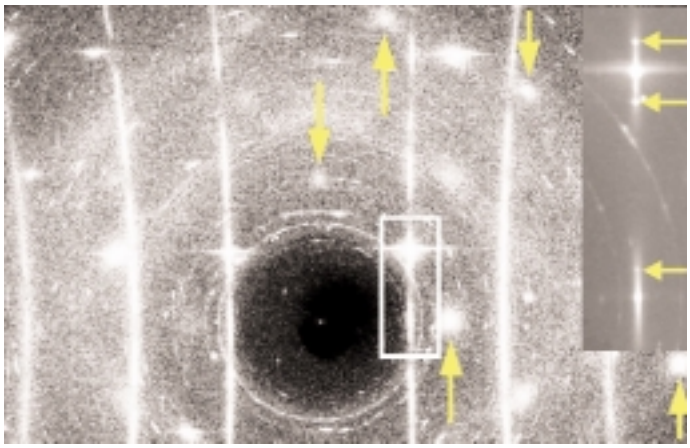

Fig. 1: 2-D diffraction pattern from a single-crystal of Ba-IV at 12 GPa. The inset enlarges the marked area. Vertical arrows mark host reflections, and arrows in the inset mark satellite reflections from the monoclinic guest adjacent to stronger reflections from the tetragonal guest.

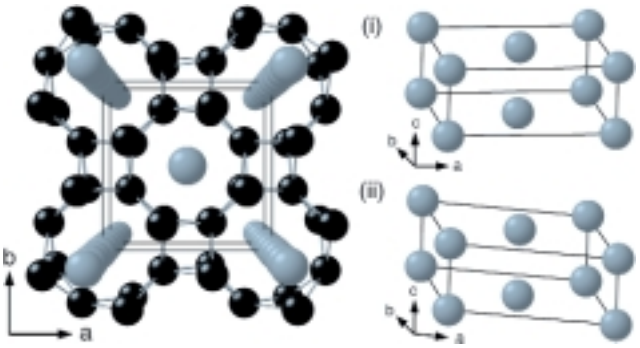

Fig. 2: The composite structure of Ba-IV. The host structure (dark atoms), with guest-atom chains (light atoms), is shown in a c-axis projection. The inset shows the tetragonal and monoclinic guest structures.

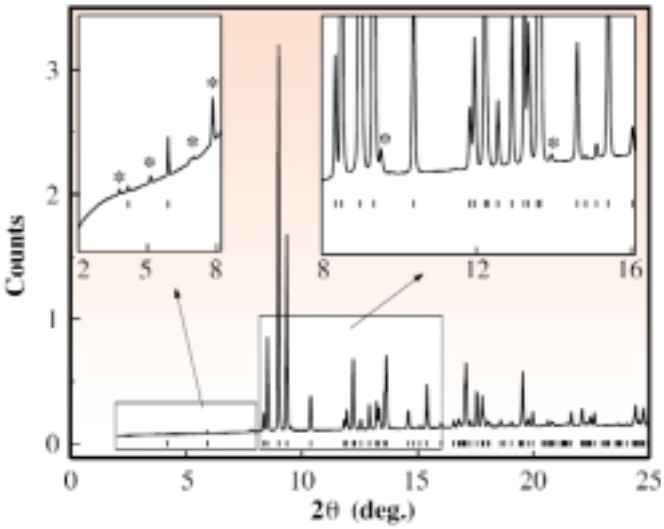

Fig. 3: Integrated profile from Sb-II at 10.3 GPa [7]. The tick marks show the positions of reflections from the host-guest composite structure. The strongest of the additional reflections are marked by asterisks.

Sr-V is stable above 46 GPa and known to have a similar diffraction pattern to Ba-IV. Studies at the SRS and on ID9 at the ESRF have revealed that it too has a composite host-guest incommensurate structure of the Ba-IV type, with c_H/c_G = 1.404 at 56 GPa [3]. We have also found that Sr-V undergoes an intra-phase transition at 71(1) GPa [3]. However, the structure of the guest phase above this pressure remains unknown.

The structure shown in Figure 2 bears a striking resemblance to the (commensurate) structure proposed previously for Bi-III and Sb-II [4], but which cannot be correct on density considerations. Powder and single-crystal studies of Bi-III and Sb-II have shown that in both cases, the true structure is a composite incommensurate structure with the same tetragonal host as Ba-IV and Sr-V, but with a different, body-centred tetragonal, guest [5]. The calculated densities of these incommensurate phases agree extremely well with those determined directly over 40 years ago by Bridgman and others. Recent studies of As-III at the ESRF and the SRS have shown that while it also has the same tetragonal host as Ba, Sr, Bi and Sb, the guest is monoclinic.

While the composite host-guest structures fit all the main features in the observed Bi-III and Sb-II diffraction profiles, there are a number of extremely weak reflections in profiles collected at the ESRF (see Figure 3) that are not accounted for. These peaks are from a furthur modulation of the structure [7]. It is clear that there are further levels of complexity yet to be uncovered in these strange phases!

