

21 December 2004

Proposal of
High-Resolution Powder Diffraction and Microfocus
Beamline
at ALBA
for Structural Crystallography and Hard Condensed Matter
Studies.

A proposal prepared for the SAC March 2005

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The collaboration of Juan Rodríguez Carvajal (Saclay, Paris) and Germán Castro (ICMM-ESRF, Grenoble) is gratefully acknowledged.

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1. Introduction

The current trend in most advanced European countries is to build own third generation synchrotrons to complement their participation in large multinational facilities. Recent examples are SOLEIL in France, DIAMOND in UK and SLS in Switzerland. In the case of Spain, the authorities decided to build the synchrotron ALBA. In order to define the needs of the Spanish synchrotron community, a meeting of synchrotron users was held in Málaga last February. The present scientific case corresponds to the needs expressed by the users grouped under the generic name "Hard Condensed Matter: Structure". A preliminary report summarising their needs was already published in the website of AUSE (Asociación de Usuarios de Sincrotrón Españoles) in February 2004. Inspection of this report clearly indicates that the beamline satisfying most requirements is a multipurpose one placed on an insertion device (ID) with two stations, the first one for high-angular resolution powder diffraction (HRPD) and the second one for microfocusing and devoted primarily to microcrystal diffraction (MD) and XRD experiments under high pressure at moderate energies.

As shown by the large number of users in section 5., HRPD is supported by a large number of research groups with proved experience. This large number evidences the maturity reached by the Spanish community in this technique. Besides the application of high-resolution powder diffractometry to the solution and refinement of crystal structures and to microstructural analysis, one aspect stressed by many groups is the possibility of carrying out *in situ* experiments under non-ambient conditions. The availability of such a HRPD station will allow performing longer and/or more risky measurements or also preliminary studies, for which it is difficult to find measuring time in very competitive facilities like the ESRF. HRPD plays an important role not only in academic research but also in industrial branches such as chemicals, cements, metallurgy and pharmaceuticals, all of them well represented in Spain.

The principal application of the microfocus station is microcrystal diffraction. Although currently the number of users is rather low, a great deal of researchers consider this technique as indispensable for the future. This technique enables the determination of crystal structures of very small crystals (down to 10 μm) with a great impact on fields like zeolites, supramolecular chemistry or pharmaceutical compounds, among others. The possibility of studying these compounds without needing large single-crystals (if feasible at all), is very often decisive for the success of a research project or an industrial development. One explanation for the still low number of Spanish users of MD can be found in the large demand for measuring time at the few dedicated MD beamlines existing at international facilities. However, due to the similarity between the experimental set-ups for microcrystal and for conventional single-crystal measurements, it is to be expected that once MD is available at ALBA, the number of MD users will rapidly increase. An additional interesting point is the fact that the proposed microfocusing diffraction station complements the diffraction capabilities of the less brilliant Spanish beamline SPLINE at ESRF which is placed at a bending magnet.

Although the design of the beamline has been optimised for HRPD and MD, some needs expressed by a number of research groups working on high pressure have also been taking into account. The idea is to provide a platform where to perform experiments with diamond anvil cell at high pressures. In many cases the high pressure experiments will satisfy the user demands and in others these preliminary measurements will help to apply for measuring time at dedicated high-pressure beamlines with higher energies. In the case of Spain, an additional expected benefit will be the enlargement of the high-pressure community that should end, in the future, with a dedicated high-pressure beamline at ALBA.

2. Scientific case

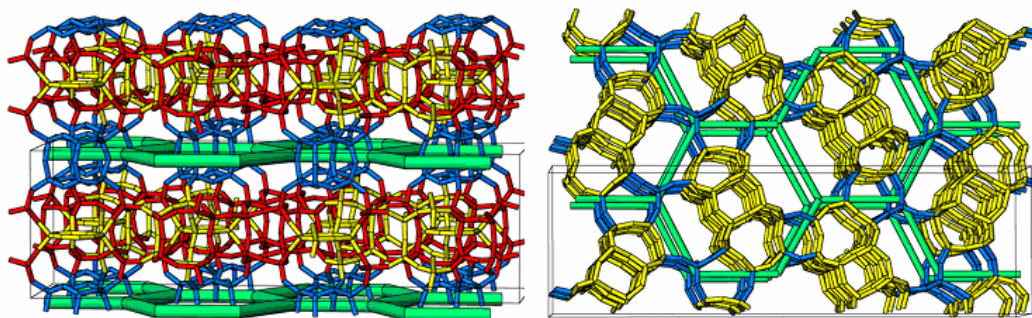
2.1. Experiments using the high-angular resolution of the powder diffractometer

The planned experiments can be grouped in the three following categories although they are very often interrelated:

2.1.1. Determination of crystal structures

In many research fields it is often very important to know the detailed crystal structure of a compound. Only with this knowledge the properties of the compound can be fully understood or improved. The usual way of solving a crystal structure when large enough crystals are available, is with single-crystal X-ray diffraction methods. In the last years, the possibility of studying very small single-crystals has become a reality by combining third generation synchrotrons with insertion devices, microfocusing mirrors and new detection technologies (CCD's). However, for volumes less than approximately $125\mu\text{m}^3$, manipulation of such microcrystals becomes problematic and powder diffraction methods must be used. The rather large volume of sample illuminated (typically in the order of mm^3) provides an averaged view of the sample which is often advantageous. The normal data collection procedure consists on dividing the total measurement time in shorter scans. At the end the counts of the individual scans are added. In this way, any change in the sample can be easily monitored. The principal limitation of powder diffraction is the peak overlapping that becomes very severe at high Bragg angles, especially for compounds with large unit cells. To attack this problem there are two obvious strategies: Either to solve the peak overlapping, or to work with the complete pattern by refining instead of the phases, the structural parameters (origin of the fragments and respective orientations, torsion angles, etc.). Both strategies have their own advantages and limitations and constitute active research fields. In both cases, however, the better resolved the diffraction peaks in the patterns, the better are the results obtained.

The simplest and more general way to solve relatively complex structures from powder data is the application of the single-crystal methodology (the so called direct methods) to powder diffraction data. These methods are model-free and can handle atomic disorder. One example of efficient and robust direct-methods phase-refinement function, especially well suited for coping with powder data and actively using the known large and weak intensities in the phasing process, is the origin-free modulus sum function implemented in the XLENS package (Rius, 1993; 1999; 2004). The key for the success of direct methods is a nearly complete intensity data set. If a structure contains dominant scatterers with a minimum separation s , then direct methods work well if the minimum d -spacing of the data set fulfills the criterion $d_{\text{min}} \leq s \cdot 0.72 \text{ \AA}$ (Rius, 1995). Direct methods are most effective for inorganic compounds (longer interatomic distances than organic compounds), and in general for compounds in which dominant scatterers are usually present (heavy atom method). One notorious example shown in the figure below is the solution of zeolite ITQ-22, an ordered zeolitic material with 16 independent T atoms showing unique catalytic properties (Corma *et al.*, 2003). The presence of 50% Ge substitution at four T sites greatly facilitated the elucidation. The data were measured at beamline DW22 (LURE) and the peaks showed practically no sample broadening effects (FWHM= 0.02° at $\lambda=0.9611\text{\AA}$). Due to the good crystallinity of the material, data collection on a high resolution powder diffractometer had simplified enormously the determination and the accuracy of the subsequent refinement.



Side (left) and upper views (right) of zeolite ITQ-22 solved by direct methods with the heavy atom method by using powder synchrotron diffraction data.

It was with the introduction of the automated intensity extraction procedures of Pawley and LeBail (Pawley, 1981; Rius *et al.*, 1996) both based on the known *metric* and *peak shapes* as constraints, that direct methods became widely used. **The automated extraction process is greatly simplified with high-angular resolution synchrotron powder diffraction as a consequence of the narrower instrumental function ($\Delta\lambda/\lambda \cong 10^{-4}$).** Since peaks are narrower, peak positions can be estimated more accurately, peak overlapping diminishes and a more complete intensity data set can be extracted. Consequently, for crystal structure with large unit cells, the availability of high-angular resolution powder patterns to reduce accidental peak overlapping is a necessity. Traditionally, presence of systematic peak overlapping has been considered a serious handicap. However, as recently demonstrated, direct methods can still be applied (Rius *et al.*, 1999). Recent examples are provided by the crystal structure solutions of a large-cavity zeolite with wide pore windows and potential interest as an oil refining catalyst (Corma *et al.*, 2002) and of the blue pigment of the catalan-andorran romanesc paintings 'aerinite' (Rius *et al.*, 2004). Paradoxically, since inorganic compounds with systematic overlap are less affected by accidental overlap, these compounds should be solved more easily from high resolution synchrotron powder data. Finally, there are also other reciprocal-space structure solution methods that would benefit from high resolution data e.g. a strategy specially thought for zeolites consisting on the iterative Fourier refinement of starting random phases followed by a cluster analysis of the resulting topologies (Grosse-Kunstleve *et al.*, 1999).

The intensity extraction procedures so far mentioned are based on a unique powder pattern. However, since powder patterns are easy to measure, it is tempting to combine the information of multiple patterns to reduce the incidence of peak overlap. In textured samples, for example, different patterns at different sample orientations can be collected and the pole function for a few well separated reflections calculated. With this information the orientation distribution function for each reflection can be found, so that a set of linear equations can be established, in which the integrated intensities of the texture-free sample are the unknowns. Zeolite UTD-1 has been solved in this way (Wessels *et al.*, 1999; Baerlocher *et al.*, 2004). This method is very elegant, although it has a number of practical difficulties that are still being worked out, e.g. how to induce texture. A different experimental approach that can be applied to samples showing anisotropic expansion is the measurement of patterns at different temperatures (Shankland *et al.*, 1997). Peak positions in the respective patterns are slightly different, so that for large enough variations the intensity correlations between neighbouring peaks can be diminished. Anisotropic expansion occurs quite often in organic materials (Wright, 2004) but not only in them. Indeed, it has been observed that many microporous solids show an anisotropic thermal behaviour (Woodcock *et al.*, 1999; Lightfoot *et al.*, 2001; Villaescusa *et al.*, 2001). Therefore, extraction of the intensities of overlapped peaks can be greatly improved by combining XRD patterns obtained at different temperatures. To afford this type of studies a similar set-up than that described for *in situ* catalytic experiments can be used. This procedure should be particularly relevant for the structural elucidation of complex microporous solids that can not be synthesised as single or even microcrystals. A variant of such methods, especially thought for the study of protein powders and based on soaking the protein powder into a suitable solution containing metal atoms, is being actively investigated nowadays. Depending on the metal quantity taken up by the powder, the unit cell dimensions and hence the peak position in the pattern will change (Von Dreele, 2001). With the proposed beamline, new ways of exploiting the information contained in multiple high resolution powder diffraction patterns could be carried out, e.g. the collection of several high resolution patterns at different pressures. Other sources of progress to be explored will be the use of isomorphous replacement and anomalous diffraction. In Spain, there are groups with proved experience in the field that can profit from these new capabilities.

In pharmaceutical research, the processes of crystallisation of polymorph phases to grow single-crystals of good quality, are made following equilibrium states. Therefore the phases that normally develop to microcrystals or to crystals of enough quality for laboratory diffractometers, are usually the stable ones, while the non-stable are rarely obtained even as microcrystals. In such cases the structures must be solved by powder diffraction techniques (Giovanni *et al.*, 2000). In principle, direct methods, in combination with intensities extracted from powder data, can be also applied to pharmaceuticals and other organic compounds. For this type of compounds, however, there is a serious risk of radiation damage. To reduce the radiation dose, it is advisable to move the capillary along the capillary axis during the measurement. If the amount of peak overlapping is still too severe, the second structure solution strategy working with the complete pattern and refining structural parameters can be applied. Also here high resolution powder data are advantageous: Firstly, for indexing purposes and for finding out the correct space group; secondly, for a more detailed knowledge of the high-angle portion of the pattern. While data in the low 2θ region are very sensitive to variations in molecular orientations and in torsion angles, molecular shift variations

predominantly affect data in the high 2θ region. Therefore, the accurate knowledge of this high angle region is of paramount importance for the effectiveness and reliability of the figure-of-merit. The most commonly employed figure-of-merit measures the discrepancy between observed and calculated powder patterns (Markvadsen *et al.*, 2002). If the high-angle portion is not informative enough, the residual can not discriminate between correct and incorrect solutions. Initially, organic structures were solved from powder data with Patterson search methods which require large rigid fragments (Rius & Miravittles, 1988; Rius *et al.*, 1990; Cirujeda *et al.*, 1995; Ochando *et al.*, 1997; Sañé *et al.*, 1997). At present, most commonly used cost functions use the residual between observed and calculated patterns or, alternatively, the correlated integrated intensity function. Molecular geometries are normally described in terms of the known interatomic distances, angles and torsion angles, so that besides the orientation and positioning of the fragments, the only variables are a reduced number of torsion angles. The most widely used Monte Carlo method for optimising the cost function is simulated annealing (Hsu *et al.*, 2001). There are some computer programs implementing these procedures [Johnston *et al.* (2002), Harris *et al.* (1998), Putz *et al.* (1999), Favre-Nicolin *et al.* (2002), Falcione *et al.* (1999) ...]. Obviously, the success of this second strategy highly depends on the available software. Unlike the direct methods case, there are practically no groups in Spain currently working in the development of such software, so that this would be a good opportunity for the Spanish community to fill this gap.

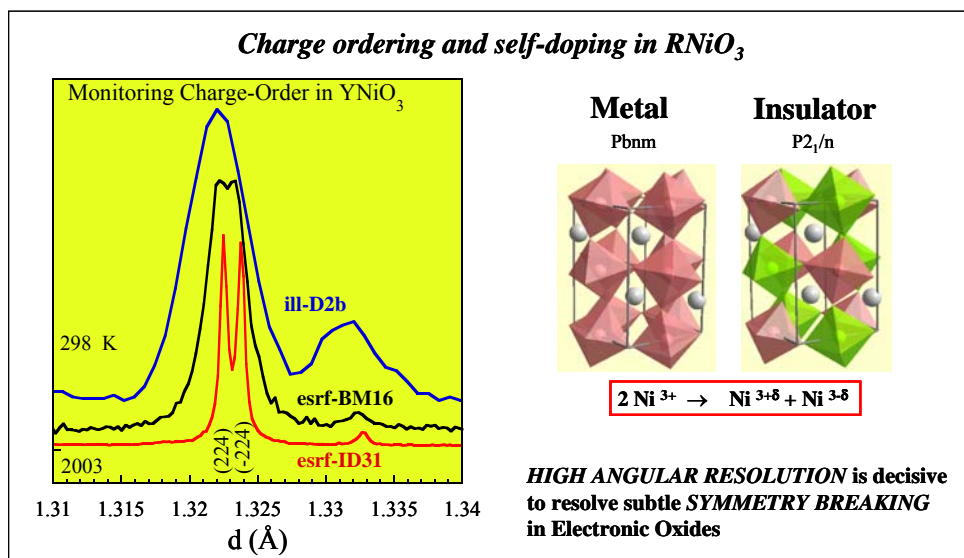
2.1.2. Structural studies on correlated materials showing phase transitions

One area of key fundamental and technological importance is the wide variety of extraordinary phenomena that occur in transition metal oxides. Some well-known examples are colossal and giant magneto-resistance, high-temperature superconductivity, charge/orbital ordering (orbital physics), polarized conduction, giant thermoelectric response, polar distortions and ferroelectricity, magnetoelectric effects, etc. The research activities in this growing area include the provision of materials for magnetoelectric, spintronic, superconducting, ferroelectric, dielectric, magnetic, thermoelectric, fuel cell and battery applications. A detailed knowledge of the structural aspects is essential to determine the microscopic mechanisms governing the unusual behavior and new phenomena of this important group of inorganic materials. Their enormous interest for functional applications is based in a gigantic response to small variations of physical and chemical parameters, and to an extraordinary effective coupling between the electric, magnetic and lattice degrees of freedom in the system. In many cases they undergo a range of order-disorder transitions commonly associated with changes in charge, spin, orbital or lattice degrees of freedom, and very often leading to diffuse scattering, which contains a wealth of information about interaction between atoms. Characterization of new orders usually requires diffraction data of extremely high quality and use of high-angular resolution synchrotron X-ray diffractometers is decisive and indispensable.

