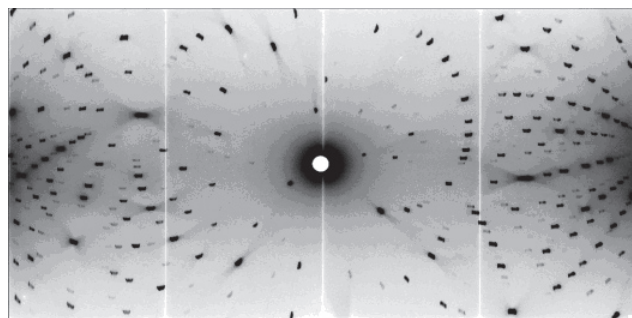


geometrical aspects of the manifestation of thermal diffuse scattering, and yield values of the sound velocities in good accord with values obtained by ultrasound attenuation measurements.



A typical long-exposure neutron Laue pattern for Al₂O₃

[1] G.J. McIntyre, M.-H. Lemée-Cailleau, C. Wilkinson *Physica B* **2006**, 385-386, 1055-1058. [2] P.D.W. Boyd, A.J. Edwards, M.G. Gardiner, C.C. Ho, M.-H. Lemée-Cailleau, D.S. McGuinness, A. Riapanitra, J.W. Steed, D.N. Stringer, B.F. Yates *Angew. Chem.* **2010**, 49, 6315-6318. [3] C.J. Carlile, B.T.M. Willis *Acta Cryst. A* **1989**, 45, 708-715.

Keywords: neutron_Laue_diffraction, image-plate_detectors thermal_diffuse_scattering

MS.56.1

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Structural identification and antiproliferative activity of metallodrugs

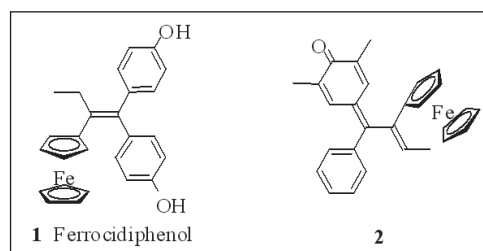
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The first line drug used to combat hormone-dependent breast cancers is tamoxifen, the archetypal selective estrogen receptor modulator (SERM). Since tamoxifen is active only against tumours that are estrogen receptor positive (ER+), and frequently gives rise to resistance after prolonged use, the search for related but different agents has intensified considerably over the last few years.

We have designed novel therapeutic agents which are based on organometallic compounds that express high antiproliferative activity against breast cancer cells [1], [2]. We found that ferrocidiphenol **1** is characterized in vitro by a strong antiproliferative effect on both hormone-dependent (MCF-7) and hormone-independent (MDA-MB-231) breast cancer cells (IC₅₀ values around 0.5 μM), whereas OH-Tam has an effect only on hormone-dependent cells.

Many complexes have been synthesized, allowing the study of the structure-activity relationship. Electrochemical experiments have suggested that the active metabolite of these compounds is a quinone methide. This hypothesis is now supported by isolation and X-ray structural determination of the quinone methide **2** [3].

The structural requirements for activity seem to be 1) the presence of a ferrocene group, 2) a conjugated linker, 3) aromatic para-substitution by a protic function and 4) an ethyl group residing on the same carbon as the ferrocene group. X-ray absorption spectroscopy has been used to obtain addition information on these compounds.



XANES spectra of ferrocidiphenol and its diphenyl analogue (2-ferrocenyl-1,1-diphenyl-but-1-ene) have been compared to XANES of ferrocene. Spectra indicate that the iron electronic properties are affected by the group that replaces a hydrogen of the unsubstituted Cp ring [4].

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Keywords: organometallic, anticancer, XANES

MS.56.2

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XANES spectroscopy for determination of the 3D nanoscale atomic structure

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The status of modern theoretical analysis of the experimental x-ray absorption spectra to extract structural parameters will be presented. Novel method for extracting of 3D structural information on the basis of advanced quantitative analysis of X-ray absorption near edge structure (XANES) realized in “FitIt” software [1] is described. The approach is based on the fitting of experimental XANES data using multidimensional interpolation of spectra as a function of structural parameters and advanced “ab-initio” XANES simulations. Small number of required ab-initio calculations is the main advantage of the approach, which allows one to use computationally time-expensive non-muffin-tin methods. The possibility to extract information on bond angles and bond-lengths is demonstrated and it opens new perspectives of quantitative XANES analysis as a 3D local structure probe. As XANES spectrum can be measured simultaneously, one can use XANES to study the local structure in time-dependent experiments within a time domain of 100 picoseconds and less.