It is a challenge for theoretical study to understand why such complex structures are stable over pressure ranges as large as 5 - 30 GPa and more. This challenge is made more difficult by the incommensurate nature of the structures. Heine has suggested possible critical factors for incommensuration such as charge density waves and the strength of the host-guest interaction [1]. First insight into the stability of Ba-IV has been obtained from calculations of a commensurate approximation [6]. Some other insight might come from an intriguing similarity with commensurate analogues found in binary alloys such as Al_2Cu and In_5Bi_3, which raises the interesting possibility that the Ba-IV-type phase might also be considered as an 'alloy' – comprising atoms with, perhaps, two different electronic arrangements. There is much yet to do, including further diffraction work to search for more of these 'weird metals' in other elements. ■

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STRUCTURAL GENOMICS: PITFALLS AND PROSPECTS

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Presentation given at the ESRF Workshop "High Throughput Structural Biology", 20-21 February 2001.

A discussion of the issues and feasibility of truly high-throughput expression, purification and structural determination using current technologies, highlighting potential bottlenecks in the existing process of gene to structure.

The solving of the human genome sequence, and the genomes of many other species, has resulted in a huge increase in the number of clinically-relevant targets (proteins) of interest to pharmaceutical companies. The production of targets for structural analysis has typically been a very slow process, mainly due to the very high purity and large quantities of protein required. To give the highest impact in a drug design process, structural information should ideally be available when lead compounds are identified from high-throughput screens. However, the solving of structures of proteins of interest can frequently occur at a very late stage within drug development projects permitting only limited input to structure-based drug synthesis and optimisation.

Large pharmaceutical companies are often interested in targets from diverse protein classes, ranging from microbial enzymes to kinases, membrane bound proteins such as 7-transmembrane receptors and ion channels. Expression of these proteins increases in difficulty - microbial proteins are relatively easy to express and crystallise, soluble mammalian proteins can be much harder to obtain, and integral membrane proteins are extremely difficult to generate in an active, folded form in sufficient quantities for structural determination.

There are many different systems available for expression of genes of interest. *E. coli* is the quickest and most economical, being easy to scale to large volumes and suitable for generation of labelled protein. However, *E. coli* does not perform post-translational modifications that may be required for functional activity. Over-expression in yeast is also fast and straightforward to scale, though the first choice for mammalian proteins is often baculovirus expression. This is much more expensive than yeast and *E. coli*, especially at large scale, but this system does perform post-translational modifications such as phosphorylation. Expression of eukaryotic proteins in mammalian cells will usually produce the native protein, but is a very slow, expensive procedure and only infrequently produces proteins in high enough yield for structural determination.

Generation and expression of proteins for structural analysis has usually been performed as an iterative process. One to three constructs - alternative forms of the gene, either truncated or mutated - are generated from the full-length gene and expressed in the 'best bet' system, usually *E. coli*. The first construct will often be that generated for high-throughput screening, which is not necessarily ideal for crystallisation. If the constructs express well, and can be supplied to the crystallographers in the required purity and concentration, a second round of construct generation is not necessary unless crystallisation fails or the crystals are of poor quality. However, if the proteins fail at any step during the supply (purification or expression), further rounds of construct generation or use of an alternative expression system is required. This iterative process clearly lengthens the time taken to produce structures, decreasing its impact on the drug design process.

It is clear that the time from gene to structure must be improved to take advantage of the many new targets in the completed human genome. Homology modelling can produce putative structures for genes within families, but the structures currently deposited in the PDB (Brookhaven Protein Data Bank) represent only a fraction of the populated folds, characteristic tertiary structure elements, such as helix-loop-helix, ß-barrel, thought to exist in natural proteins [1]. This limits the usefulness of homology modelling as a predictive tool. There are many initiatives worldwide to determine structures of unknown proteins from the various genomes, and it is estimated that solving a minimum of 10,000 structures within 10 years should produce at least one example of the folds from each family of proteins [2].

To determine such a large number of structures within a relatively short time frame requires a re-think of the current methods of protein generation. Instead of working with one to three constructs, and performing several rounds of generation and purification to generate all of the constructs of interest to the crystallographers, multiple constructs could be produced in one go (including constructs designed for high-throughput screening). These could be cloned into powerful *E. coli* expression systems, and expressed in multiple *E. coli* strains. There are many new strains designed to improve expression and folding of proteins. One or two affinity tags could be included (both N- and C-terminal) to assist in purification, and protease cleavage sites

(such as TEV or PreScission) could also be encoded to remove large flexible regions from the N-termini of the proteins which would potentially interfere with crystallisation. In addition, site-directed mutagenesis could be employed to remove undesirable surface residues or loops. Using this approach, it could be anticipated that many constructs of a particular protein in a form suitable for crystallisation may be generated.

What would be the implications of this increase in the number of proteins for crystallisation? It is estimated that the production of 1000 crystal structures per year would require approximately 10,000 proteins to be screened for crystallisation (about 800 crystallisation screens per month). If each crystallisation screen comprised 200-500 conditions, then each screen would require 2-5mg of protein at a concentration of 10mg/ml and 95% purity. In order to collect sufficient X-ray data to solve this quantity of crystal structures a dedicated MAD (Multiple-wavelength Anomalous Diffraction) beamline would be essential. Using current structure solution methods, automated electron density map interpretation and refinement packages each structure would take approximately 2-4 weeks to complete. A team of 50-100 protein crystallographers would be required to undertake a task of this magnitude.

The key to completion of this number of structures is miniaturisation and automation at every step of the process. Cloning, expression and purification is relatively straightforward to automate; robots exist to perform liquid handling, but expression analysis would be time consuming by electrophoresis (SDS-PAGE), so an alternative must be developed. Crystallisation can also be automated (possibly at the nanolitre scale), but crystal mounting and freezing is currently a time-consuming and manual procedure, and therefore a serious bottleneck in this process. Finally, new programs need to be developed to automate structure solving and perform docking in a high-throughput mode.