One of the common basic structural features of the “ordered phases” is the development of weak commensurate or incommensurate peaks and/or the appearance of subtle changes in symmetry the symmetry of the material. Very illustrative examples are (i) the charge and orbital order transitions in magnetoresistive R-A-Mn-O manganites (Radaelli *et al.*, 1997; García-Muñoz *et al.*, 2001; Daoud-Aladine *et al.*, 2002; Frontera *et al.*, 2003), rutenates, vanadates, cobaltites (Suard *et al.*, 2000), cuprates (Abbamonte *et al.*, 2004) etc.; (ii) the Verwey-type transitions in iron oxides (Fe_3O_4 , $\text{R}\text{BaFe}_2\text{O}_x$, Wright *et al.*, 2001; Karen *et al.*, 2001; García *et al.*, 2004) and nickel perovskites (RNiO_3 , Alonso *et al.*, 1999; Gracia-Muñoz *et al.*, 2004); (iii) the spin-state order and spin-state transitions in cobaltites ($\text{R}\text{BaCo}_2\text{O}_3$, Suard *et al.*, 2000; Frontera *et al.*, 2000) or (iv) the magnetoelastically induced lattice modulation in some magnetic ferroelectric RMO_3 oxides ($\text{M}=\text{Mn,Fe}, \dots$, Kimura *et al.*, 2003; Van Aken *et al.*, 2004; Lottermoser *et al.*, 2004), which produces gigantic magnetoelectric and magnetocapacitance effects. Often these phenomena are accompanied by the development of very weak superstructure Bragg reflections in the X-ray diffraction patterns that are the signature of very small (but vital for their physical response) structural distortions: Jahn-Teller distortions, orbital order, martensitic-type coherent atomic displacements, Peierls-like transitions, polar distortions, etc. In these interesting materials the intensity of the superstructure reflections associated to the emerging structural distortions is very often 10^3 times lesser than the strongest main peaks. It is therefore of great importance to combine high count rates with very good signal to noise ratio.

In virtue of the electronic origin (electron-electron and electron-lattice interactions) of many of the relevant phase transitions, a proper determination of the key structural details/changes requires high ($\Delta d/d \sim 10^{-3}$) or very high ($\Delta d/d \sim 10^{-4}$) resolution. High angular resolution is of great importance to (i)

resolve the overlap of lines, (ii) detect subtle symmetry breaking, and (iii) perform microstructural and peak broadening studies. The following examples illustrate how very high angular resolution is decisive to detect the existence of charge-order below the metal-insulator transition of $R\text{NiO}_3$ compounds. Charge disproportionation in this family produces a subtle symmetry change from orthorhombic to monoclinic. During more than 10 years these compounds were satisfactorily refined as orthorhombic and the existence of charge-order was ignored. The monoclinic splitting (\equiv charge-order) became apparent with the enhanced resolution of the new ID31 at ESRF.



Last years research on functional oxides has shown the emergence of competing multi-scale phenomena in a rich variety of materials. This is the case of nanoscopic, mesoscopic and macroscopic phase segregation in metal oxides with strong tendency to adopt inhomogeneous charge and orbital distributions (such as charge-order and stripe formation in perovskite oxides: high- T_c superconductors, manganates, etc; Tranquada *et al.*, 1977; Uehara *et al.*, 1999; Fernández-Díaz *et al.*, 1999). The spontaneous phase separation in colossal magnetoresistive perovskites is a good example of the advantages of the high-angular resolution synchrotron powder diffraction (Llobet *et al.*, 2000). Reorganization of the periodic orbital occupancy (transitions between different orbitally ordered states) has been proved to be very common in transition metal compounds with electron-lattice coupling. Phase separation is behind unusually large change of resistivity observed in certain materials following application of magnetic field. By varying external physical parameters such as the temperature, pressure, magnetic or electrical fields, a definite structural phase can transform into a multiphase coexistence sharing the average structure but each phase presenting different distortions, superstructures or modulations (Kajimoto *et al.*, 1999; Ritter *et al.*, 2000; Algarabel *et al.*, 2002). Such multiphase segregation (coexistence of metallic-insulating phases, ferroelectric-paraelectric, or superconducting-insulating) is the key for the understanding of the overall properties of the material. The structural differences between the emerging phases and their cell parameters can be very subtle and cannot be distinguished using conventional X-ray diffraction techniques. Thus, one of the advantages of powder diffraction using synchrotron radiation is the enhanced angular resolution, e.g. FWHM (2θ) $\sim 0.005^\circ$ in the old BM16 of the ESRF and FWHM (2θ) $\sim 0.001^\circ$ in the new ID31 diffractometer.

Incommensurate phases are often associated with phase transitions and the study of microscopic mechanisms driving transitions is of great interest. The most important feature in diffraction patterns of incommensurate structures is the appearance of satellite reflections at positions determined by the wavevector q . These reflections contain the most important information on the distortion or modulation characteristics of the incommensurate phase and, in general, they are very weak, being several orders of magnitude below the intensity of main reflections associated with the average structure. Thus, it is evident that a careful measurement of the intensities of satellite reflections is necessary to determine fine details of the structural model or to follow their behaviour depending on external conditions (p , T). However, weakness of satellites increases the experimental difficulties when high order satellites are involved

and/or when they are close to strong main reflections. Some examples of active research fields in the topic of incommensurate structures are:

1/ the phase transitions in the Aurivillius compounds: Subject of these investigations are a series of Bi-based compounds with regular intergrowth of Bi_2O_2 blocks and perovskite blocks, exhibiting a ferroelectric-paraelectric transition. For some compounds like $\text{SrBi}_2\text{Nb}_2\text{O}_9$ or $\text{SrBi}_2\text{Ta}_2\text{O}_9$, the nature of this transition has remained unclear and a two-step transition via an intermediate phase has been proposed. The existence of this new phase has been recently suggested based on a Rietveld analysis of powder neutron diffraction data at different temperatures, distinguishing between a centered and a non-centered space group (Snedden et al., 2003). The phase transition and the possible anomalies can also be studied following the temperature dependence of different types of reflections: superstructure reflections vanishing at the well known high T phase and reflections containing the structural information on the distortion associated with the expected intermediate phase.

2/ Soliton regime in the incommensurate structure of RbZnCl_4 : Although this compound is not a transition metal oxide it has been included here because it exhibits an incommensurate phase followed by a commensurate modulated lock-in phase. Characteristic of this transition is the appearance of a region close to the lock-in phase where high order satellites are developed as a feature of the so called soliton regime (Aramburu, 1997). The low intensity and the partial overlap of satellites and/or main reflections make the combination of synchrotron radiation and high-resolution diffractometry the ideal choice for observing this region and understanding this regime.

Although many oxides can be obtained as single crystals, it is important to recall that their characteristic distortions represent in many cases a serious obstacle for obtaining high-quality (untwinned) single crystals. Consequently, many studies are carried out on powders or micro-crystals because good single crystals are not easily available. Compared with single crystal, powder diffraction presents some advantages in the case of materials that intrinsically grow presenting twinned multidomains. Another obstacle for studying single crystals comes from the intrinsic difficulties of sample preparation: typical examples are the transition metal oxides with unusual valences or forced structures (certain families of titanates, nickelates, pyrochlores, vanadates, complex cuprate phases, etc.). In conclusion, a dedicated high-intensity, high-resolution synchrotron X-ray powder diffraction beamline is a crucial instrumentation for the characterization of this very wide group of inorganic materials. An optimized compromise between high count rates and high resolution in a wavelength window 0.5-1.3 Å is required. In addition, the use of the instrument for resonant scattering, microstructural studies (peak shape analysis), residual strain and dynamic/*in situ* measurements must be also feasible.

2.1.3. Microstructural studies

These experiments take advantage of the high-angular (or also wave-vector q) resolution (10^{-4} Å) which allows (i.) obtaining intrinsic peak profiles (domain sizes and shapes, strains, etc.) without any deconvolution operations, (ii.) measuring very small peak shifts and (iii.) also determining the diffuse scattering close to the Bragg peak positions.

Phase transitions of layered compounds exhibiting polytypism

Comparatively little is known about the structural phase transitions of layered compounds exhibiting polytypism. Typical characteristics of these compounds is a diffuse intensity distribution in the form of one-dimensional streaks containing the information about the stacking sequences of generally well ordered layers. The lattice parameters corresponding to the axis perpendicular to the layers can be very large, easily reaching up to values of 60-100 Å. The situation is further aggravated by the fact that the Bragg reflections defining these directions are superimposed on the diffuse intensities or streaks. The use of single crystal samples for all these experimental cases allows extracting the maximum of information but, under certain conditions (synthetic difficulties, breakdown of the crystal associated to the phase transition) only powder samples are available. For the investigation of these compounds the high intensity and excellent resolution makes synchrotron radiation the ideal method of choice. One example is the study of the polytypic disorder exhibit by ternary sulphides. The synchrotron measurements of both Bragg reflections and one-dimensional diffuse intensities in $(\text{LaS})_{1.18}\text{VS}_2$ allowed to determine the structures of two coexisting polytypic modifications and to characterize the stacking disorder of their respective layers (Friese et al., 1997). Similar synchrotron experiments are planned for other ternary sulphides (RbInS_2 , KGaS_2 etc.)

'In situ' studies of growth of nanoparticles in confined spaces

For nanotechnology purposes, the use of well organised porous materials is becoming an useful way of controlling the size and shape of the final nanoparticles. Metal nanoparticles are useful for intelligent-drug delivery, cancer treatment, sensors, magnetic devices, microelectronic, optoelectronic applications, etc. (Caruso, 2003; Mornet et al., 2004; Yang et al., 2003). Some recent examples of nanocasting in molecular sieves are the growth of Pt nanowires (Fukuoka et al., 2003) or magnetic Co nanoparticles (Gross et al., 2003) inside of ordered mesoporous solids. A recent Spanish publication of formation of a continuous metal synthesised inside of pure silica zeolite ITQ-7 was given by Ichimura et al. (2002). Also, microporous zeolites have been used as templates of the smallest single-walled carbon nanotube synthesised up to now (Wang et al., 2000; Tang et al., 2003). These carbon nanotubes have shown impressive properties such as superconductivity, ion conductivity and unusual optic properties. The number of microporous structures with different pore apertures can be applied to control the diameter of the resulting nanotubes. At this beamline, *in situ* XRD techniques could provide relevant microstructural information from the analysis of the diffraction peak shapes, like the evolution of the grain size, the grain-size distribution and the micro-strain. Due to the smaller instrumental broadening at synchrotrons, sample-broadening effects can be already detected in particles with sizes even larger than 0.4 μm . For laboratory equipment with the highest resolution, the limit is 0.1 μm .

In Spain there are some groups with the necessary know-how for carrying out this kind of experiments, but it is expected that this will be a growing area based on the National Strategic Program on Nanoscience and Nanotechnology, recently presented by the Spanish Ministry of Education and Science.

Disordered Phases in molecular alloys

The better understanding of the mechanisms that govern the miscibility in solid state help to design new molecular materials with specific applications: the molecular alloys. Molecular alloys offer opportunities as Phase Change Materials (MAPCM) in fields like the energy storage and the thermal protection among others (Tamarit et al., 1997). Orientationally disordered crystals, also known as plastic crystals, are molecular materials where within the rotator, high-temperature phase, molecular reorientations take place with the molecules having their centers-of-mass sitting on crystal lattice points. Recent interest in these materials stems from the fact that these rotator phase crystals, when cooled down at moderate rates, may reach an orientational glassy state in which rotations are frozen and thus exhibit static orientational disorder. Transitions between these two states involve a genuine, glass-transition and therefore this offers the possibility of studying glassy phenomena on long-range-ordered systems, which by their very nature are simpler than structural glasses.

2.2. Experiments using the high flux of the powder diffraction station

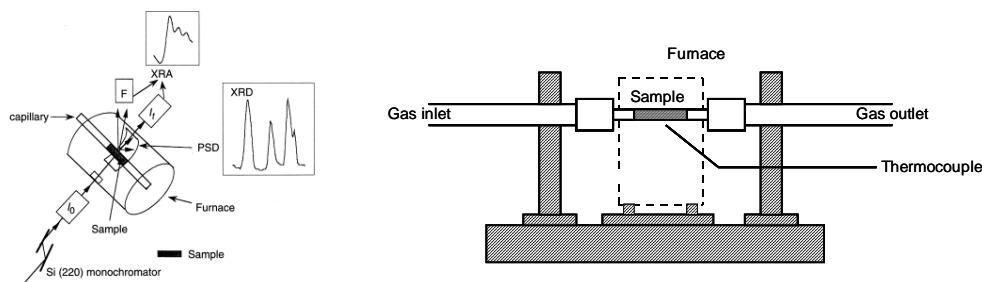
In most cases, the experiments described in this section take advantage besides of the high-angular resolution, of the high density of photon flux that allows the detailed characterisation of small amounts of sample included in a capillary by X-ray powder diffraction (typical volume is close to 1mm^3).

2.2.1. *In situ* diffraction studies of catalysts under operating conditions

The combination of *in situ* powder diffraction (ISPD) with high-flux synchrotron radiation sources has important applications in materials science. Powder diffraction (PD) is for example particularly well suited for the investigation of the structure of catalysts under reaction conditions. Indeed, high-temperature PD measurements under controlled environmental conditions provide information about phase transformations and the existence of metastable phases, which could be the active species in the catalytic processes. The coupling of *in situ* techniques (powder diffraction and absorption spectroscopies such as IR, UV-vis, photoluminescence, etc) and the analysis of the products will give a complete picture of the catalytic processes by providing information of the macrokinetic, microkinetic and active sites. Two examples of this methodology were employed in the study of Cu-supported catalysts for DeNox [Shannon et al. (1996)] and also, Cu/ZnO catalysts were studied during the methanol steam reforming process [Günter et al. (2001)]. In both reactions the correlation between final activity and selectivity with the nature of the active species were unambiguously established. Due to their importance such combined techniques surpass the academic interest, and also industries could be motivated to apply this type of studies. Particularly, petrochemistry industries that perform selective oxidation reactions of light hydrocarbons could be sensitive to this technology, since these processes use transition metal oxides or

polyoxometallate catalysts at high temperature and reductive (hydrocarbons) or oxidative (air or oxygen) conditions. Under these conditions it is usually unknown which is the active phase responsible for the hydrocarbon conversion.

Typical temperatures for *in situ* reaction studies are comprised between 300–600 °C and pressures from atmospheric to 50 bars. ISPD experiments require relatively fast acquisition times (s to min), a considerable penetration depth of the radiation, especially when using metal-walled capillaries and for high-absorbing materials, and also wavelength tuneability for allowing the separation of the active sites of the various metals with anomalous diffraction experiments. Use of capillaries for this kind of experiments is advantageous since it reduces the inhomogeneity problems and allows the possibility of gas flowing through the solid at high pressures, similar to those employed in industry (e.g. 50 bars). The subsequent analysis of the outgoing gas provides valuable information about the hydrocarbon transformations occurring inside the capillary (macrokinetic). Use of quartz capillaries also permits to apply additional spectroscopic techniques, like UV-vis, photoluminescence or Raman spectroscopies, which give information about both organic and inorganic species, allowing to complete the whole picture of the catalytic process, starting from the nature of the active species under operating conditions, going then to the intermediate states formed in the course of reaction (photoluminescence and Raman spectroscopies) and finally giving information about the total conversion and selectivity of the overall catalytic processes (mass spectroscopy, GC, etc). The experimental set-up for this type of experiments is schematised in the figure below .