Advanced theoretical analysis based either on self-consistent muffin-tin model or full potential (non-muffin-tin) theory, coupled with DFT geometry optimization have been applied to extract structural information from experimental XANES data. The status of modern research shows that XANES spectroscopy and its “ab initio” theoretical analysis can be a useful tool for the investigation of both local structure and electronic subsystem of many advanced materials without long range order. The present approach can provide a subatomic level (i.e., 0.01- 0.03 angstrom) of accuracy in the determination of the interatomic distances and several of degrees in the determination of the bonding angles at specific atomic site of nanostructured materials without long range order.

In the framework of this approach, results of recent studies of local atomic and electronic structure for several types of nanostructures: free and supported Cu nanoclusters, magnetic nanoclusters, and irradiated by C and Si ions ZnO thin films are reported. The parameters of local atomic structure obtained from the XANES spectra analysis have been controlled by using theoretical optimization of the atomic structures on the basis of density function theory. The research is supported by RFBR 10-02-92658-IND_a and the President of Russian Federation MK-4283.2010.2 grants.

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Keywords: XANES

MS.56.3

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Graphene, electrons, plasmons, and quantum: A perfect match

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Electron beams constitute excellent tools to probe both propagating and localized plasmons with outstanding spatial resolution. The inelastic events recorded in electron energy-loss spectroscopy (EELS) and in light emission during electron-plasmon interaction (cathodoluminescence, CL) have been recently used to resolve plasmon excitations and to yield maps with detailed spatial distributions [1]. Here, we will illustrate several recent examples of plasmon mapping via EELS and CL in both extended metallic nanostructures and in nanoparticles. We will also discuss plasmons in graphene as an emerging powerful framework to study the interaction between photon, plasmons, and electrons at the single particle level, with potential applications to areas as varied as ultrasensitive biosensing, nonlinear optics, and quantum information processing.

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Keywords: plasmon, EELS, cathodoluminescence

MS.56.4

Acta Cryst. (2011) **A67**, C131

Amphipathic and amphidynamic crystalline materials: an XRD and MAS NMR study

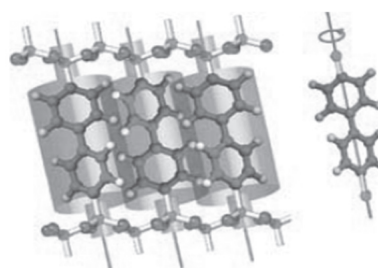
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Molecular self-assembled crystalline materials are promising in several fields, including gas storage, selective recognition and modulation of functions of active molecules. The tandem X-ray diffraction and solid state NMR approach allowed us to study amphipathic or amphidynamic materials i.e. crystalline structures that exhibit an intrinsic duality within the same periodic architecture [1-4]. In particular, we realized self-assembled crystalline architectures with guest molecules compartmentalized in two amphipathic nanospaces with distinct geometries and polarities [5]. The effect of these distinct environments on the NMR properties of the guest molecules is evident from chemical shift data and 2D heterocorrelated NMR techniques that could discriminate identical guest molecules embedded in distinct structural environments - one highly polar and the other nonpolar. The large magnetic susceptibility effect, due to ring currents of the

aromatic host, enabled the determination of the host-guest distances and corroborated the variable-temperature crystal structure resolution. A dual behavior was also highlighted in a block copolymer. The molecular recognition of specific blocks of triblock copolymers by a host molecule led to the formation of hierarchical periodic structures [2]. The end blocks of the triblock copolymer were locked into the inclusion crystals whilst the central block was excluded, creating a new material of assembled nanocrystals regularly superimposed on one another. The formation of the supramolecular architectures was followed *in situ* synchrotron X-ray diffraction while fast-¹H MAS NMR provided direct evidence of selective inclusion of the blocks.

Notably, amphidynamic materials could be recognized in hybrid organic-inorganic crystalline materials [1]. The precise engineering of highly-organized porous materials containing organic elements pivoted on inorganic layers enabled the fabrication of fast molecular rotors entirely exposed to the guest molecules exploring the cavities. Powder X-ray diffraction highlighted the crystalline order on both the meso- and molecular scales. Spin-echo deuterium NMR gave direct proof of the reorientation rate of the aligned rotors and demonstrated the active role of the guests in modulating the rotor dynamics.

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Keywords: NMR, inclusion, dynamics

MS.56.5

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Metal-semiconductor surface phase transitions: A photoelectron – diffraction study

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The origin of surface phase transitions has been a matter of intense dispute among theoreticians and experimentalists, during the last years. Concurrently, inside surface science, systematic studies of simple model systems has successfully provided remarkable advances during the last 40 years. In spite of this, the emergence of novel powerful techniques has made attainable a more truthful representation of those “well-known” traditional systems. The improved new pictures confirm that complex phenomena take place at surface originally described as simple model systems. In particular, notions as Peierls distortions, Fermi surface nesting, Jahn-Teller distortions, metal-insulator fluctuations, disproportionation and charge and spin density waves, have been pointed out as responsible mechanisms of reported Surface Phase Transitions. In this sense, pioneer studies have focused their attention on the traditional Pb or Sn adsorbed on Ge(111) surfaces,