It is not impossible to do high-throughput structural determination. Indeed, there are several biotech companies (*e.g.* Syrrx, Structural Genomics) with business plans based on structural genomics. Large pharmaceutical companies have a slightly different focus, with needs closer to 'functional' genomics. Although crystal structures of pure proteins can be used for compound docking and SAR (Structure-Activity Relationship studies), more information for drug design and optimisation can be obtained from structures of protein/ligand or protein/ inhibitor complexes. This is particularly true if inhibitors of many structural classes are available for co-crystallisation. However, this is just a difference in emphasis in the needs of structural genomics projects versus drug discovery, and the methods discussed in this article can be applied and adapted to achieve both sets of aims. ■

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ACKNOWLEDGEMENTS

We would like to thank all of the members of the Structural Biology, Gene Expression Sciences, Protein Biochemistry and Computational Chemistry departments at GSK in Harlow that took part in the discussions described in this article.

Automated Data Collection and Processing for Macromolecular Crystallography

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Presentation given at the ESRF Workshop "High Throughput Structural Biology", 20-21 February 2001.

Fully automated data collection and processing is an achievable and highly desirable objective for modern synchrotron protein crystallography beamlines. A possible scheme for reaching a high level of automation with modest programming resources is outlined.

Structural genomics initiatives such as that recently funded by the National Institute of General Medical Sciences in the USA will lead to a dramatic increase in the rate at which macromolecular structures are determined. This increase in throughput will be achieved by applying automation to almost all steps in the structure determination pathway,

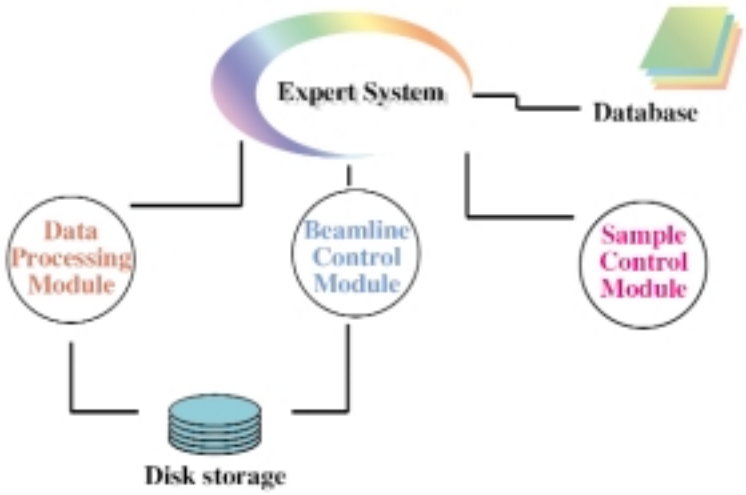

Fig. 1: A schematic representation of the control software for an automated protein crystallography beamline.

from protein expression and purification through to model building and refinement. Inevitably, the steps involving collection and processing of the diffraction data will also need to become far more automated than at present, if these steps are not to become rate limiting. Based on conservative estimates of exposure time and detector readout time (10 s each per 1° image), a typical third-generation beamline equipped with automated sample loading is capable of producing 24 complete (180° rotation) datasets per day. This could represent 12 *ab inito* structures (based on 2 wavelength MAD phasing) which translates into over 3000 structures per annum. In practice, the requirement to screen multiple crystals prior to commencing data collection and the fact that not all MAD datasets will lead to a structure, will significantly reduce this number. Nevertheless, this example helps to illustrate that data collection and processing must become more automated if the potential throughput of such a beamline is to be achieved.

At present, the scientists working on the beamline are responsible for mounting samples, for operating the beamline control software and for running the data processing software. They decide whether or not to collect data from a particular crystal on the basis of visual inspection of images and information obtained from the data processing programs. They set the optimal data collection parameters (resolution, exposure time, oscillation angle, phi range) and ideally try to process at least some of the images as they are collected. In an automated system, crystal mounting and centring would be performed robotically, and "intelligent" software (an expert system) would take the decisions currently made by the scientists, based on information provided by the processing software and "project parameter information" stored in a database. One possible scheme is outlined in Figure 1. Its modular nature is deliberate because a more monolithic or integrated structure would take longer to develop and could not easily be installed on different beamlines, which typically have their own version of the beamline control software. Communication between the modules would be at a high level such that the expert system could instruct the processing module to characterise a crystal using images from a certain directory. In response, the processing module would return information such as crystal cell parameters, possible space group, mosaicity, and resolution limit. On the basis of this information, the expert system could then choose the acquisition parameters and instruct the beamline control module to proceed with the data acquisition.

To assess the feasibility of this type of automation, it is necessary to examine the steps involved in manually characterising a crystal for data collection. The first step is to collect two images, separated by 90° in rotation angle, and to verify whether the crystal diffracts to a useful resolution, whether it is a single lattice, and whether the mosaicity and spot shapes are acceptable. If the crystal passes this "quality check", the images are autoindexed to derive a unit cell and possible spacegroup(s). The autoindexing is also checked by predicting the spots for the two images. A more quantitative estimate of the mosaicity is determined, and a data collection strategy is worked out (total phi range(s), oscillation angle required to avoid spatial overlaps). The images are integrated to obtain an estimate of the true resolution limit, and the exposure time and resolution for data collection are chosen. Finally, the data are collected and, ideally, processed simultaneously.