Schematic experimental set-up for an in-situ X-Ray diffraction cell with the possibility of applying a second spectroscopic technique during the course of catalytic experiments.

It would be highly valuable if the high-resolution powder diffraction station could provide this type of instrumentation to the users. If this were possible, a large number of groups and industries working in catalysis would be motivated to apply for beam time at ALBA instead of other synchrotrons, since as far as we know, this is not offered by any light source facility in the world.

Exactly the same set-up can be employed for tracking the crystallisation of solids under hydrothermal conditions. Zeolites, germanates and metal-phosphonates, which are porous solids widely employed for different industrial applications, are generally obtained under hydrothermal conditions, i.e., in aqueous media at temperature above the boiling point of water and pressures higher than the atmospheric, requiring the use of autoclaves as reaction vessels.

Then, crystallisation studies of these materials must be done by quenching the system at different crystallisation times, being submitted the collected solids for *ex situ* characterisation (mainly Powder diffraction techniques). The main problem of this general approach is that very often crystallisation of the microporous solids occurs in minutes and therefore no kinetic data can be obtained by using *ex situ* techniques. This limitation can be overcome by employing high-flux X-ray sources in combination with fast acquisition detectors. This allows to obtain real time Powder diffraction patterns under crystallisation conditions and the subsequent analysis of the kinetics of crystallisation. When this is combined with a second spectroscopic technique also the incorporation of heteroatoms or organic moieties can be followed under *in situ* conditions [Sankar et al. (1995)].

2.2.2. Kinetic studies of chemical reactions and dynamic studies of phase transitions in organics

Since organic compounds are weaker scatterers than inorganic ones, the kinetic studies of reactions and the dynamic studies of phase transitions are only affordable using synchrotron radiation, especially for real time measurements. On the other hand, the coexistence of two phases near the transition point or reaction point causes an increment of the overlapping which hinders its evaluation. The higher resolution of synchrotron radiation should facilitate the correct indexing of the reflections and the obtention of the cell parameters for the different phases. In addition, the variation of the parameters with temperature permits the calculation of the thermal expansion tensor and, consequently, of the deformation directions in each phase transition. Finally structure models can be built from bibliographic data and energy minimisation calculations for the different observed forms carried out. These structure models can be refined by the Rietveld method using the synchrotron data.

The research groups in pharmaceutical products also share a common interest with other groups working with phase diagrams (especially for molecular compounds) to study the phase changes (polymorphism). A better understanding of the mechanisms that govern the miscibility in solid state help to design new materials with specific applications: the molecular alloys. The properties of these new materials may be modulated as a function of their composition. Molecular alloys offer opportunities as Phase Change Materials (MAPCM) in fields like the energy storage and the thermal protection among others (Tamarit et al., 1997). The knowledge of the mechanisms of formation and the conditions of stability is indispensable. From the fundamental point of view the problem is not trivial if we keep in mind that the different mixed buildings are made of a common basic entity, the molecule. In the final materials conformational, substitution or position disorder may coexist, being, at the end, a polymorphism problem associated to the isomorphism (Mondieig et al., 2004; Ventolà et al., 2002; Rajabalee et al., 2002). These experiments would require an oven for capillaries and flat sample holders and a cryostat system. The data collection with an efficient position-sensitive detector to follow fast phase transitions or relatively quick reactions would be necessary.

2.2.3. Quantitative diffractometry (non-conventional conditions and minor amounts)

Knowledge of the crystalline phase/mineralogical composition of a given material is vital to understand their performances. X-ray powder diffractometry is the best suited and easy-to-use technique to determine the phase composition. When all phases present in the sample have been identified and when their crystal structures are known, then powder diffraction can be coupled to the Rietveld method and the resulting quantitative method becomes standardless (in the absence of amorphous content) (Hill, 1987). Nowadays, this methodology is starting to be applied not only to crystalline laboratory mixtures but to complex industrial materials such as cements, alloys, ceramics, minerals, slags, etc. Laboratory X-ray Powder Diffraction is the most available (and cheap) technique for quantitative phase analysis and the final goal is to implement it routinely. However, laboratory data may contain systematic errors such as strong preferred orientation, 2θ -dependent optical aberrations, microabsorption and severe peak overlapping of the different phases. Furthermore, the small mean penetration depth ($\sim 20\text{-}40\ \mu\text{m}$ for $\text{CuK}\alpha$ and samples with medium and heavy elements) in reflection geometry may lead to poor particle statistic. Hence, it is necessary to validate the quantitative analysis from laboratory data with High-angular Resolution Synchrotron Powder Diffraction. Rotating capillary geometry (transmission) avoids preferred orientation. High energy X-rays minimise microabsorption and guarantee good particle statistic as a larger amount of sample is tested in wide capillaries. High resolution data also minimise the overlapping (detection of traces) and parallel synchrotron X-rays geometry, with an analyser crystal in the diffracted beam, do not show optical aberrations. Thus, high resolution powder diffraction is being used to *validate the quantitative phase analysis* of industrial materials. Moreover, it is used to *determine the phase assemblage under relevant industrial conditions* (temperature, pressure, gases, etc.). Here, due to the complex sample environments, laboratory powder data are not reliable. An example of this is provided by the belite Portland cements (de la Torre et al., 2001; 2002; 2003).

In spite of its universal use in contemporary construction, Ordinary Portland Cement (OPC) is one of the most environmentally contentious materials. For every tone of cement produced, 60-130 kg of fuel and an additional 110 kWh of electricity are used, and 0.83 tones of carbon dioxide are directly emitted from the kiln into the atmosphere. Because of the effect of this CO_2 as greenhouse gas, cement chemists and technologists are making great efforts to find ways to reduce the environmental impact of the cement-

production process. The main components in OPC are: alite Ca_3SiO_5 60%; belite Ca_2SiO_4 15%; ferrite $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ 10%; aluminate $\text{Ca}_3\text{Al}_2\text{O}_6$ 10 wt%; and minor constituents. The formation of the main component in OPC, alite, requires a temperature in the kiln of 1450 °C. However, belite Portland cements [with phases assemblage close to: belite 60%; alite 20%; aluminate 10%, and ferrite $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ 10 wt%] would reduce heat requirement as it is possible to prepare it at 1350°C. Importantly, CO_2 emissions may be lowered up to a 20%. Moreover, belite cements are expected to lead to more durable buildings as the hydration reactions give a less basic pH. However, belite is harder which requires more energy at the cement mills and it reacts slowly with water and thus strength development at early stages is affected. Recently, the reactivity of belite cements is been increased by adding alkalis which stabilizes high-temperature more-reactive belite polymorphs and by quenching which decreases the crystal sizes. *In situ* diffraction studies of belite Portland cements will invariably require the use of high-angular resolution synchrotron powder diffraction as the experiments must be carried out at high temperatures (~1350 °C) in specially confined environments as the samples contains ~20% of liquid phase.

Quantitative phase analysis can also play an important role in studies such as: i. *In situ* solid-state reactions and phase transitions of ceramics and cementitious materials at temperatures ranging from ambient to 1400 °C (Castellote *et al.*, 2002; Rodríguez *et al.*, 2002; DeAza *et al.*, 2002; Guirado *et al.*, 1999); ii. *In situ* monitoring of the reactions taking place in metal-cement interfaces submitted to accelerated corrosion by applying electric fields (Castellote *et al.*, 2002); iii. Characterisation of ancient ceramics and paintings (Cultural Heritage) (De Aza *et al.*, 2004; Pradell *et al.*, 2004; Rius *et al.*, 2004). For studies i. and ii., special ancillary is needed such as furnaces or unusual containers and sampleholders. The experiments related to phase transitions or ceramics sintering require a furnace that can reach temperatures up to 1500 °C. Two recent high temperature studies showing the viability of what is proposed are O'Connor *et al.*, 1997; Yashima *et al.*, 2002). For the corrosion studies the possibility of placing a reaction cell with the appropriate wiring should be feasible in the high-pressure experimental set-up.

Notice that not only the quantitative diffraction methods based on Rietveld refinements work better with high resolution data. Since the intensities of many individual reflections are accessible now, alternative methods working with the intensities of the resolved reflections can be also applied e.g. the standardless X-ray diffraction method for the quantitative analysis of multiphase mixtures (Rius *et al.*, 1987). This method uses the compositional fluctuations present in several samples to derive the calibration constants of the phases without prior knowledge of their respective crystal structures. It can be used for example to find the unknown calibration constants of clay minerals in ceramic raw materials. Methods based on individual intensities are also useful when not all phases in the sample have been identified.

Sometimes, the difficulty is simply caused by the limited amount of available sample. This situation is often encountered when analysing fragments of pieces of art, forensic materials or solid pollutants (Gómez *et al.*, 2003), e.g. the fine fractions of airborne dust particles for which long collection times are required. In comparison with a less brilliant source, the higher flux of the beam enables to work with smaller sample volumes ($<1\text{mm}^3$) without sacrificing the accuracy of the analysis. This means that the duration of the measuring period can be shortened and, consequently, the representativity of the analytical result increased.

2.2.4. Residual Stress Measurements

Residual stresses (RS) are one of the causes of failures in structural components. It has been reported that failures due to stress corrosion, fatigue and corrosion-fatigue have been triggered, in most cases, by the presence of tensile RS (Elices *et al.*, 1983; Webster *et al.*, 1997). RS are self-equilibrating internal stresses existing in a free body which has no external forces or constraints acting on its boundary. These stresses may be generated in the fabrication process, in additional heat treatments or just during the mechanical loading of a component in use (Noyan *et al.*, 1987). So, they are not “visible”, only their consequences are observed and they are often ignored in the design or quality control of a component. This is the reason why RS need to be carefully measured, especially in components designed for high-risk applications. The non-destructive measurements of RS are based on X-ray (Ruiz *et al.*, 2003) or neutron diffraction (Pyzalla, 2000). In this method, the change in the interplanar lattice spacing with respect to the “stress-free” reference value is employed to calculate the strain, whence the stress is derived. Soft X-ray radiation allows the assessment of surface RS in engineering materials (due to low penetration) while neutron or

hard X-rays are to be employed to measure RS inside an engineering material or component. It is obvious that this beamline is not the best choice for in depth studies. However, for surface RS determination the proposed beamline is competitive, since the high photon density of flux not only reduces the acquisition time in surface RS determinations when compared to laboratory diffractometers but also permits the use of small entrance slits and, consequently, to achieve a high lateral resolution. In contrast, the applications to in-depth studies are very limited. Since typical penetration depths for 25 keV photons are in the order of 2mm in Al and 0.1mm in Fe, strain scanning inside the material could only be carried out in low-Z metal alloys, by defining a gauge volume by means of fine entrance and exit slits (up to 50-100 μm high). Finally, to determine the diffraction elastic constants, a stress rig to apply mechanical load while measuring the residual strain would be necessary. Ideally, the load capacity should be around the 100 kN and it should be designed not to interfere with the beam path.

2.3. Experiments using the microfocusing capability

2.3.1. Microcrystal diffraction studies at ambient and non-ambient conditions

Pharmaceutical and organic chemistry.

Most research groups interested in doing microcrystal diffraction experiments are developing compounds with pharmaceutical interest, and in many cases these groups work for the pharmaceutical industry. Since a great number of pharmaceutical compounds are organic compounds, the research groups dealing with organic products have the same structural characterisation problems than the previous ones, and hence the corresponding experiments will be handled, hereafter, in a unified way. As the knowledge on the activity mechanisms of chemical compounds with therapeutic properties progresses, e.g. which functional groups are the really active ones, the role of each adopted conformation, the dependence of the activity on each specific polymorph form,..., it becomes more and more important to determine precisely the structure of the new obtained drugs, either as original products, either as derivatives with already known pharmacological applications (Schlunzen *et al.*, 2003). There are a large variety of experiments involving pharmaceutical and organic compounds that require X-ray diffraction techniques. Some of them have been already discussed in previously. Some additional ones that require synchrotron radiation are:

1/ Accurate determination of crystal structures and absolute configuration: structure-activity and chirality-activity relationships.

If the quality of the single-crystal is not good enough to use classic X-ray sources (laboratory diffractometers) because of its size or its crystallinity. This is the typical case that can be solved with microfocussed synchrotron radiation onto a single microcrystal (Shankland *et al.*, 2000), since the increased flux greatly improves the peak-to-background ratio. The structural characterization is the first and decisive step on which all subsequent studies of the different phases will rely. Another aspect of special interest in the field of pharmacological products is the ab initio determination of the absolute configuration of the compound from microcrystals or crystals of low quality. In this connection, it is noteworthy to mention the study of the macrolide azitromicine system by means of microcrystal diffraction (Montejo-Bernardo *et al.*, 2003). This product is an antibiotic that displays, at least, three different crystalline forms (the anhydrous, the monohydrate and the dihydrate one), and that also gives various pseudo-polymorphs with different solvent (mainly alcohols). Some of them could not be solved by standard single-crystal techniques, and the determination of the absolute configuration of the chiral compound was only possible using microcrystals or crystals of low quality.

2/ Determination and topological study of the electron density.

It constitutes another important aspect that will grow exponentially in the coming years. The interest of this study lies in the information on reactivity that it gives. It requires high-resolution data, so that use of synchrotron radiation is necessary.

In order to improve the quality of the measured data or to study the structure evolution with temperature, the microfocus station should be provided with a gas stream cooler (25-30K) and a heater system.

Microporous materials

Microporous materials are of great interest because of their diverse applications in catalysis, absorption, separation, ion exchange, hydrogen and methane storage. Zeolites and aluminophosphates are well known

examples (Bekkm et al., 1991), but more recently two kind of new microporous compounds have been discovered. One of them are called “zeotypes”: germanates (Cascales et al., 1999), borates (Hensen et al., 1994), etc., and the other are organo-inorganic polymers, also called metal-organic frameworks (MOFs) (Rosi et al., 2003; Snejko et al., 2002). So far the most important hit was to know the topology of the frameworks. In the last years, however, the exploration of the microporous space has received a lot of attention in order to determine the accurate position of the guest species to explain the interaction among the framework and the internal molecules and ions. Thus, the guests can play the role of template species during the synthesis, selectively sorbed species, or cations balancing the charge. To carry out these studies single crystals are normally needed.

The data collected with microcrystals are of enough quality to be used for the structural characterisation of twinned microcrystals (Jensen et al., 2002) and for the location of metal dopants by means of detailed electronic density maps (Norberg et al., 2000). Two recent examples of the structural elucidation of zeolites employing microfocusing X-ray diffraction techniques reported by Spanish groups are the SSZ-23 [Cambor et al., (1998)] and ITQ-13 [Corma et al. (2003)]. The SSZ-23 was solved by collecting X-ray diffraction data on a microcrystal of 20 x 20 x 5 microns and consists in the unique example of a microporous solids possessing a bi-directional channels system formed by 7 and 9 members ring pores. The structural elucidation of ITQ-13 zeolite was carried out on a crystal with dimensions of 40 x 30 x 20 microns. Its structure exhibits three sets of intercrossed medium-pore channels; a 9-ring channel that runs parallel to the crystallographic a axis, a 10-ring channel system parallel to the c axis, and another 10-ring set of channels parallel to the b axis. The employ of microfocusing X-ray diffraction techniques allowed to exactly locate the occluded organic cations and fluoride anions, providing highly valuable information to understand the role of these species during the crystallization of ITQ-13 zeolites. Two additional examples of extremely small microcrystals solved by microfocusing diffraction are the microporous material ZP-4 ($K_2ZnPO_4 \cdot 0.8H_2O$) (Broach et al., 1999) and the K_4Li_4 compound ($32\mu m^3$) (Celestian et al., 2003). Use of synchrotron radiation in resonant diffraction experiments to increase the contrast between neighboring elements (Warner et al., 1991) and hence to resolve the multiple occupancy of cations in extra-framework sites (Wilkinson et al., 1992) is a powerful but still not so usual technique.

Organometallics

Problems related to scattering power/crystal size can be found when trying to determine the crystal structures of organometallic compounds, or also in the field of coordination and bioorganic chemistry, in particular in connection with the applications of metall complexes to homogeneous and heterogeneous catalysis. This corresponds to situations where the crystal growth is notoriously hindered, so that only small-sized crystals are obtained ($<1000\mu m^3$) with insufficient scattering power to be measured using conventional X-ray sources.

Study of polycrystals

In spite of the continuous progress in powder diffraction, it is obvious that peak overlap will always remain a limitation of the technique. This is the price to be paid for its experimental simplicity. Recently the viability of a new method for studying polycrystals has been shown that exploits the high flux of the beam, the microfocusing capability and the high instrumental resolution of two-dimensional detectors (Schmidt *et al.*, 2003; Vaughan *et al.*, 2004). A polycrystal may be regarded as a collection of microcrystals with fixed mutual orientations. The experiment illustrating its viability consisted on irradiating a volume of $250 \times 250 \times 180 \mu m^3$ of a sintered plate of pure Al_2O_3 (average grain diameter of $20 \mu m$ and mosaic spread of the reflections of the order of 0.2°) with a homogeneous X-ray beam of 50 keV. The oscillation images were recorded over a ϕ range of 90° in 0.1° steps at a κ -diffractometer (instrumental resolution is 0.4° in 2θ on the CCD detector face). Using the known metric as constraint and by means of sophisticated filtering and sorting procedure based on various reasonable assumptions, 57 grains could be indexed. From these, 17 grains were associated with 510 reflections. The R1 value (Sheldrick, 1997) for the merged set of 17 grains was 0.034. This result is promising and could represent a significant advance in the structure solution from polycrystals. The main limitation of the method is anticipated to be spot overlap that can become very important for very large unit cells or for a large number of grains in the gauge volume. In principle, there is no problem to handle mixtures of two (previously) indexed phases or to treat undetachable mixtures of crystalline and amorphous materials. According to the authors, this procedure can handle a maximum of 1500 grains. Aspects such as homogeneity of the beam or also the detector efficiency and resolution will become more relevant for smaller gauge volumes. This is a new and promising technique with multiple applications e.g. for

studying both the atomic structure and the microstructure of the individual grains as a function of their relative orientation, that should be feasible on the microfocus station.

2.3.2. Powder diffraction studies at high pressures

Pressure is a powerful thermodynamical variable that allows the direct control of the interatomic distances and hence of the interaction potentials. Consequently, the results from experiments done under pressure (state equations, elastic constants, Grüneisen parameters...) are very decisive and demanding on the electronic structure calculations. These measurements are also important for understanding the effect of the interaction potentials on physical phenomena like superconductivity, colossal magnetoresistance, metal-insulator transitions, etc. From a more practical standpoint, only pressure (combined with temperature) generates the appropriate thermodynamical conditions for the synthesis of technologically interesting ultrahard, superconducting or magnetoresistive materials, among others, or for the study of materials in the inner Earth. According to this, Spanish groups working in high-pressure plan to carry out experiments on the following scientific topics:

1/ Structure, equation of state and structural phase diagrams (polymorphism) of materials with technological interest as test for *ab-initio* models and as aid in the prediction of the effects of chemical substitutions (hydrostatic v.s. 'chemical' pressure). The materials will belong to large gap semiconductors (Pellicer-Porres *et al.*, 2002; 2004), dielectrics for solid-state lasers or scintillators (Aguado *et al.*, 2003), transition metal oxides (Le Godec *et al.*, 2000; García-Muñoz *et al.*, 2004), ultrahard materials (Le Godec *et al.*, 2000; Amulele *et al.*, 2004), metals (Errandonea *et al.*, 2003) and layered structures with magneto-optical properties (Rodríguez *et al.*, 2001; 2003).

2/ *In situ* study on the synthesis of HT_c superconductors, CMR perovskites and ultrahard materials (García Jaca *et al.*, 2000).

3/ Study of the structure, equation of state and elastic moduli of natural materials under similar thermodynamical conditions as found in nature (Earth crust and in the inner of other planets) (Santamaria-Perez *et al.*, 2004; Errandonea *et al.*, 2002).

4/ Kinetics of phase transitions and pressure induced reactions (Grzechnik *et al.*, 2003).

5/ In connection with the high-pressure structural studies it is worth pointing out the existence in Spain of several very prestigious groups of *ab-initio* theorists that collaborate regularly with experimental groups (prediction of equations of state and phase transitions in very complex (Mujica *et al.*, 2003).

High-pressure diffraction experiments employing heatable diamond anvil cells are very demanding and require the use of microfocused synchrotron radiation in combination with a laser heating system. Since this is not a dedicated high-pressure beamline, an indication of the maximum attainable pressure values is in order. To achieve pressures higher than 100GPa (1000kbar) a focus size smaller than $10 \times 10 \mu\text{m}^2$ is required (ideally $5 \times 5 \mu\text{m}^2$). Since the focus of the proposed beamline is $20 \times 20 \mu\text{m}^2$ (it can be further reduced with slits), the value of 100 GPa can be considered a realistic upper limit. On the other hand the purpose of the diffraction experiment is to measure reflections as high as possible in 2θ . The two main limiting factors are the angular opening of the anvil cell and the energy of the incident photons. The accessible 2θ values for usual diamond anvil cells are 30° for pressures up to 20 GPa and 20° for the megabar region. By assuming a photon energy of 25 keV and an angular opening of 50° , patterns down to 1.15Å resolution should be measurable, so that many of the planned experiments would be feasible. In this connection it is interesting to mention that 50% of the asked Spanish high-pressure users said that their measurements would be mostly below 20GPa. For these particular experiments a resolution close to 1Å will be easily attainable.

For illustrative purposes some examples of experiments that should be feasible are provided. Two of them could be only performed at synchrotron sources with microfocused beams (APS, ESRF, Spring-8).

Example 1: Structures of non-metallic catalysts for diamond synthesis under extreme conditions.

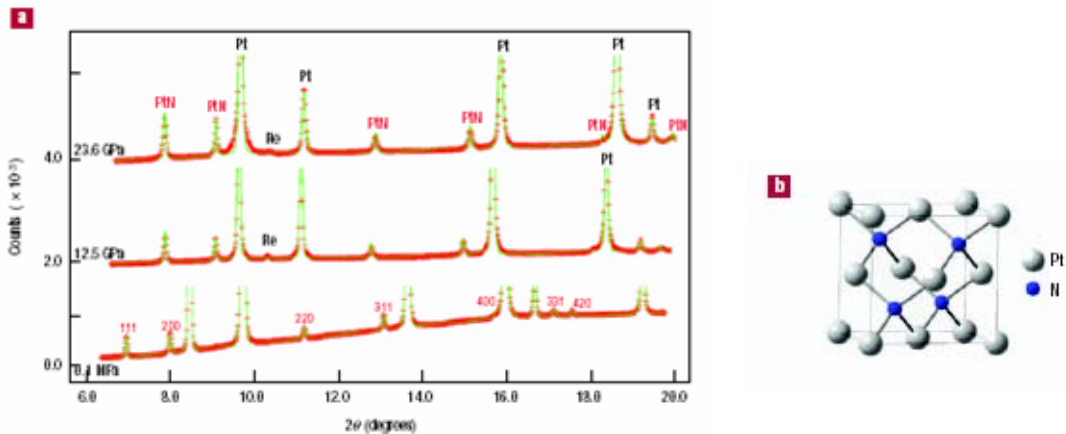
The direct graphite-diamond transformation occurs above 12 GPa and 1873 K. The standard use of metallic catalysts lowers the required pressures and temperatures, the major drawback being that the diamond synthesis can only be performed under highly reducing conditions. However, non-metallic catalysts offer a possibility of diamond formation in a wide range of redox conditions. The efficiency of these non-metallic catalysts depends on whether (and how) their activity is influenced by their chemical and structural instabilities.

The precise knowledge of phase diagrams, structural phase transitions, decomposition, and chemical reactions of the catalysts provides fundamental insight into the growth of diamonds under natural and laboratory conditions and shall improve their synthesis at lower pressures and temperatures.

A new non-quenchable hexagonal polymorph ($P6_3/mcm$, $Z = 2$) of Li_2CO_3 occurring above 10 GPa has been solved from synchrotron angle-dispersive powder X-ray diffraction (Grzechnik *et al.*, 2003). The sample of the carbonate was annealed at 10 GPa using a YAG laser to obtain better quality powder X-ray patterns for structural analysis. The carbonate groups are in a staggered configuration along the c axis in this new modification. Two columns of face-shared distorted octahedra around the Li atoms are linked through octahedral edges. This study has shown that upon compression up to about 25 GPa at room temperature lithium carbonate (at atmospheric conditions $C2/c$ and $Z = 4$) does not transform to any crystal structures derived from the hexagonal aristotype ($P6_3/mmc$, $Z = 2$) of other alkali metal carbonates Me_2CO_3 (Me: Na, K, Rb, Cs) at ambient conditions. Synchrotron investigations on other carbonates, which exhibit modulated structures at atmospheric pressure, are planned in the future.

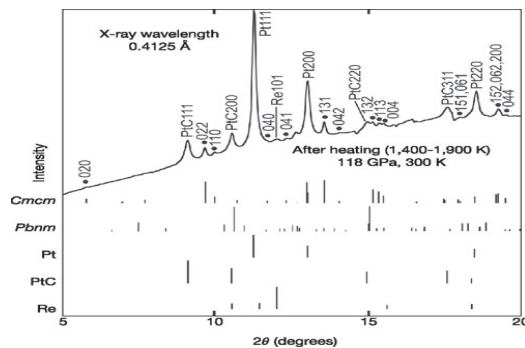
Example 2: Synthesis of platinum nitride, the first ultrahard compound made of a precious metal.

This study performed by E. Gregoryanz *et al.* (2004) is an example of what can be done at the proposed beamline. PtN was synthesised in a diamond anvil cell at 50 GPa and 2000K. It is metastable in ambient conditions and its bulk modulus is 372 GPa. The experiment was performed with a microfocused beam ($10 \mu\text{m} \times 10 \mu\text{m}$, $\lambda = 0.3738 \text{ \AA}$). The crystal structure belongs to the sphalerite structure type with $a = 4.8041 \text{ \AA}$. The figures below show PtN powder diffraction patterns at different pressures, and the PtN unit cell. Data up to $2\theta = 18.60^\circ$ could be measured on a cell with a 50° wide window at 25 keV.



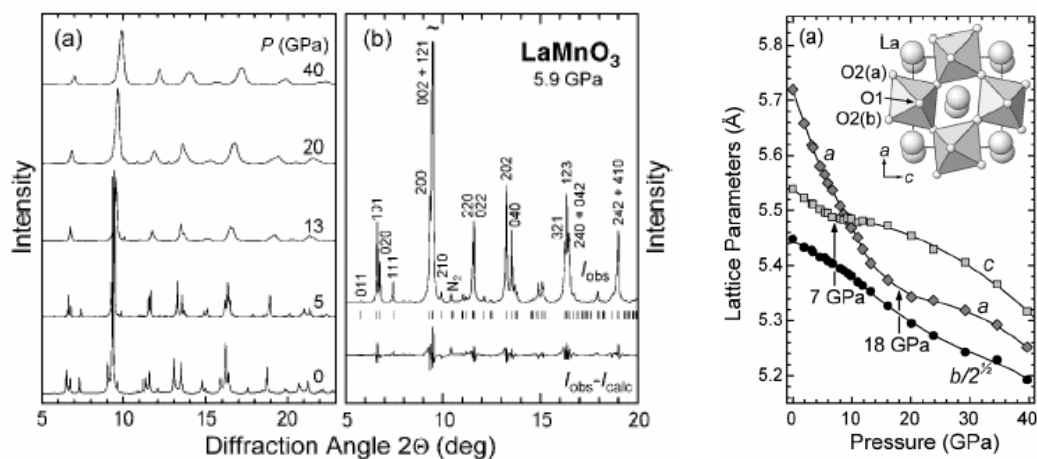
Example 3: A new post-perovskite phase of MgSiO_3 formed at mantle-core interphase conditions.

Recently, it has been shown (Oganov *et al.*, 2004) that MgSiO_3 , one of the major constituents of the Earth mantle with perovskite structure type, transforms into a layered structure type (CaIrO₃-type with $Cmcm$ symmetry) when pressure and temperature conditions similar to those found at the mantle-core interphase are reached (D'' sheet). The elastic properties of this new post-perovskite phase and its stability range explain many properties of the D'' sheet as for example its seismic anisotropy and the shear-waves discontinuity. The figure below reproduces the diffraction pattern of this new phase measured at 118 GPa (this value is found 150 Km deep).



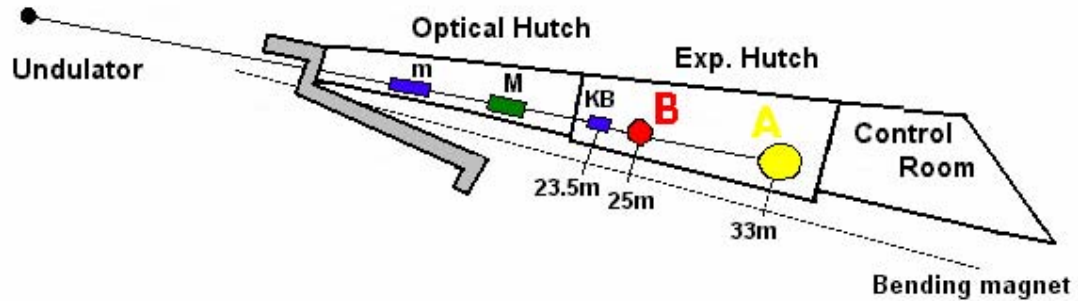
Example 4: Pressure-Induced Quenching of the Jahn-Teller Distortion and Insulator-to-Metal Transition in LaMnO₃.

Perovskite-type manganites have recently received renewed interest after the observation of a “colossal” negative magneto-resistance (CMR) effect in La_{1-x}Ca_xMnO₃. The complex electronic properties of doped manganites originate from an intimate interplay of lattice and electronic degrees of freedom in which the Jahn-Teller distortion and the Mn-O-Mn tilting angle play an important role. However, recent structural studies on LaMnO₃ by neutron diffraction (Pinsard-Gaubert *et al.*, 2001), synchrotron X-ray diffraction, optical spectroscopies, and transport measurements (Loa *et al.*, 2001) under pressures up to 40 GPa report controversial results. Either the progressive reduction of the cooperative Jahn-Teller (JT) distortion leading to suppression of the JT effect above 18 GPa (Loa *et al.*, 2001) or the stability of the JT distortion under pressure (Pinsard-Gaubert *et al.*, 2001) was found from high-pressure diffraction studies. This controversy, which often occurs in the realm of high-pressure diffraction, illustrates the adequacy of carrying out precise structural studies on manganites and related oxides to elucidate the role of the JT distortion and tilting on their electrical and magnetic properties as well as the occurrence of pressure-induced Insulator-to-Metal transition. Dedicated beamline facilities providing suitable powder diffraction patterns are necessary for structural analysis and, particularly, determining variations of internal atomic coordinates. High-pressure experiments around 50 GPa will also provide direct ways of exploring high-spin to low-spin phenomena in transition metal oxides (Pasternak *et al.*, 1999).