The most challenging step to automate in this procedure is an assessment of the "quality" of the two initial diffraction images. This is something that is quite straightforward for an experienced crystallographer, but it would require rather sophisticated image processing techniques to extract the same information automatically. A possible solution to this problem is to extract this information indirectly, based on the success or failure of the autoindexing of the two images. Algorithms for autoindexing are now generally very robust and further improvements should help to reduce the occurrence of algorithm failure. An examination of the situations in which the autoindexing fails reveals the following causes: incorrect direct beam co-ordinates, crystal-to-detector distance or wavelength; insufficient spots found (implying weak diffraction); multiple lattices or split spots; excessive mosaic spread or too large a rotation angle. On an automated beamline, the physical parameters would be passed from the beamline control software and therefore should not be erroneous. Many of the other reasons for the failure of autoindexing would suggest that the sample is actually unsuitable for

data collection. The two images should be autoindexed separately (to detect lattice imperfections which are not visible in some regions of reciprocal space) and also together, to give more accurate cell parameters. Rejection criteria based on the rms positional residual of indexed spots and the number of spots rejected from both the indexing and the cell parameter refinement will be applied to select successful solutions. Samples which fail this test are flagged for visual inspection (possible at a later time) by the beamline operator who may (*e.g.* by manual spot editing) be able to find a satisfactory solution. Autoindexing will produce a list of possible solutions with different symmetries, each with its own penalty score which evaluates how well the cell parameters comply with the restrictions appropriate for that spacegroup. Generally (unless the true symmetry is triclinic) there will be a clear separation between a number of solutions with low penalties and other solutions with much higher penalties. The solution with the highest lattice symmetry from the group with low penalties will normally be selected as an initial hypothesis for the true symmetry.

The next step is to obtain an estimate of the mosaic spread. The algorithm implemented in MOSFLM [1] relies on integrating an image with different values of mosaic spread and evaluating the total intensity of all predicted reflections. This total intensity will reach a plateau when the true mosaic spread is reached.

A data collection strategy can now be determined based on the assumed spacegroup, the known spot size and the mosaic spread. Initially, a minimum total rotation range, typically divided into two or three wedges of data that should result in a high (*e.g.* 90-95%) completeness, will be calculated. For this rotation range(s) the maximum oscillation angle that will avoid spatial overlap will also be calculated as a function of the phi angle. This data will be collected first, in order to minimise radiation damage. A second data collection range, designed to bring the completeness to 100% and increase the multiplicity of the observations, will also be calculated. For appropriate cases (MAD data collection), the completeness of the anomalous data will be maximised. All the functionality for these calculations already exists in MOSFLM. Finally, the exposure time and resolution of the dataset need to be defined. To do this, the two initial images are integrated and the mean $I/\sigma(I)$ is calculated as a function of resolution. The effective resolution is defined as that at which the mean $I/\sigma(I)$ drops below a cutoff value (e.g. 2). Using Poisson statistics, it is possible to estimate the exposure time required to achieve the desired $I/\sigma(I)$ value at any particular resolution. This would be compared with the "maximum allowable" exposure time to arrive at a final choice of resolution and actual exposure time. Data collection can then be started. For lower symmetry spacegroups (orthorhombic or below), a few images should be collected 90° away in Φ from the first data wedge. These images, together with images from the first wedge, are used to determine accurate cell parameters by post-refinement. Using these cell parameters the images are processed as they are collected. During the data collection the first two images are re-collected at regular intervals to monitor radiation damage. The images should also be scaled and merged at the earliest opportunity, to check the initial assumption of the spacegroup symmetry. If it turns out to be incorrect, the data collection strategy will need to be recalculated, taking into account the data that has already been collected.

The modularity of the system should allow maximum flexibility in implementation while minimising the programming effort. The expert system should be beamline and synchrotron independent and could be a focal point for collaboration between different synchrotron sites. Only a command "translator" module would be required to interface a standard expert system with different beamline control software. Information specific to a given sample or project will need to be supplied to the expert system in order to assist in decision making. Some of the possible project parameters are listed below:

(a) Minimum acceptable resolution (defined as $I/\sigma(I)>X$)
(b) Highest resolution required
(c) Maximum exposure time per dataset
(d) Maximum acceptable mosaic spread
(e) Maximum acceptable anisotropy
(f) Maximum acceptable radiation damage (expressed as a B factor or $\Delta I/\sigma(I)$ at the highest resolution)
(g) Number of wavelengths required
(h) Anomalous scatterer
(i) Minimum exposure time per image
(j) Maximum number of overloaded reflections
(k) Minimum acceptable completeness (anomalous or overall)

The number of project parameters and their default values would have to be determined on the basis of experience.

Beamline performance could be monitored by evaluating a standard sample at regular intervals. Any deterioration in quality would result in a message being passed to the beamline operator, possibly via a mobile phone.

The different processes outlined in Figure 1 would probably run on different computers. In particular, a high performance machine with rapid disk access would be required for the data processing if this is to keep pace with data collection. Given the continual improvement in performance, it is not unrealistic to expect data collection and processing to proceed in step. A collaboration is currently being established with personnel at the ESRF and SRS (UK) to work towards a practical implementation of the scheme outlined above. ■

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I would like to thank P. Evans and H. Powell for many useful discussions.