3. Beamline description

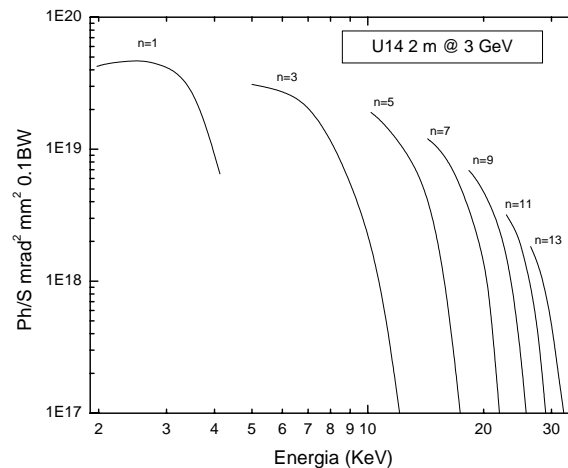
The basic components of the beamline are the source, the optical hutch containing the primary mirror, the monochromator and the pair of focusing mirrors, the experimental hutch with two stations and the control room placed at the end. The figure shows the schematic layout of the beamline and includes the foreseen location of the two end stations in the experimental hutch. The disposition of the elements in the figure is approximate, since the calculations to define the exact positions are not finished.



Schematic layout of the proposed beamline. m: primary mirror, M: double crystal monochromator, KB: removable Kirkpatrick-Baez focusing mirrors, A: high-resolution powder diffraction station, B: microfocus station.

3.1. Insertion device and beam requirements

To satisfy the scientific purposes of the beamline, the source has to deliver X-ray photons within the range 5 to 25 KeV. The insertion device that better fits our needs is the minigap undulator (in-vacuum) U14 (2 m long, $\lambda = 14$ mm, gap = 5 mm, $k = 1.0 - 2.0$). The figure below illustrates the brilliance of the 2m U14 undulator at 3 GeV as a function of the energy.



It can be seen that the energy of the first harmonic ranges from 1.9 to 4.2 KeV, while the third to eleventh harmonics provide a calculated continuous spectrum ranging from 5 to 25 KeV (to 30keV for the 13th

harmonic). The calculated on axis peak brilliance is 4×10^{19} ph/sec/mrad²/mm²/0.1%bw at 3KeV. For an in-vacuum undulator installed in a 4m straight section of Alba the photon beam dimensions and divergences (FWHM) are approximately:

$$\begin{aligned} \Sigma_x &= 323 \mu\text{m} & \Sigma_z &= 15 \mu\text{m} \\ \Sigma'_x &= 98 \mu\text{rad} & \Sigma'_z &= 22 \mu\text{rad} \end{aligned}$$

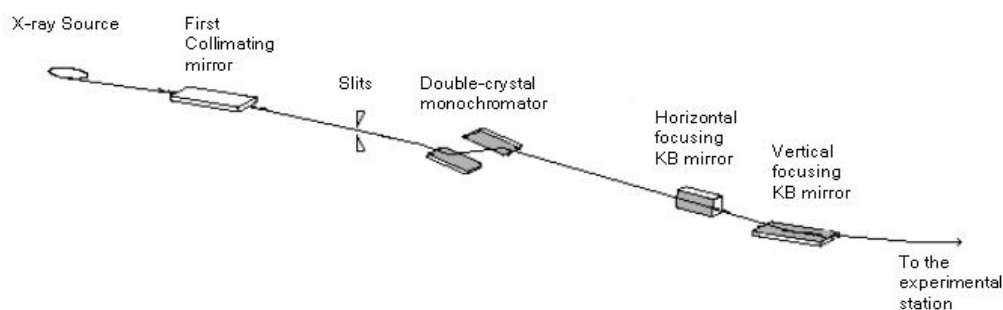
The minimum beam requirements are:

Brilliance	2.8×10^{19} ph/sec/mrad ² /mm ² /0.1%bw at 6KeV
Photon energy	5 - 25 keV tuneable for resonant and anomalous studies
Energy stability	0.1 eV
Bandpass ($\Delta E/E$)	approx. 2×10^{-4}
Beam size at powder sample	between 3.0 - 5.0 mm (H) and between 0.5 - 1.0 mm (V)
Flux at powder sample	at 10 keV at 10^{-4} bandpass: approx. 8.2×10^{13} (ph/sec/mm ² /250mA) at 25KeV “ “ “ : approx. 10^{13} “
Position stability	$\pm 2 \mu\text{m}$ for the $20 \mu\text{m} \times 20 \mu\text{m}$ microfocus.

3.2 Optics

The principal components of the optics are:

- a primary metal Pt (or Rh)-coated mirror (water-cooled) to eliminate the high order harmonics as well as the heat load on the monochromator.
- a water-cooled double-crystal monochromator of spectroscopic quality with flat crystals that allows tuning the wavelength between 5 to 30KeV. Two sets of crystals must be provided, Si(111) for $E < 20$ keV and Si(311) for $E > 20$ keV.
- a pair of Kirkpatrick-Baez mirrors to focus the incident beam for the microcrystal diffraction experiments to an area of $20 \times 20 \mu\text{m}^2$. For high-angular resolution powder diffractometry these mirrors will be removed from the beam path to produce a parallel incident beam on the powder sample. The photon flux (ph/sec/250 mA) through the $20 \times 20 \mu\text{m}^2$ area should be on the order of 1.7×10^{14} at 10keV and 1.3×10^{13} at 25 keV.



Scheme of optical hutch showing beam path with inserted KB mirrors

3.3. Experimental stations

As can be seen in the previous figure showing the beamline layout, the beamline consists of two experimental stations: Station A dedicated to powder diffraction, and the microfocus station B devoted to microcrystal and high-pressure diffraction. To ensure the best conditions for both microcrystal and high-pressure diffraction studies, two independent set-ups are required that are mounted on a common stage. This allows the two set-ups to be put alternatively in the beam path by simply shifting the stage in the direction normal to the beam. This is one easy way to encompass the requirements imposed by the small sphere of coincidence in microcrystal experiments (5 microns) and the large load carrying capacity needed in high-pressure experiments when the Edimburgh-Paris cell is used (approx. 50N).

3.3.1. Station A (powder diffraction)

The dedicated high-angular resolution powder diffractometer is based on three heavy-duty high precision rotary tables mounted and aligned coaxially on a base plate with levelling jacks and locking screws. From the tables, via coaxial shafts that lay horizontal, are supported one outer plate (\varnothing approx. 1.8m) carrying the multi-analiser/detector set-up, one middle plate holding the position-sensitive detector (\varnothing approx. 1.5m) and one inner plate (\varnothing approx. 0.75m) with the sample support. The outer and inner table must have a resolution of 0.0001° (0.36 arcsec) with an accuracy of 2 arcsec. The reproducibility of the middle table carrying the wide-angle solid-state detector can be relaxed to 5 arcsec. The wide-angle detector should span approximately 60° of 2θ and will be placed at the negative part of 2θ .

The finality of the diffractometer is firstly to collect high resolution powder diffraction pattern (instrumental FWHM in the order of $0.003^\circ 2\theta$ for 15 KeV) in a reasonable time (2 hours) and secondly to enable the fast measurement (ms) of powder pattern portions in order to follow fast phase transitions without losing too much angular resolution. The critical point is the selection of the most appropriate position-sensitive detector. The open geometry of the powder diffractometer allows mounting various sample supports on the inner plate e.g. an additional Eulerian arc, or placing different sample environments on a lifting table that can be easily moved to the diffractometer on a rail system.

Sample supports:

1. Holder for rotating capillaries with optional movement along the capillary axis. (The possibility of this movement must be considered in the final design of the diffractometer).
2. Flat-plate sample holder with spinner.
3. Eulerian arc/cradle

Sample environments:

1. Liquid-nitrogen cryostream. Temperature range: 80K-350K (for example Oxford Cryosystems). Temperature stability 0.1K.
2. Hot air stream heater for capillaries. Temperature stability 0.1K, operating in the temperature range: 300-1250K.
3. Reaction cell for *in situ* studies and capillary samples.
4. Diode laser furnace for capillaries (Temperature range up to 1500 °C). Those experiments related to phase transitions or ceramics sintering require a furnace that could reach temperatures up to 1500 °C. Although some models are commercially available they are not off the shelf pieces of equipment. In practice in-house development and modifications around a commercial model would be needed to adapt it to the particular specifications of the beamline.
5. Continuous liquid-helium flow cryostat with spinning capillary and flat-plate adaptors (rotating sample rod). Temperature range: 2.2K-350K (for example, Optistat-type (Janis),...). Temperature stability 0.1K. With cryogenic transfer line and pumping systems (gas flow and rotary pumps).
6. Stress rig to apply mechanical load while measuring the residual strain, to determine the diffraction elastic constants. Ideally, the load capacity should be around 100kN and it should be designed not to interfere with the beam path.

3.3.2. Station B (microfocus)

Microcrystal diffraction:

For microcrystal diffraction measurements a full four-axis instrument for flexible sample orientation and complete data collection to high theta values at very small crystal-to-detector distances has been selected. The sphere of confusion should not exceed the 5 microns in order to be in accordance with the focus size of $20 \times 20 \mu\text{m}^2$. The selection of the Kappa-geometry permits easy access to the sample, so that the attachment of accessories is greatly simplified. The rest of most relevant technical specifications of the goniometer should be at least:

Sample to detector distance (DX): 35 – 250 mm with 2000 mm/min positioning speed.

Kappa axis: -175° to $+175^\circ$ (chi equivalent -99.85° to $+99.85^\circ$)

2-Theta axis: -90° to $+135^\circ$

Omega axis: -210° to 210°

Phi axis: $n \times 360^\circ$

Positioning speeds; positioning accuracy :

DX : 2-Theta, Omega and Kappa: from $0.0009^\circ/\text{min}$ to $2000^\circ/\text{min}$; 0.01°

Phi: from $0.0012^\circ/\text{min}$ to $3000^\circ/\text{min}$; 0.015° with 0.0003° resolution.

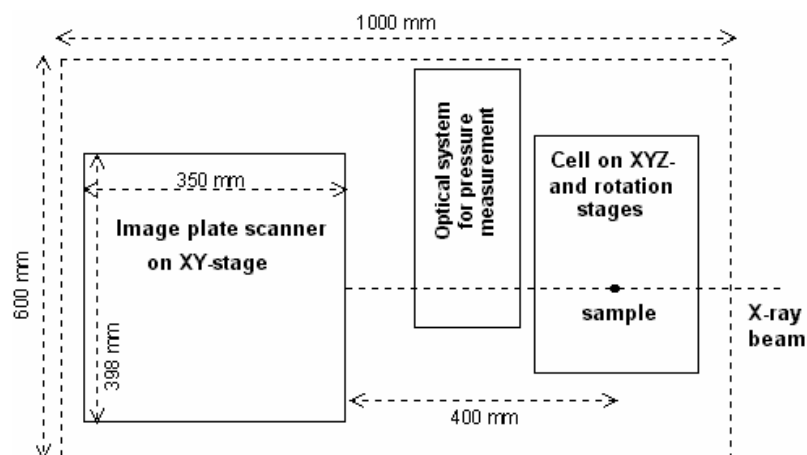
Reproducibility: better than 0.005°

Sphere of intersection of axes: less than 5 microns.

If possible, a commercial goniometer is to be preferred. The goniometer is mounted at one end of the translation stage. The specifications of the CCD detector to be used in combination with this goniometer are described in 3.4.2. The equipment must be supplied with the following usual additional requirements /accessories: Fully collision hardware and software, completely integrated data collection strategy software, alignment tools, goniometer heads, test crystal, cryo-vial with magnetic base adaptation to Kappa-goniometer, server computer to control goniometer and detector system and crystal mounting and alignment in an appropriate interface, video microscope with magnification, etc. The low temperature system must be low-consuming (<0.5 l/hr), highly stable (± 0.1 K) and with a temperature range from 75 K to 300 K.

High-pressure diffraction:

For high-pressure diffraction measurements the instrumental set-up basically consists of a tower formed by a rotation stage to increase the grain statistics, and, on top of it, one z-stage and one x-y stage. These two last stages help to position the sample in the beam. This high-pressure equipment will be mainly used in combination with an image-plate detector that also requires an x-y stage. The minimum detector requirements are described in 3.4.2. A schematic layout showing the distribution of the high-pressure components is given below.



The whole set-up is mounted at one end of the translation stage which shift normal to the beam (to allow easy exchange with the Kappa-goniometer) and vertical. The minimum lateral shift is approximately 25cm plus the shift needed by the Kappa-goniometer.

One important part of the high-pressure set-up is the pressure measurement by an optical system. Basic accessories are a diamond anvil cell, a microscope and a hole drilling.

3.4. Detectors

3.4.1. For powder diffraction experiments

High-angular resolution mode:

A minimum of a 5- channel analyser/scintillator detection set-up producing a nominal offset of 2° (for Si(111) and Ge(111)) for each detector in a single 2θ -scan. The multi-analyser/scintillator set-up should be designed for photon energies between 5-30 KeV. The Bragg conditions for all 5 crystals is fulfilled by rotating in a 1:2 ratio the crystals support and the detectors bank, so that in principle no individual adjustment of the crystals is needed when changing the wavelength. A similar set-up is already working in the powder diffractometer at the Materials Science Beamline (SLS). The detectors are NaI(Tl) scintillator crystals optically coupled to photomultipliers followed by a preamplifier.

Fast data collection mode:

There exist the wide-angle solid-state position-sensitive gas-filled detector RAPID2 developed at Daresbury that spans 60° of 2θ with a high count rate and giving 5 pixels over a peak with FWHM of 0.06° . It is ideal in many ways for studying reaction kinetics but not for high resolution studies. One alternative is the solid-state position-sensitive microstrip detector developed at the SLS that has many advantages over gas detectors, especially with respect to the spatial resolution. An improved version of it will be soon in operation. In general, the ideal detector should have good spatial resolution ($< 0.004^\circ 2\theta$) not requiring demagnification optics, a very high count-rate allowing real time experiments (read-out time < 1 ms) and high energy resolution. A new robust solid-state position-sensitive detector called DIFFEX that is expected to fulfil the above criteria, is currently designed and built at Daresbury. It is to be expected that when the powder diffraction station will be commissioned, this new solid-state detector will be commercially available.

3.4.2. For microcrystal diffraction experiments

For microcrystal diffraction a high-performance, high-resolution CCD X-ray detector is needed. Although the technology of these type of detectors is continually evolving, some relevant minimum specifications that the wanted CCD detector must satisfy, are:

Sensitive surface: diameter larger or equal than 165 mm
Resolution: better or equal than 4096 x 4096 pixels
Pixel size (on the screen): less or equal than 40 μm
Read-out time (binned): faster or equal than 2.5 – 0.5 seconds

3.4.3. For high-pressure diffraction experiments

For high-pressure diffraction an Image Plate Scanner is needed. The most relevant technical specifications are:

Plate diameter: approx. 345 mm
Usable detector area: greater or equal than 93.480 mm^2
Pixel size: less or equal than 100 μm x 100 μm
Sensitivity: higher or equal than 1 X-ray photon per ADC-unit at 8 keV
Intrinsic noise: less than 1-2 photon equivalents
Minimum dynamic range: between 0 and 131000 (17 bits)
Scan time: faster or equal than 108 seconds

At present the mar345 Image Plate Scanner fulfills the above requirements.