AUTOMATION OF THE MACROMOLECULAR CRYSTALLOGRAPHY BEAMLINES AT THE ESRF

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THE JOINT ESRF AND EMBL STRUCTURAL BIOLOGY GROUP (JSBG)

Presentation given at the ESRF Workshop "High Throughput Structural Biology", 20-21 February 2001.

Macromolecular crystallography is now a routine tool in academia and industry alike. Automation is required to maximise throughput on the available beamlines and to cope sensibly with the increasing influx of measurements.

Since the first ESRF beamline for macromolecular crystallography, ID2B, came on-line in September 1994, macromolecular crystallography has developed into a standard tool for scientists in academia and industry alike. It now has a routine role in the drug development cycle and is an intrinsic component of the burgeoning structural genomics field. In order to maintain pace with this explosive growth and augment throughput of generic experiments, such as ligand soaking and <100 kDa structure solution, the beamlines must become automated, reliable and easy to use. Automation will clear the path for the challenging long-term projects requiring many shifts of beam time that will follow structural genomics: the membrane proteins, the functional studies and, perhaps most crucially, the study of complexes of proteins and macromolecules that is central to the understanding of their real-life interactions.

THE CURRENT BEAMLINES

Five JSBG (Joint Structural Biology Group) beamlines are available for macromolecular crystallography: the ID14 complex with four end-stations and ID29 which, since the end of 2000, has superseded BM14 (now an Anglo-Spanish CRG line). Every six months these beamlines handle over five hundred projects and demand is on the increase, requiring improved efficiency and throughput.

Beamline	Detector	Wavelength range (Å)
ID14-1	165mm MAR CCD	Fixed: 0.93
ID14-2	ADSC Q4 Matrix CCD	Fixed: 0.93
ID14-3	165mm MAR CCD	Fixed: 0.93
ID14-4	ADSC Q4R Matrix CCD	MAD: routinely* 0.94 - 1.15
ID-29	ADSC210 Matrix CCD	MAD: routinely* 0.80 - 2.1

*other wavelengths possible by prior arrangement.

GOAL: GENERIC HIGH THROUGHPUT

Crystallographic data collection represents only a small time slice on the structural genomics pathway, but automation at the beamline is not only concerned with this facet of the process. Beamlines increasingly resemble factory assembly lines, with the goal of automation to streamline the entire structure solution process from sample mounting, alignment and collection strategy through to data processing, reduction, phasing and even initial 3-D model construction (Figure 1). To accomplish this will require a close collaboration between instrumentationalists and software engineers.

Automation also goes to the heart of the beamline, in the optics hutch. It is of little use automating the experiment if the underlying optical elements are not as optimised and reliable as possible. The suite of JSBG beamlines will be made consistent in terms of software and

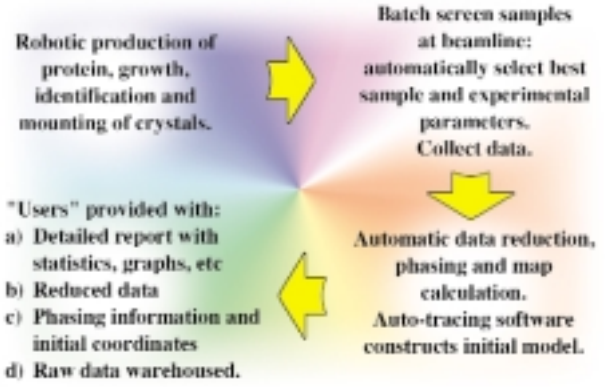

Fig. 1: Target protein to initial 3-D model for generic structure solution.

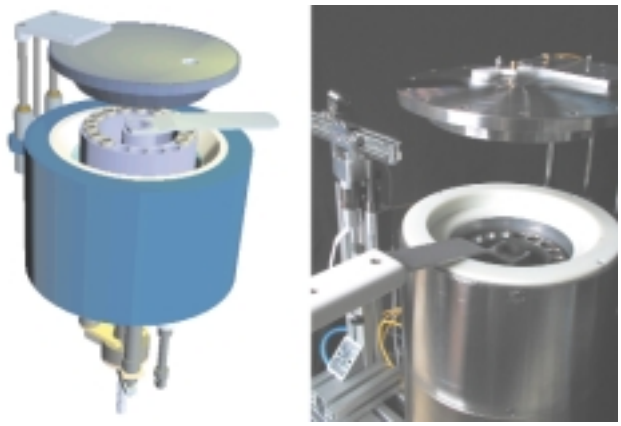

Fig. 2: (Left) schematic of sample changer cassette and cold box. (Right) the complete changer unit ready to move to a beamline.

hardware, with built-in diagnostic tools to allow rapid alignment or intervention in the event of a breakdown.

Optics hutch and experiment automation together will reduce human error: tired users in the small hours can make unwise decisions, deteriorating their data quality and eventual structural information or indeed the beamline itself.

IN THE PIPELINE: HARDWARE

Plans are already underway to use ID14-3 as a test-bed for beamline automation. New equipment will be installed on the line over the coming months and then rolled out over the other stations once thoroughly tested and proven. The Automation Task Force have designs in hand and the first steps will be taken shortly with particular regard to the beamline optics where automatic alignment tools and instrumentation will be added.

For the experimental hutch, the Joint Instrumentation Group (JIG) of the ESRF and EMBL has developed an automated sample changer. Currently, user groups can take many minutes to retrieve, mount and align a pre-frozen sample, with this process becoming harder as average sample sizes drop from 200 μm several years ago to around 80 μm now. The sample changer is under final bench checks and will soon move to a beamline for on-line testing. The current device, the design of which is extendable, can hold up to twenty samples in Hampton Research cryo-vials (Figure 2) and is simple in conception as well as robust, compact and rapid. With the footprint of a dry-transport dewar and standing lower, it can place or remove a sample in under two seconds on the experiment goniometer. Once mounted, automatic alignment routines can precisely centre the sample for data collection. Work on this aspect is underway, though pattern recognition of the cryo-cooled crystal in supporting loop will not be simple.

The changer is compatible with a microdiffractometer, also developed by the JIG, and already used for scheduled experiments on the ID13 and ID14 lines much to the delight of users. The microdiffractometer can work with samples down to 5 μm in size and allows remote accurate centring in small beams. A commercialised version is under development.

IN THE PIPELINE: SOFTWARE

With the revolution in data collection speeds, the ergonomics and ease of use of a beamline have become paramount. To this end, the ProDC interface, the user's beamline communication and control centre, is now installed on all beamlines providing a unified interface no matter which detector or equipment is installed. The software takes care of routine data collection tasks, such as safety shutter opening, beam loss checks, auto beam realign and one button edge scans for anomalous diffraction data.

The beamline software also interacts with databases in order to store experiment and beamline parameters. This can allow subsequent automated data processing using stored parameters either on-site or remotely through web-based interfaces, and also the recovery of known beamline configurarations in the event of failures. These web interfaces are going through the second generation of development using the ZOPE environment and eventually users can expect to use the interfaces to query databases with questions such as:

- What did I collect around 28 Feb 2001?
- Can I take a look at the images?
- I'd like to process the data using software X and script Y.
- What are the data processing statistics?
- Can I see the Pattersons?
- Can I trace a 3-D structure?

These questions highlight the advantages and flexibility of a database environment, in comparison to complementary information storage in the headers of image files, where parameters and results can be changed or added at a later date.

THE FUTURE

The beamlines are continuously evolving and projects, such as the automated sample mounting and alignment, are underway to further advance beamline efficiency. The JSBG is aiming for a fully automated beamline to be operational in two to three years' time. In the future, user presence may not be necessary for all measurements with samples routinely sent to beamlines, handled by robots and the processed data (or initial coordinates) sent electronically back to the research groups at home.

WHAT COULD BE DONE?

Assuming one useful structure data set (MAD, SAD, ligand soak, etc.) per hour, an optimised suite of JSBG beamlines could produce 125 structures per day or 25,000 per year. Multiply this by the European synchrotrons and their macromolecular crystallography resources and over 100,000 structures could be produced per year. Even if only one quarter of this total were to be realised, the input of structural information to world databases would be extraordinary. Imagine what could be achieved with that amount of knowledge! ■

Further Information

The JSBG is a joint ESRF and EMBL team of technicians, engineers and scientists operating and maintaining the JSBG beamlines, together with technical developments and in-house research.
(http://www.esrf.fr/exp_facilities/jsbg/jsbg_beamlines.html)

Damping Links to Attenuate Vibrations of Magnet Girder Assemblies

L. Zhang

ESRF, Technical Services Division

Installation of damping links to reduce quadrupole magnet vibrations was completed at the ESRF during the March 2001 shutdown. The results from measurement clearly show attenuation of vibration of the quadrupole magnets, and significant improvement of electron beam and X-ray beam stability.

In the ESRF storage ring, there are three types of magnet girder assemblies (MGA) involving quadrupole magnets: G10, G20, G30. The G10 and G30 MGAs each contain five magnets, whereas the G20 MGA is longer and consists of seven magnets. The fundamental resonant frequency of these magnet girder assemblies is in the frequency range of 6.5 to 9 Hz, with a lateral rocking motion. This resonant rocking motion of the MGAs induces the electron beam motion with a dominant frequency of 6.8 Hz mainly in the lateral direction. The rms displacement in the frequency range of 4 to 12 Hz is typically 0.2 µm for quadrupoles, and 12 µm for the electron beam at high-ß section. The electron beam motion influences the position stability of the X-ray beam, the intensity stability of the X-ray beam after a monochromator, especially for a horizontally diffracting monochromator. Intensity variation of the X-ray beam with a peak frequency around 7 Hz has been observed in some beamlines, for instance, ID14, ID24 and ID26. In order to improve electron beam and X-ray beam stability, it is necessary to attenuate the vibrations of the magnet girder assembly in the storage ring.

A damping device, the so-called 'damping link', has been developed to attenuate the vibrations of the magnet girder assembly. It consists of three parts (Figure 1):

- a sandwich structure with aluminum plates and ViscoElastic Material (VEM): Al + VEM + Al
- a girder mounting fixture (GMF) which allows the sandwich structure to be linked to the girder
- a floor mounting fixture (FMF) which allows the sandwich structure to be linked to the floor