4. Estimated Beamline Costs

	Price (in kEuro)
Source	
Insertion device + front end	900 ± 150 (1)
Beamline & Optics	
Mirrors (primary + KB) and Mechanisms	130 ± 15
Monochromator System	240 ± 20
Other equipment (colled slits, flight tubes, pumps,...)	100 ± 20
Infrastructure	
Hutches + Fluid + Wiring +Safety	350 ± 50 (2)
Experiment	
Station A	
High angular resolution powder diffractometer (3 coaxial axis)	180
5-analyser/detector bank	50
Wide-angle position-sensitive detector	380
Sample supports and sample environment	84
Continuous He cryostat system	60±10
Stress rig	60
Station B	
Kappa Diffractometer	120
CCD detector	210
L-N ₂ cooling system (common with powder diffraction)	50
Tower (rotation + X-Y + Z-stages) for high-pressure cell	41
Image plate + XY-stage	98
Pressure measurement system + XYZ-stage	37
Basic accessories + diamond anvil cell	25 + 24
Translation stage	40

(1) depending if locally constructed or if bought already mounted

(2) very approximately

5. Users with expertise

Laboratories with expertise in high resolution powder diffraction:

Alonso Alonso, José Antonio	Grupo de síntesis a altas presiones, Dpto. de Síntesis y Estructura de Óxidos CSIC- Instituto de Ciencia de Materiales de Madrid	ja.alonso@icmm.csic.es
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Palacín, María Rosa	Grupo de Química del Estado Sólido (Materiales para baterías), Dpto. de Cristalografía y Química del Estado Sólido CSIC- Instituto de Ciencia de Materiales de Barcelona	rosa.palacin@icmab.es
Pizarro, José Luis Arriortúa, María Isabel	Dpto. de Mineralogía y Petrología Fac. de Ciencia y Tecnología Univ. del País Vasco, UPV / EHU	npppisaj@lg.ehu.es npparmai@lg.ehu.es
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Laboratories with expertise in microcrystal diffraction:

Santiago García Granda	Dpt. de Química-Física Universidad de Oviedo	sgg@fq.uniovi.es
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Miguel Maestro Saavedra	Universidade da Coruña	
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Fernando Rey	CSIC-UPV Instituto de Tecnología Química de Valencia	frey@icmab.es

Laboratories with expertise in high-pressure powder diffraction:

Alfredo Segura Daniel Errandonea	Grupo de Semiconductores y Altas Presiones Dpto. de Física Aplicada Universidad de Valencia	Alfredo.Segura@uv.es daniel.errandonea@uv.es
Fernando Rodríguez	DCITIMAC- Grupo de Propiedades Ópticas de Materiales, Facultad de Ciencias Universidad de Cantabria	rodriguf@unican.es
Emilio Morán	Grupo de Química del Estado Sólido-Lab. complutense de altas presiones Dpto. de Química Inorgánica Universidad Complutense	
Angel Vegas	Grupo de estructuras de óxidos CSIC- Instituto de Física "Rocasolano"	avegas@iqfr.csic.es
Alfonso Muñoz Gonzalez	Dpto. de Física Fundamental II Univ. de La Laguna	

6. Potential users

Groups normally working or familiar with Powder Diffraction:

CSIC-Instituto de Ciencia de Materiales de Madrid: José Luis Martínez, Francisco Javier Palomares
CSIC-Instituto de Ciencia de Materiales de Madrid: Jesús Sanz
CSIC- Instituto de Ciencia de Materiales de Sevilla: M^a Dolores Alba Carranza
CSIC- Instituto "Jaime Almera" de Ciencias de la Tierra: Ignaci Queralt, Feliciano Plana
ESRF: Monica Amboage, Gema Martinez
Univ. de Barcelona: Dra. Lourdes Mestres Dpto. de Química Inorgánica
Univ. de Barcelona: Dpto. de Física Fundamental: Aleaciones Metálicas: Prof. Luis Mañosa
Univ. de Barcelona - Servicios Científico-Técnicos: Xavier Alcobé, Josep Bassas
Univ. Aut. de Barcelona: Dpto. de Geología, Angel Alvarez, Eugenia Estop, Aureli Alvarez, J.M^a Briansó
Univ. Aut. de Barcelona: Dpto. de Física: Física Aplicada I: J.Rodríguez-Viejo, M.T. Claveguera-Mora
Univ. Aut. de Barcelona: Dpto. de Física: Física Aplicada II: M^a Dolors Baró
Univ. Aut. de Barcelona: Dpto. de Química: Química Inorgánica: Josefina Pons
Univ. Aut. de Barcelona: Dpto. de Química: Química Orgánica: Marcial Moreno
Univ. Carlos III de Madrid: Dpto. de Ciencia de Materiales e Ingeniería Metalúrgica: Alejandro Varez.
Univ. Jaume I: Dpto. de Química Inorgánica y Orgánica: Vicente Esteve, M^a Angeles Tena
Univ. Jaume I: Dpto. de Química Inorgánica Medioambiental y Materiales cerámicos: Teófilo Sanfeliu
Univ. de Oviedo: Facultad de Ciencias: Jesús Blanco
Univ. Pol. Catalunya:Facultat de Nautica: Antonio Isalgué
Univ. Pol. Catalunya: Dpt. de Ciència de Materials i Enginyeria Metalúrgica: Prof. Marc Anglada
Univ. Rovira Virgili: Dpto. de Física y Cristalografía de Materiales: Magdalena Aguiló, Francesc Díaz
Univ. Rovira Virgili: Servicios Científico-Técnicos: Francesc Guirado
Univ. de Sevilla-CSIC: Dpto. de Química Inorgánica: Ana Isabel Becerro
Univ. de Valencia:Dpto. de Geología: Jose M^a Amigó, José Luis Ochando
Univ. de Valencia:Dpto. de Física Aplicada: Daniel Errandonea, Domingo Martínez
Univ. de Valencia: Ed. de Investigación. Julio Pellicer

In Spain, there is an important industrial and academic community interested in the engineering applications of the synchrotron radiation, especially in the measurement of RS and texture. Some potential industrial users are the following: Emesa-Trefilería, Renfe, Tecnatom, Izar, Aceralia (grupo Arcelor), Roldán (Acerinox) and Cidaut. Regarding the scientific users, the following groups support the present proposal: Departamento de Ciencia de Materiales (UPM), Departamento de Metalurgia Física (CENIM-CSIC), Departamento de Ciencia de Materiales (Universidad de Oviedo), Departamento de Ingeniería Mecánica y de Materiales (Universidad de Sevilla), Departamento de Ciencias de los Materiales e Ingeniería Metalúrgica (UPC), Departamento de Materiales (CEIT), Departamento de Fisión Nuclear (CIEMAT), Departamento de Propiedades Ópticas, Magnéticas y de Transporte (ICMM-CSIC), Departamento de Cerámica (ICV-CSIC), INASMET, CASA-espacio and some others.

Groups interested in studying Pharmaceuticals/Organics by synchrotron radiation:

CSIC-Inst. de Ciencias de la Tierra, Granada: Grupo de Crecimiento Cristalino: Juan Manuel García Ruíz
CSIC-Inst. Ciencia de Materiales de Barcelona.: Grupo Consolidado de la Generalitat de Catalunya: Elies Molins, Jordi Rius
CSIC-Inst. Química Médica, Madrid: Grupo de José Elguero
CSIC-Inst. Rocasolano: Grupo de Concepción Foces-Foces
Univ. Aut. de Barcelona: Grupo Consolidado de la Generalitat de Catalunya: Joan Francesc Piniella
Univ. de Barcelona: Grupo Consolidado por la Generalitat de Catalunya; Xavier Solans
Univ. de Barcelona: REALM -Eur. Net of molecular Alloys. Coordinator: Miquel Àngel Cuevas Diarte
Univ. de Granada: Grupo de Miguel Quirós
Univ. de Oviedo: Grupo de Excelencia del Principado de Asturias: Santiago Gracia Granda
Univ. Pol. Catalunya: Grupo de transiciones de fase, metaestabilidad y polimorfismo: José Luis Tamarit
Univ. de Sevilla: M^a. Dolores Estrada, M^a. Jesús Diañez
Univ. de Valencia: Grupo de José M^a Amigó, Luis Ochando

All these groups have ongoing research projects and collaborations with pharmaceutical companies and companies of other sectors. There are also numerous research groups in pharmaceutical-organic chemistry or in bio-inorganic chemistry that usually collaborate with Crystallography groups in diffraction experiments. Some of these groups are: José Barluenga, Vicente Gotor and José Manuel Concellón of the University of Oviedo, Pelayo Camps, Virtudes Moreno of the University of Barcelona, M. Carmen Navarro, Autonomous University of Madrid, Dr. Noheda of the Institute of Organic Chemistry of the CSIC (Madrid) or Joaquín Erases of the University of Valencia.

Pharmaceutical companies.

At present the Spanish pharmaceutical companies have no diffraction facilities; therefore they subcontract their crystallographic studies to universities or to CSIC institutes. Their need for diffraction experiments in the future is unquestionable, but it is difficult to predict if they will create their own research teams and hence become direct users of the synchrotron radiation facility, or if they will still continue subcontracting the research to groups at the University or the CSIC. In any case, there will be pharmaceutical samples to be studied at the beamline in the future. The companies that have shown their interest in this beamline are Lab. Dr. Esteve, Almirall, and Group Ferrer in Barcelona, Asturpharma in the Principality of Asturias, Pharmamar in Madrid and Aventis in France (subcontracting research to Spanish groups).

Organometallic and coordination chemistry groups with ongoing projects:

The diffraction studies are carried out by organometallic and coordination chemistry groups mostly in collaboration with crystallography and quantum chemistry/molecular modelling groups. Although at present use of synchrotron facilities by these groups is rather low, the future potential participation of this community in microcrystal synchrotron diffraction is very high. The following list only includes a short number of such groups:

Universidad de Oviedo, José Gimeno, Victor Riera, S. García-Granda; Grupos de la Universidades Gallegas, Casas y Sordo, Castiñeiras, Llamas-Sainz; Grupos de Universidades Andaluzas, Ernesto Carmona, Fernando López-Ortiz, Juan Niclós, Juan Manuel Salas, Miguel Quirós, Enrique Colacio; Grupos de la Universidad de Zaragoza, Luis Oro, Juan Fornies, Fernando Lahoz, Larry Falvello; Grupos de Universidades Catalanas, Oriol Rosell, Jaume Granells, Margarita Crespo, Concepción López, Josefina Pons, Josep Ros, Pilar González, Juan F. Piniella, Elías Molins y Xavier Solans; Grupos de las Universidades de Valencia, Eugenio Coronado, Miguel Julve, Pascual Lahuerta, Joaquín Borrás; Grupos de la Universidad del País Vasco, Pascual Román; Grupos de las Universidades Madrileñas, Esther Delgado, Antonia Mendiola, David Tudela, Carmen Navarro, Isabel Cuadrado, Loreto Ballester, Mercedes Cano; Grupo de la Universidad de Murcia, José Vicente; Grupos de Universidades Canarias como el de Catalina Ruiz-Pérez; Grupos del CSIC, J. Delgado-Martín, Margarita Paneque.

A search for those groups working with topics related to organometallic and coordination chemistry and being interested in microcrystal synchrotron diffraction, gives more than hundred groups, all of them with ongoing research projects.

People with interest in high pressure powder diffraction:

Centro Federal de Investigación en Nutrición y Alimentos (Karlsruhe): Avelina Fernández García
CSIC- Instituto de Agroquímica y Tecnología de los Alimentos de Valencia: Ramón Catalá Moragrega
CSIC-Instituto del Frío: Dpto. de Ingeniería: Pedro Sanz Martínez
CSIC- Instituto de Ciencia de Materiales de Barcelona: José Luis García Muñoz
CSIC- Instituto de Ciencia de Materiales de Madrid: Jose Alonso Alonso
CSIC- Instituto de Ciencia de Materiales de Sevilla: M^a Dolores Alba Carranza
INTA-CSIC: Centro de Astrobiología. Lab. de Geología Planetaria: Olga Prieto Ballesteros
Univ. Aut. de Barcelona: CER Planta Tecnología de Alimentos. Buenaventura Guamis Lopez
Universidad Complutense: Dpto. de Química Física I : Valentín García Baonza, Mercedes Cáceres Alonso
Universidad de "La Laguna": Dpto. Física Fundamental II.: Javier Gonzalez-Platas
Universidad de Oviedo: Dpto. de Química, Física y Analítica: José Manuel Recio Muñiz
Universidad de País Vasco: : Dpto. Física de la Materia Condensada: Gotzon Madariaga Menéndez
Universidad Politécnica de Valencia: : Dpto. Física Aplicada: Francisco Javier Manjón Herrera
Universidad de Valencia: Dpto. de Química Inorgánica: José Antonio Real Cabezas

7. List of scientists wishing to participate in the design and construction of the experimental stations.

The scientist that have expressed their wish to participate, are:

Powder diffraction:	J.Rius F.Rey (expertise in reaction cells) J.L. Jordá X.Turrillas (expertise in high-temperature)
Microcrystal:	F.J. Zúñiga K. Friese S. García Granda
High-pressure:	A. Segura D.Errandonea A.Grzechnik D.Martínez J. Pellicer

The details of the participation will be discussed later.