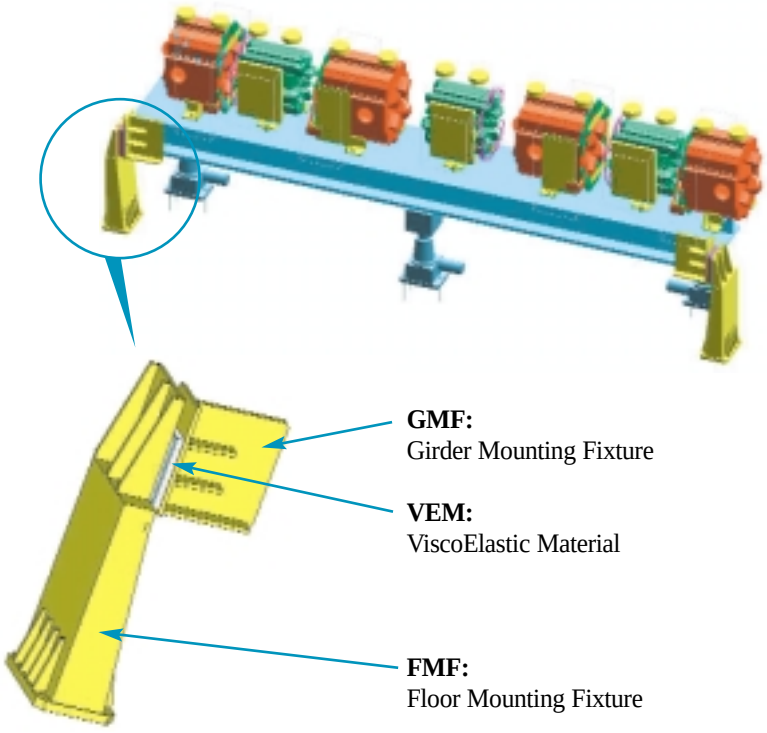

Fig. 1: Damping link and location on a storage ring girder.

The idea is to use the sandwich structure with VEM to absorb the dynamic strain energy of the MGA. The damping links are installed on the two extremities of the girder and floor as shown in Figure 1. The mounting fixtures (GMF, FMF) should both accommodate the environment in the tunnel and be stiff enough to transmit maximal dynamic strain energy of the MGA to the VEM layer which then dissipates this energy. Mechanical properties of the VEM are key parameters for the successful design of damping link.

Significant efforts were necessary for the installation. The available space was very limited such that cooling pipes and some electrical tracks had to be moved. The installation of damping links at all locations in the ESRF storage ring was

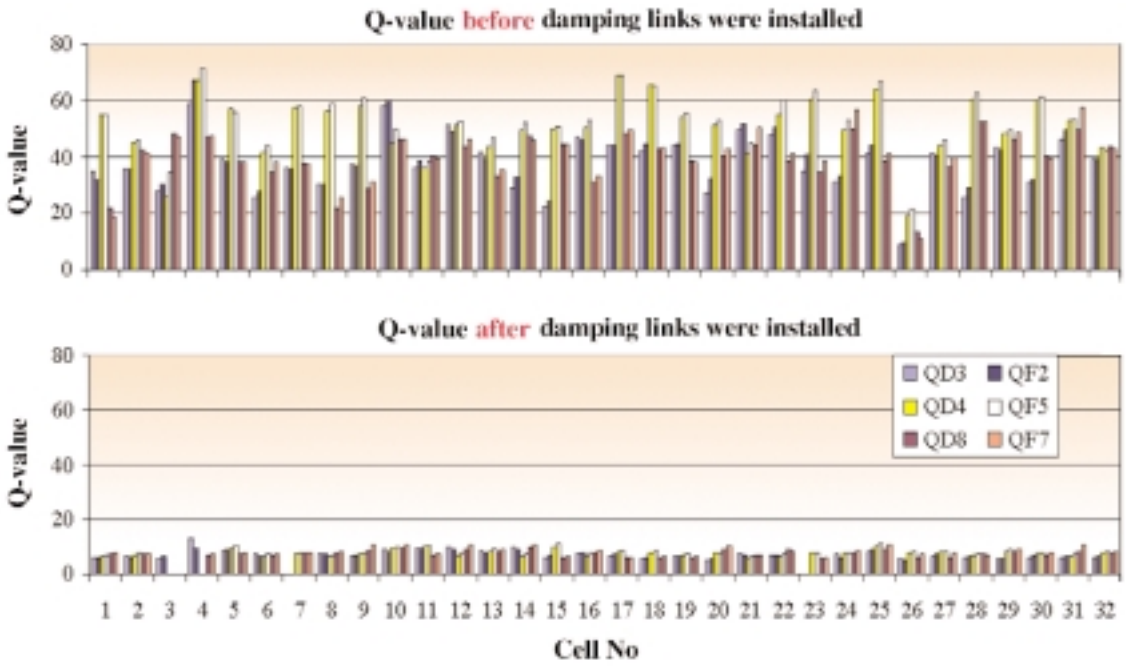

Fig. 2: Q-value of quadrupoles before and after the installation of the damping links in the storage ring.

completed during the March 2001 shutdown.

Vibration tests have been performed on quadrupoles before and after damping link installation. Results in terms of Q-value (peak value in the transfer function at fundamental resonant frequency) of quadrupoles are shown in Figure 2. Note that there are 32 cells in the storage ring, and 3 MGAs with quadrupoles per cell. Results are given here for 2 quadrupoles per MGA: QF2 and QD3 for G10, QD4 and QF5 for G20, QF7 and QD8 for G30. The Q-value of the quadrupoles was about 50 before installation of the damping links, and was reduced to about 10 after installation of the damping links.

In cell 26, damping plates (another damping device) were installed between the jacks and the floor in 1997. The jacks were bolted to the floor. The damping plates were partially shunted by the bolts, but there are still some damping effects. This explains why the Q-values before installation of the damping links in cell 26 were significantly smaller than in other cells.