References

- P.Abbamonte, G.Blumberg, A.Rusydi, A.Gozar, P.G.Evans, T.Siegrist, L.Venema, H.Eisaki, E. D.Isaacs, G.A.Sawatzky, "Crystallization of charge holes in the spin ladder of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ ", *Nature* 431, 1078, 2004.
- F.Aguado, F.Rodríguez, R.Valiente, J.P.Itite, P.Munsch, "Pressure-induced closure of the Jahn-Teller distortion in $\text{Rb}_2\text{CuCl}_4(\text{H}_2\text{O})_2$ ", *High Pressure Research* 23, 181, 2003.
- B.B.Van Aken, T.M.Palstra, "Influence of magnetic on ferroelectric ordering in LuMnO_3 ", *Phys. Rev. B* 69, 134113, 2004.
- P.A.Algarabel, J.M.DeTeresa, B.García-Landa, L.Morellon, M.R.Ibarra, C.Ritter, R.Mahendiran, A.Maignan, M.Hervieu, C.Martin, B.Raveau, A.Kurbakov, V.Trounov, "Field effect on phase segregation in the electron-doped mixed-valence manganites near a structural instability", *Phys. Rev. B.* 65, 104437, 2002.
- J.A.Alonso, J.L.García-Muñoz, M.T.Fernández-Díaz, M.A.G.Aranda, M.J.Martínez-Lope, M.T.Casais, "Charge disproportionation in RNiO_3 perovskites: Simultaneous metal-insulator and structural transition in YNiO_3 ", *Phys. Rev. Lett.* 82, 3871-3874, 1999.
- G.Amulele, M.Maghnani, B.Li, D.Errandonea, Y.Meng, M.Somayazulu, "High-pressure ultrasonic and X-ray studies of SiC composite", *J.of Appl. Phys.* 95, 1086, 2004.
- I.Aramburu, G.Madariaga, D.Grebille, J.M.Perez-Mato, T.Breczewski, "High-Order Diffraction Satellites and Temperature Variation of the Modulation in the Incommensurate Phase of Rb_2ZnCl_4 ", *J. Phys I France*, 7, 371-374, 1997.
- A.H.De Aza, M.A.Rodríguez, J.L.Rodríguez, S.De Aza, P.Pena, P.Convert, T.Hansen, X.Turrillas, "Decomposition of Dolomite Monitored by Neutron Thermodiffraction", *J. Am. Ceram. Soc.*, 85, 881-88, 2002.
- A. H. De Aza, A. G. De La Torre, M. A. G. Aranda, F. J. Valle, S. De Aza, "Rietveld Quantitative Analysis of Buen Retiro Porcelains", *J. Am. Ceram. Soc.*, 87, 449-54, 2004.
- Ch.Baerlocher, L.B.McCusker, S.Prokic, T.Wessels, "Exploiting texture to estimate the relative intensities of overlapping reflections", *Z. Kristallogr.*, 219, issue 12, 2004 (in press).
- H.Van Bekkum, E.M.Flaningen, J.C.Jansen Eds., "Studies in Surface Science and Catalysis", Elsevier. Vol 58, 1991.
- R.W.Broach, R.L.Bedard, S.G.Song, "Synthesis and characterization of ZP-4 ($\text{KZnPO}_4 \cdot 0.8\text{H}_2\text{O}$), a new zincophosphate microporous material: Structure solution from $2.5 \times 3.5 \times 8 \mu\text{m}$ single crystal using a third generation synchrotron X-ray source", *Chem. of Materials*, 11, 2076-2080, 1999.
- M.A.Cambor, M-J.Diaz-Cabanas, J.Perez-Pariente, S.J.Teate, W.Clegg, I.J.Shannon, P.Lightfoot, P.A.Wright, R.E.Morris, "SSZ-23: An odd zeolite with pore openings of seven and nine tetrahedral atoms", *Angew. Chem. Int. Ed.*, 37, 2122-2126, 1998.
- C.Cascales, E.Gutiérrez-Puebla, M.Iglesias, A.Monge, C.Ruiz-Valero, "A Germanium Zeotype Containing Intratunnel Transition Metal Complexes", *Angew. Chem. Int. Ed.*, 38, 1999, 2436-2439, 1999.
- M.Castellote, C.Alonso, C.Andrade, J.Campo, X.Turrillas, "*In situ* hydration of Portland cement monitored by neutron diffraction", *Appl. Phys.* A74, s1224-6, 2002.
- M.Castellote, C.Andrade, C.Alonso, X.Turrillas, Å.Kvick, A.Terry, G.Vaughan, J.Campo, "Synchrotron Radiation Diffraction Study of the Microstructure Changes in Cement Paste due to Accelerated Leaching by Application of Electrical Fields", *J. Am. Ceram. Soc.*, 85, 631-35, 2002.

- A.J.Celestian, J.B.Parise, A.Tripathi, A.Kvick, G.M.Vaughan, “(K₄Li₄)Al₈Ge₈O₃₂·8H₂O: an Li⁺exchanged potassium aluminogermanate with the zeolite gismondine (GIS) topology”, *Acta Cryst. C* 59, 74-76, 2003.
- J.Cirujeda, L.E.Ochando, J.M.Amigó, C.Rovira, J.Rius, J.Veciana, "Structure Determination from Powder Diffraction Data of a Hydrogen-Bonded Molecular Solid with Competing Ferromagnetic and Anti-ferromagnetic Interactions: The (2-(3,4-Dihydroxyphenyl)- α -Nitronyl Nitroxide Radical", *Angew. Chem. Int. Ed.*, 34, 55-57, 1995.
- A.Corma, M.J.Diaz-Cabañas, J.Martinez-Triguero, F.Rey, J.Rius “A large-cavity zeolite with wide pore windows and potential as an oil refining catalyst”, *Nature*, 418(6897), 514-517, 2002.
- A.Corma, M.Puche, F.Rey, G.Sankar, S.J.Teet, "A zeolite structure (ITQ-13) with three sets of medium pore crossing channels formed by 9 and 10-rings", *Angew. Chem. Int. Ed.*, 42, 1156-1159, 2003.
- A.Corma, F. Rey, S.Valencia, J.L.Jordá, J.Rius, "A zeolite with interconnected 8-, 10- and 12-ring pores and its unique catalytic selectivity", *Nature Materials*, 2, 493-497, 2003.
- R. A.Caruso, ‘Nanocasting and nanocoating.’ *Topics Current Chem.*, 226, 91-118, 2003.
- A.Daoud-Aladine, J.Rodríguez-Carvajal, L.Pinsard-Gaudart, M.T.Fernández-Díaz, A.Revcolevschi, “Zener Polaron Ordering in Half-Doped Manganites”, *Phys. Rev. Lett.* 89, 097205, 2002.
- R.B.Von Dreele, “Binding of *N*-acetylglucosamine to chicken egg lysozyme: a powder diffraction study“, *Acta Cryst.*, D57, 1836-1942, 2001.
- M.Elices, G.Maeder, V.Sanchez-Galvez, “Effect of surface residual stress on hydrogen embrittlement of prestressing steels”, *Brit. Corr. J.* 18, 80, 1983.
- D.Errandonea, Y.Meng, D.Häusermann, T.Uchida, “Study of the phase transformations and equation of state of magnesium by synchrotron X-ray diffraction”, *J. Phys.: Condens. Matter* 15, 1277, 2003.
- D.Errandonea, B.Schwager, R.Boehler, M.Ross, "Angle-dispersive diffraction on solid Krypton and Xenon to 50 GPa", *Phys. Rev. B* 65, 214110, 2002.
- D.Errandonea, M.Somayazulu, D.Häusermann and H.K.Mao, "Melting of tantalum at high pressure determined by angle dispersive X-ray diffraction in a double-sided laser-heated diamond-anvil cell", *J. of Physics: Condensed Matter* 15, 7635, 2003.
- M.Falcioni and M.Deem, “A biased Monte Carlo scheme for zeolite structure solution”, *J. Chem. Phys.*, 110, 1754-1766, 1999.
- V.Favre-Nicolin, R.Cerny, “FOX, ‘free objects crystallography’: a modular approach to ab initio structure determination from powder diffraction”, *J.Appl.Cryst.*, 35, 734-735, 2002.
- M.T.Fernández-Díaz, J.L.Martínez, J.M.Alonso, E.Herrero, “Structural, thermal, transport, and magnetic properties of the charge-ordered La_{1/3}Ca_{2/3}MnO₃ oxide”, *Phys. Rev. B* 59, 1277, 1999.
- K.Friese, O.Jarchow, K.Kato, “Die Struktur des fehlgeordneten Kompositkristalls (LaS)_{1.18}VS₂: Eine Betrachtung als Domänenstruktur”, *Z. Kristallogr.* **212**, 648-655, 1997.
- C.Frontera, J. L.García-Muñoz, M.Hervieu, M.A.G.Aranda, C.Ritter, Ll.Mañosa, X.G.Capdevila and A. Calleja, “Charge and Zener polaron order in Bi_{3/4}Sr_{1/4}MnO₃”, *Phys. Rev. B* 68, 0134408, 2003.
- C.Frontera, J.L.García-Muñoz, A.Llobet, M.A.G.Aranda, “Selective Spin-State Switch and Metal-Insulator Transition in GdBaCo₂O_{5.5}”, *Phys. Rev. B* 65, 180405(R), 2002.
- A.Fukuoka, Y.Sakamoto, H.Araki, N.Sugimoto, S.Inagaki, Y.Fukushima, M.Ichikawa, “Template synthesis and catalysis of metal nanowires in mesoporous silicas”, *Studies in Surface Science and Catalysis*, 146, 23-28, 2003.

- J.García and G.Subías, "The Verwey transition-a new perspective", J. Phys.: Condens. Matter 16, R145, 2004.
- J.García-Jaca, X.Turrillas, S.M.Clark, E.Moran, M.A.Alario-Franco, "*In situ* study of the formation and decomposition processes, under high pressure, of an infinite-layer cuprate: Ca_{0.5}Sr_{0.5}CuO₂", Physica C 341, 779, 2000.
- J.L.García-Muñoz, M.Amboage, M.Hanfland, J.A.Alonso, M.J.Martínez-Lope, R.Mortimer, "Pressure-induced Melting of Charge-Order in the Self-doped Mott Insulator YNiO₃", Phys. Rev. B 69, 067405, 2004.
- J.L.García-Muñoz, C.Frontera, M.A.García-Aranda, A.Llobet, C.Ritter, "High temperature charge and orbital ordering in Bi_{1/2}Sr_{1/2}MnO₃", Phys. Rev. B 63, 064415, 2001.
- J.Giovannini, M.-A.Perrin, D.Louer, F.Levellier, "Ab-initio Crystal Structure Determination of Three Pharmaceutical Compounds from X-ray Powder Diffraction Data", EPDIC-7 Meeting. Barcelona. Spain. 2000.
- Y.LeGodec, D.Martínez-García, V.L.Solozhenko, M.Mezouar, G.Syfosse, J.M.Besson, "Compression and thermal expansion of rhombohedral boron nitride at high pressures and temperatures", Journal of Physics and Chemistry of Solids 61, 1935, 2000.
- E.Gomez, T.Sanfelíu, J.Rius, "A standardless X-ray diffraction method for the quantitative analysis of multiphase mixtures. II. Application to non-infinitely thick samples", J. Appl. Cryst. 35, 600-605, 2002.
- E.Gregoryanz, C.Sanloup, M.Somayazulu, J.Badro, G.Fiquet, H.K.Mao, R.J.Hemley, "Synthesis and characterization of a binary noble metal nitride", Nature Materials 3, 294, 2004.
- A.Grzechnik, P.Bouvier, L.Farina, "High-pressure structure of Li₂CO₃", J. Solid State Chem. 173, 13-19, 2003.
- A. F. Gross, M. R. Diehl, K. C. Beverly, E. K. Richman, S. H. Tolbert, "Controlling Magnetic Coupling between Cobalt Nanoparticles through Nanoscale Confinement in Hexagonal Mesoporous Silica", Journal of Physical Chemistry B, 107(23), 5475-5482, 2003.
- R.W.Grosse-Kunstleve, L.B.McCusker, Ch.Baerlocher, "Zeolite structure determination from powder diffraction data: applications of the FOCUS method", J.Appl.Cryst. 32, 536-542, 1999.
- M.M.Guenter, T.Ressler, R.E.Jentoft, B.Bems, "Redox Behavior of Copper Oxide/Zinc Oxide Catalysts in the Steam Reforming of Methanol Studied by *in situ* X-ray Diffraction and Absorption Spectroscopy", Journal of Catalysis, 203(1), 133-149, 2001.
- F.Guirado, S.Galí, S.Chinchón, J.Rius, "Crystal structure solution of hydrated high alumina cement from powder X-ray diffraction data", Angew. Chem. Int. Ed. Engl. 37, 72-75, 1998.
- Y.J.Han, J.M.Kim, G.D.Stucky, "Preparation of Noble Metal Nanowires Using Hexagonal Mesoporous Silica SBA-15", Chem. Mater., 12(8), 2068-2069, 2000.
- K.Harris, R.Johnston, B.Kariuki, "The Genetic Algorithm: Foundations and Applications in Structure Solution from Powder Diffraction Data", Acta Cryst. A54, 632-645, 1998.
- N.J.Hensen, A.K.Cheetham, J.D.Gale, "Theoretical Calculations on Silica Frameworks and their Correlation with Experiment", Chem. Mater. 6, 1647, 1994.
- R.Hill, "Quantitative phase analysis from neutron powder diffraction data using the Rietveld method", J. Appl. Cryst. 20, 467-474, 1987.
- H.P.Hsu, U.H.E.Hansmann, S.C.Lin, "Structure determination of organic molecules from diffraction data by simulated annealing", Phys. Rev. E64, 056707, 2001.

- A.S.Ichimura, J.L.Dye, M.A.Cambor, L.A.Villaescusa, "Toward Inorganic Electrides", *J. Am. Chem. Soc.*, 124(7), 1170-1171, 2002.
- T.R.Jensen, R.G.Hazell, A.N.Christensen, J.C.Hason, "Hydrothermal synthesis of lithium zinc phosphates: Structural investigation of twinned α - $\text{Li}_4\text{Zn}(\text{PO}_4)_2$ and a high temperature polymorph β - $\text{Li}_4\text{Zn}(\text{PO}_4)_2$ ", *J. Solid State Chem.*, 166, 341-351, 2002.
- J.Johnston, W.David, A.Markvardsen, K.Shankland, "A hybrid Monte Carlo method for crystal structure determination from powder diffraction data", *Acta Cryst. A58*, 441-447, 2002.
- R. Kajimoto, H. Yoshizawa, H. Kawano, H. Kuwahara, Y. Tokura, K. Ohoyama, M. Ohashi, "Hole-concentration-induced transformation of the magnetic and orbital structures in $\text{Nd}_{1/2-x}\text{Sr}_x\text{MnO}_3$ ", *Phys. Rev. B*. 60, 9506, 1999.
- P.Karen, P.M.Woodward, J.Linden, T.Vogt, A.Studer, "Verwey transition in mixed-valence $\text{TbBaFe}_2\text{O}_5$: Two attempts to order charges", *Phys. Rev. B* 64, 214405, 2001.
- T.Kimura, T.Goto, H.Shintani, K.Ishizaka, T.Arima, Y.Tokura, "Magnetic control of ferroelectric polarization", *Nature* 426, 55, 2003.
- P.Lightfoot, D.A.Woodcock, M.J.Maple, L.A.Villaescusa, P.A.Wright, "The widespread occurrence of negative thermal expansion in zeolites", *Journal of Materials Chemistry*, 11(1), 212-216, 2001.
- A.Llobet, C.Frontera, J.L.García-Muñoz, C.Ritter, M.A.G.Aranda, "Chemical Heterogeneity in a Single Phase: $\text{Bi}_{0.15}\text{Ca}_{0.85}\text{MnO}_3$ a Case Example of Macroscopic Phase Segregation", *Chem.Mater.* 12, 3648, 2000.
- I.Loa, P.Adler, A.Grzechnik, K.Syassen, U.Schwarz, M.Hanfland, G.Kh.Rozenberg, P.Gorodetsky, P.Pasternak, "Pressure-induced quenching of the Jahn-Teller distortion and insulator-to-metal transition in LaMnO_3 ", *Phys. Rev. Lett.* 87, 125501, 2001.
- T.Lottermoser, T.Lonkai, U.Amann, D.Hohlwein, J.Ihringer, M.Fiebig, "Magnetic phase control by an electric field", *Nature* 430, 541, 2004.
- A.Markvardsen, W.David, K.Shankland, "A maximum-likelihood method for global optimisation-based structure determination from powder diffraction data", *Acta Cryst. A58*, 316-326, 2002.
- D.Mondieig, F.Rajabalee, V.Metivaud, H.A.J.Oonk, M.A.Cuevas-Diarte, "n-Alkane Binary Molecular Alloys", *Chem. Mater.*, 16, 786-798, 2004.
- J.Montejo-Bernardo, S.García-Granda, M.Bayod, L.Llavona, I.Llorente, "X-ray study of the pseudopolymorphism of the azithromycin monohydrate", *Z. Kristallogr.* 218, 703-707, 2003.
- S.Mornet, S.Vasseur, F.Grasset, E.Duguet, "Magnetic nanoparticle design for medical diagnosis and therapy.", *J. Mater. Chem.*, 14, 2161-2175, 2004.
- A.Mujica, A.Rubio, A.Munoz, R.J.Needs, "High-pressure phases of group-IV, III-V, and II-VI compounds", *Reviews of Modern Physics* 75, 863, 2003.
- S.T. Norberg, V.A. Streltson, G.Svensson, J.Albertsson, "Dopant positions in strontium/chromium- and barium-doped KTP, determined with synchrotron X-radiation", *Acta Cryst.*, B56, 980-987, 2000.
- I.C.Noyan, J.B.Cohen, "Residual Stress: Measurement by Diffraction and Interpretation", Springer-Verlag, New York, NY, 1987.
- L.E.Ochando, J.Rius, D.Louër, R.M.Claramunt, C.Lopez, J.Elguero, J.M.Amigó, "Phase Transitions in Tris(3,5-dimethylpyrazol-1-yl) methane. The structure of the High-Temperature Phase from X-ray powder Diffraction", *Acta Cryst. B53*, 939-944, 1997.

- B. H. O'Connor, A. van Riessen, J. Carter, G. R. Burton, D. J. Cookson, R. F. Garrett, "Characterization of Ceramic Materials with BIGDIFF: A Synchrotron Radiation DebyeScherrer Powder Diffractometer", *J. Am. Ceram. Soc.*, 80, 1373-1381, 1997.
- A.R.Oganov, S.Ono, "Theoretical and experimental evidence for a post-perovskite phase of MgSiO₃ in Earth's D" layer Nature", *Nature* 430, 445 (2004).
- M.P.Pasternak, G.Kh.Rozenberg, G.Yu.Machavariani, O.Naaman, R.D.Taylor, R.Jeanloz, "Breakdown of the Mott-Hubbard State in Fe₂O₃: A First-Order Insulator-Metal Transition with Collapse of Magnetism at 50 Gpa", *Phys. Rev. Lett.* 82, 4663, 1999.
- G.S. Pawley, "Unit-cell refinement from powder diffraction scans", *J.Appl.Cryst.*, 14, 357-361, 1981.
- J.Pellicer-Porres, A.Segura, V.Muñoz, J.Zúñiga, J.P.Itie, A.Polian, P.Munsch, "Cinnabar phase in ZnSe at high pressure", *Phys. Rev. B* 65, 012109, 2002.
- J.Pellicer-Porres, A.Segura, Ch.Ferrer-Roca, D.Martínez-García, J.A.Sans, E.Martínez, J.P.Itié, A.Polian, F.Baudelet, A.Muñoz, P.Rodríguez-Hernández, P.Munsch, "Structural evolution of the CuGaO₂ delafossite under high pressure", *Physical Review B* 69, 24109, 2004.
- L.Pinsard-Gaudart, J. Rodriguez-Carvajal, A.Daoud-Aladine, I.Goucharenko, M.Medarde, R.I.Smith, A.Revcolevski, "Stability of the Jahn-Teller effect and magnetic study of LaMnO₃ under pressure", *Phys. Rev. B* 64, 064426/1-7, 2001.
- M.M.Pop, K.Goubitz, M.B.Borodi, D.J.A.DeRidder, R.Peschar, H.Schenk, "Crystal structure of the inclusion system of beta-cyclodextrin with mefenamic acid from high-resolution synchrotron powder diffraction data in combination with molecular-mechanics calculations", *Acta Cryst.* B58, 1036-1043, 2002.
- T. Pradell, J. Molera, M. Vendrell, J. Prez-Arantegui, E. Pantos, M. Roberts, M. DiMichiel, "Role of Cinnabar in Luster Production", *J. Am. Ceram. Soc.*, 87, 1018-1023, 2004.
- H.Putz, J.C.Schön, M.Jansen, "Combined method for ab initio structure solution from powder diffraction data", *J. Appl. Cryst.* 32, 864-870, 1999.
- A.Pyzalla, "Methods and feasibility of residual stress analysis by high-energy synchrotron radiation in transmission geometry using a white beam", *J. Nondest. Eval.*, 19, 21, 2000.
- P.G.Radaelli, D.E.Cox, M.Marezio, S-W.Cheong, "Charge, orbital, and magnetic ordering in La_{0.5}Ca_{0.5}MnO₃", *Phys. Rev. B* 55, 3015, 1997.
- F.Rajabalee, P.Negrier, D.Mondieig, M-A.Cuevas-Diarte, "Ordered Phases in n-Heptacosane (C₂₇H₅₆). Structure Determination of the Mdc1 Phase", *Chem. Matter.*, 14, 4081-4087, 2002.
- C.Ritter, R.Mahendiran, M.R.Ibarra, L.Morellon, A.Maignan, B.Raveau, C.N.R.Rao, "Direct evidence of phase segregation and magnetic-field-induced structural transition in Nd_{0.5}Sr_{0.5}MnO₃ by neutron diffraction", *Phys. Rev. B.* 61, R9229, 2000.
- J.Rius, F.Plana, A.Palanques, "A standardless X-ray diffraction method for the quantitative analysis of multiphase mixtures", *J. Appl.Cryst.* 20, 457-460, 1987.
- J.Rius, C.Miravittles, "Determination of crystal structures with large known fragments directly from measured X-ray powder diffraction patterns", *J.Appl.Cryst.*, 21, 224-227, 1988.
- J.Rius, C.Miravittles, E.Molins, M.Crespo, J.Veciana, "Crystal Structure of the Organic Free Radical Perchlorotriphenylmethyl from powder diffraction data. Comparison with its clathrate structures", *Mol. Cryst. Liq. Cryst.*, 187, 155-163, 1990.
- J.Rius, "Derivation of a New Tangent Formula from Patterson-Function Arguments", *Acta Cryst.* A49, 406-409, 1993.

- J.Rius, J.Sañé, C.Miravittles, J.M.Amigó, M.M.Reventós, D.Louër, "Extraction of integrated intensities from partially overlapping Bragg reflections", *Anales de Química Int. Ed.*, 92, 223-227 (Springer Verlag) 1996.
- J.Rius, "XLENS, a direct-methods program based on the origin-free modulus sum function: Its application to powder data", *Powder Diffraction*, 14, 267-273, 1999.
- J.Rius, C.Miravittles, H.Gies, J.M.Amigó, "Structure solution from powder patterns with systematic overlap", *J.Appl.Cryst.*, 32, 89-97, 1999.
- J.Rius, E.Elkaim, X.Torrelles," Structure determination of the blue mineral pigment aerinite from synchrotron powder diffraction data: The solution of an old riddle", *Eur.J.Mineral.*, 16, 127-134, 2004.
- J.Rius, "Advances and some recent applications of the origin-free modulus sum function", *Z. Kristallogr.*, 219, 826-832, 2004.
- F.Rodríguez, F. Aguado, "Correlations between structure and optical properties in Jahn–Teller Mn^{3+} fluorides: a study of $TiMnF_4$ and $NaMnF_4$ under pressure", *J. Chem. Phys.* 118, 10867, 2003.
- F.Rodríguez, M.Hanfland, J.P.Itiè, A. Polian, "Optical properties of A_2CuCl_4 layer perovskites under pressure. Structural correlations" in "Frontiers of high pressure research II. Application of high pressure to low-dimensional novel electronic materials", Ed. Kluwer Academic Publishers, Mathematics, Physics and Chemistry 48, 143, 2001.
- J.L.Rodríguez, A.H.De Aza, P.Pena, J.Campo, P.Convert, X.Turrillas, "Study of Zircon Dolomite Reactions Monitored by Neutron Thermodiffractometry", *J. Sol. State Chem.*, 166, 426-433 2002.
- N.L. Rosi, J. Eckert, M Eddaoudi, D. T. Vodak, J Kim, M. O’Keeffe, O.M. Yaghi, "Hydrogen Storage in Microporous Metal-Organic Frameworks", *Science*, 300, 1127-1129, 2003.
- J.Ruiz, J.M.Atienza, M.Elices, "Residual stresses in wires: influence of wire length", *J. Mater. Eng. Perform.*, 12, 480, 2003.
- J.Sañé, J.Rius, T.Calvet, M.A.Cuevas-Diarte, "Chiral Molecular Alloys: Patterson-Search Structure Determination of L-Carvone and DL-Carvone from Powder Diffraction Data at 218 K", *Acta Cryst. B53*, 702-707, 1997.
- G.Sankar, J.M.Thomas, F.Rey, G.N.Greaves, "Probing the onset of crystallization of a microporous catalyst by combined X-ray absorption spectroscopy and x-ray diffraction", *J. Chem. Soc., Chem. Comm.*, (24), 2549-50, 1995.
- D.Santamaria-Perez, J.Nuss, J.Haines, M.Jansen, A.Vegas, "Iron silicides and their corresponding oxides: A high-pressure study of Fe_5Si_3 ", *Solid State Sciences* 6, 673-678, 2004.
- F.Schlunzen, J.M.Harms, F.Franceschi, H.A.S.Hansen, H.Bartels, R.Zarivach, A.Yonath, "Structural basis for the antibiotic activity of ketolides and azalides", *Structure(Camb)*. 11, 329-338, 2003.
- S.Schmidt, H.F.Poulsen, G.B.M.Vaughan, "Structural refinements of the individual grains within polycrystals and powders", *J.Appl.Cryst.*, 36, 326-332, 2003.
- K.Shankland, W.I.F.David, D.S.Sivia, "Routine ab-initio structure determination of chlorothiazide by X-ray powder diffraction using optimised data collection and analysis strategies", *J.Mater.Chem.*, 7,569-572, 1997.
- N.Shankland, K.Shankland, W.I.F.David, A.J.Florence, Ch.S.Frampton, "Correlating crystal structure with physical properties of zopiclone", *ESRF Report CH-856*, 2000.
- I.J.Shannon, F.Rey, G.Sankar, J.M.Thomas, T.Maschmeyer, A.M.Waller, A.E.Palomares, A.Corma, A.J.Dent, G.N.Greaves, "Hydrotalcite-Derived Mixed Oxides Containing Copper: Catalysts for the Removal of Nitric Oxide", *J. Chem. Soc. Faraday Trans.*, 92, 4331-4336, 1996.

- G.M.Sheldrick, "SHELXTL97". University of Göttingen, Germany, 1997.
- A.Snedden, C.H.Hervoches, P.Lightfoot, "Ferroelectric phase transitions in $\text{SrBi}_2\text{Nb}_2\text{O}_9$ and $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$: A powder neutron diffraction study", *Phys. Rev. B* 67,92102-1/4, 2003.
- N.Snejko, C.Cascales, B.Gomez-Lor, E.Gutiérrez-Puebla, M.Iglesias, C.Ruiz-Valero, A.Monge, "From rational octahedron design to reticulation serendipity. A thermally stable rare earth polymeric disulfonate family with CdI_2 -like structure, bifunctional catalysis and optical properties", *Chem. Commun.*, 1366-1367, 2002.
- E.Suard, F.Fauth, V.Caignaert, I.Mirebeau, G.Baldinozzi, "Charge ordering in the layered Co-based perovskite $\text{HoBaCo}_2\text{O}_5$ ", *Phys. Rev. B* 61, R11871, 2000.
- J. Ll.Tamarit, M.Barrio, D.O.López, Y.Haget, "Packing Disordered Molecular Crystals and their Molecular Alloys", *J. Appl. Cryst.*, 30, 118–122, 1997.
- Z.K.Tang, L.Y.Zhang, N. Wang, X.X.Zhang, J.N.Wang, G.D.Li, Z.M.Li, G.H.Wen, C.T.Chan, P.Sheng, "Ultrasmall single-walled carbon nanotubes and their superconductivity properties", *Synthetic Metals*, (133-134), 689-690, 2003.
- O.Terasaki, Z.Liu, T.Ohsuna, H.J.Shin, R.Ryoo, "Electron microscopy study of novel Pt nanowires synthesized in the spaces of silica mesoporous materials", *Microscopy and Microanalysis*, 8(1), 35-39, 2002.
- A.G.delaTorre, A.Cabeza, A.Calvente, S.Bruque, M.A.G.Aranda, "Full Phase Analysis of Portland Clinker by Penetrating Synchrotron X-rays", *Analytical Chemistry*, 73, 151, 2001.
- A.G.delaTorre, S.Bruque, J.Campo, M.A.G.Aranda, "The Superstructure of C_3S from Synchrotron and Neutron Powder Diffraction and Its Role in Quantitative Phase Analyses", *Cement Concrete Research* 32, 1347, 2002.
- A.G.delaTorre, M.A.G. Aranda, "Accuracy in Rietveld Quantitative Phase Analysis of Portland Cements", *J. of Appl. Cryst.*, 36, 1169, 2003.
- J.M.Tranquada, J.D.Axe, N.Ichikawa, A.R.Moodenbaugh, Y.Nakamura, S.Uchida, "Coexistence of, and Competition between, Superconductivity and Charge-Stripe Order in $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ ", *Phys. Rev. Lett.* 78, 338, 1997.
- M.Uehara, S.Mori, C.H.Chen, S-W.Cheong, "Percolative phase separation underlies colossal magnetoresistance in mixed-valent manganites", *Nature* 399, 560, 1999.
- G.B.M.Vaughan, S.Schmidt, H.F. Poulsen, "Multicrystal approach to crystal structure solution and refinement", *Z. Kristallogr.*, 219, issue 12, 2004 (in press).
- L.Ventolà, M.Ramirez, T.Calvet, X.Solans, M.A.Cuevas-Diarte, P.Negrier, D.Mondieig, J.C.Van Miltenburg, H.A.J.Oonk, "Polymorphism of N-Alkanols: 1-Heptadecanol, 1-Octadecanol, 1-Nonadecanol and 1-Eicosanol", *Chem. Matter.*, 14, 508-517, 2002.
- L.A.Villaescusa, P.Lightfoot, S.J.Teate, R.E.Morris, "Variable-Temperature Microcrystal X-ray Diffraction Studies of Negative Thermal Expansion in the Pure Silica Zeolite IFR", *J. Am. Chem. Soc.*, 123, 5453-5459, 2001.
- N.Wang, Z.K.Tang, G.D.Li, J.S.Chen, "Materials science: Single-walled 4Å carbon nanotube arrays", *Nature*, 408(6808), 50-51, 2000.
- J. K. Warner, A.P.Wilkinson, A.K.Cheetham, D.E.Cox, "Comparative study of elemental contrast by resonant X-ray and neutron powder diffraction", *J. Phys. Chem. Solids*, 47, 155, 1991.

- P.J.Webster, G.Mills, "Residual stresses in a steel strand", Phys. B: Condens. Matter, 241-243, 1270-1273, 1997.
- T.Wessels, Ch.Baerlocher, L.McCusker, "Single-crystal-like diffraction data from polycrystalline materials", Science, 284, 477-479, 1999.
- A. P. Wilkinson, A. K. Cheetham, S. C. Tang, W.J. Reppart. J. Chem. Soc. Chem. Commun.,1485, 1992.
- D.A.Woodcock, P.Lightfoot, P.Wright, L.A.Villaescusa, M.A.Cambor, "Strong negative thermal expansion in the siliceous zeolites ITQ-1, ITQ-3 and SSZ-23", Journal of Materials Chemistry, 9(2), 349-351, 1999.
- J. P. Wright, "Extraction and use of correlated integrated intensities with powder diffraction data", Z. Kristallogr., 219, issue 12, 2004 (in press).
- J. P. Wright, J. P. Attfield, and P. G. Radaelli, "Long Range Charge Ordering in Magnetite Below the Verwey Transition", Phys. Rev. Lett. 87, 266401, 2001.
- H. Yang, Q. Shi, B. Tian, Q. Lu, F. Gao, S. Xie, J. Fan, C. Yu, B. Tu, D. Zhao, "One-Step Nanocasting Synthesis of Highly Ordered Single Crystalline Indium Oxide Nanowire Arrays from Mesoporous Frameworks", J. Am. Chem. Soc., 125, 4724-4725, 2003.
- M. Yashima, "In situ Observations of Phase Transition Using High-Temperature Neutron and Synchrotron X-ray Powder Diffractometry ", J. Am. Ceram. Soc., 85, 2925-30, 2002.