Electron beam motion has been measured before and after the installation of the damping links in the storage ring. As the installation work was done during four machine shutdowns (Summer 2000, October 2000, Winter 2000/2001, and March 2001), measurements were also made in the case where only part of storage ring was equipped with damping links. Power Spectral Density (PSD) of the horizontal displacement of the electron beam is shown in Figure 3 for four cases. Before the installation of the damping links, there was a huge peak at 6.8 Hz in the horizontal displacement PSD. When half of the storage ring was equipped with damping links, limited damping effects on the electron beam could be observed. When the storage ring was totally equipped with damping links, the peak at 6.8 Hz in the PSD was shifted to about 9 Hz and dramatically reduced by a factor greater than 40. The RMS displacement in the frequency range of 4 to 12 Hz was reduced from a typical value of 12 µm to 3 µm for the electron beam, and from 0.2 µm to 0.05 µm for the quadrupoles. In the results shown in Figure 3, there is a wide peak around 30 Hz. The damping links have no effects on this wide peak. This is because the wide peak around 30 Hz in the PSD of the electron beam is due to the lateral rocking motion of the

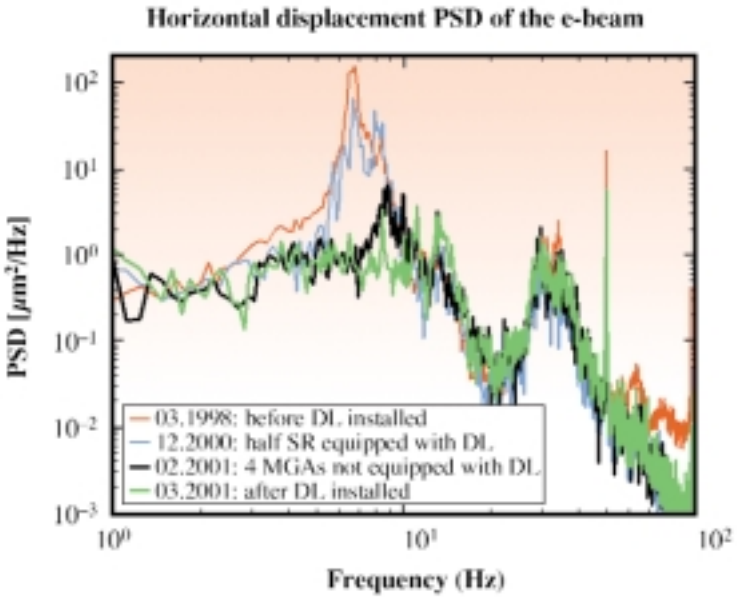

Fig. 3: Horizontal displacement PSD of the electron beam before, during and after the installation of the damping links in the storage ring.

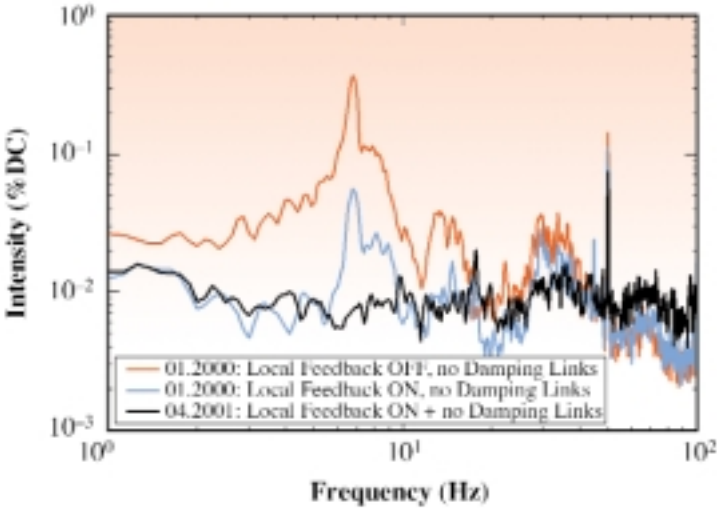

Fig. 4: Spectra of the X-ray beam intensity variation measured with the ID14-EH1 beamline.

quadrupoles QF2 and QF7 relative to the girder. As the girder does not move for this vibration mode at 30 Hz, the damping links are therefore not effective for the vibration of the quadrupoles around 30 Hz, as well as for the motion of the electron beam around 30 Hz. Some countermeasures to reduce the vibrations of quadrupoles QF2 and QF7 have been studied by finite element simulation, and could be very effective.

The significant enhancement of the electron beam stability was also observed on the X-ray beam. Figure 4 shows the spectra of the X-ray beam intensity variation measured at the ID14-EH1 beamline in January 2000 and in April 2001. Damping links for the machine girders were installed between these two dates. The spectra are expressed in percentage of the DC value. The variation of intensity should be as small as possible, so that the spectral value should be significantly smaller than unit 1. The peak at 6.8 Hz in the X-ray bean intensity spectra is removed in totality after damping links have been installed in the storage ring. Note that the local feedback on the electron beam significantly reduced the intensity variation around the peak frequency 6.8 Hz, but the peak is still visible.

In conclusion, the damping links have been successfully developed and implemented in the ESRF storage ring. Vibrations of the magnet girder assemblies were effectively attenuated. Electron beam and X-ray beam stability were significantly improved. ■

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	6129	Mechanical Engineer	24/08/01
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