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Local polarizations and the interaction between them play a crucial role in the relaxor behavior of relaxor ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN). We report the temperature evolution of the local and medium-range crystal structure of PMN from 1000K to 15K using neutron pair distribution function analysis [1]. We present evidence for both local atomic displacements (local polarization) and for medium-range ($\sim 5 \text{ \AA} - 50 \text{ \AA}$) ordering, called polar nanoregions (PNRs). These medium-range correlations are modeled using rhombohedral symmetry, enabling for the first time an estimate of the temperature dependence of the volume fraction of the PNRs. We show that this fraction steadily increases from 0% to a maximum of $\sim 30\%$ as the temperature decreases from 650K to 15K. Below $T \sim 200\text{K}$ the volume fraction of the PNRs becomes significant, and PNRs freeze into the spin-glass-like state.

[1] Jeong I.-K., Darling T. W., Lee J. K., Proffen Th., Heffner R. H., Park J. S., Hong K. S., Dmowski W., Egami T. *Phys. Rev. Lett.*, in press.

Keywords: relaxor, medium-range ordering, PDF

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Getting the most from Total Scattering

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Total scattering, an extension of the powder diffraction method, is increasingly being used to study crystalline materials. The unique combination of Bragg and diffuse scattering can be used to determine both the average structure and the short-range fluctuations from this average within a single experiment. To maximise the structural information from such data three-dimensional atomic models consistent with all aspects of the data are required. Here I present a technique for producing such models based on the reverse Monte Carlo (RMC) method. The existing RMC method has been expanded to take explicit account of the Bragg intensity profile from crystalline materials [1].

Analysis of the RMC-generated atomic models gives much more detailed information than is available directly from the data. I will give several examples where this method has been used to successfully study the structure and dynamical disorder of materials including those with the perovskite structure [2], those showing negative thermal expansion and molecular crystals. I will also show examples of low-energy phonon dispersion curves obtained from the models [3].

[1] Keen D. A., et al, *J. Phys.: Cond. Matt*, 2005, **17**, S15. [2] Hui Q., et al, *J. Phys.: Cond. Matt*, 2005, **17**, S111. [3] Goodwin A. L., et al *Phys. Rev. Lett.* **93**, 075502, 2004.

Keywords: reverse Monte Carlo, structural simulation, neutron X-ray scattering

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Characterisation of Nanoparticles

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Powder diffraction patterns of ZnO as well as CdSe/ZnS core shell nanoparticles were obtained and analysed with respect to particle size, defect density and local structure. The pair distribution function was successfully used to analyze the local structure.

The ZnO pattern was refined by the Rietveld method using a

wurtzite structure. The moderate agreement shows that the particles are of anisotropic shape and have a stacking fault density of some 20%. The nanoparticles were modelled and size, shape, stacking fault density, positional and displacement parameters fitted to the powder pattern by means of the Debye formula as well as to the respective experimental Pair Distribution Function. The two methods give similar results of some 3.5 nm parallel [100] and 2.5 nm parallel [001] in size.

The CdSe nanoparticles and CdSe/ZnS core-shell nanoparticles show diffraction patterns that qualitatively fit to a wurtzite structure. The size of 3 nm as well as stacking fault density of 25% and distortions at a surface layer degrade the powder pattern. The pattern of the CdSe/ZnS core-shell nanoparticles are widened at the high 2 θ side compared to the pure CdSe nanoparticles. The smaller metal-anion distance (Zn-X=0.235 nm, Cd-X=0.27 nm) causes a distortion of the whole particle.

Keywords: nanoparticle, pair distribution function, local structure

MS75 SURFACES

Chairperson: Laurence D. Marks

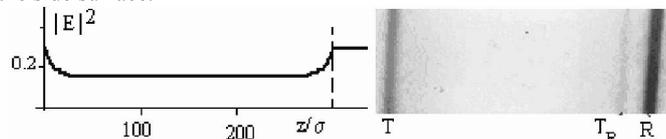
MS75.29.1

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Electromagnetic Wave Tunneling Through a Barrier With Periodical Structure

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We discuss specific features of electromagnetic wave localization inside specimen with periodical structure in diffraction regime. The problem was solved by Hambartsumian's layer addition method modified for cholesteric liquid crystal layer (CLCL)[1]. Experiment for a perfect single crystal of silicon was fulfilled when x-ray beam was reflected from atomic planes (2 $\bar{2}0$). We reveal an interesting manifestation of electromagnetic wave tunneling through barrier with periodical structure, namely, we theoretically and experimentally showed that when electromagnetic wave propagated through the barrier in the Bragg regime the wave field in the specimen was localized near the specimen boundaries, while it was practically absent inside the sample. Using this we explained the fact (observed in experiment) that absorption and scattering inside the sample are practically absent, and that reflection takes place only from the two surface layers of the sample. Fig. 1 shows electromagnetic wave intensity distribution in CLCL in the Bragg diffraction regime (a) and x-ray sectional photograph from the two block silicon systems, when the primary beam (which is reflected from the first block and incident onto the second block) then forms three beams; R is reflected from the entrance surface, T is the transmitted beam and T_R is reflected from the side surface.



[1] Gevorgyan A.H., et al., *Opt. Spectrosc.*, 2000, **88**, 647.

Keywords: diffraction, tunneling, surface physics

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Holographic Methods for Surface Crystallography

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A hologram stores information about the amplitude and phase of a wave in an interference pattern with a known reference wave. The unknown wave may be recovered through a process known as reconstruction. It has been suggested that many diffraction patterns, e.g. those formed by photoelectrons, or low energy backscattered electrons may be capable of a holographic interpretation, and

computer reconstruction algorithms were proposed to recover the 3D structure of atoms surrounding an atomic source of a (spherical) reference wave. A major limitation of all these methods is that, due to the decay of the reference wave with the inverse of the distance from the source, the reconstructed image contains information only about atoms rather close to the source. In the case of surface crystallography, a more useful direct method would be one capable of recovering the entire contents of a large surface unit cell. We will describe in this talk an alternative holographic interpretation of x-ray and electron diffraction patterns from surfaces which accomplishes this task by taking as the reference wave the delocalized one scattered by the entire bulk substrate and show some results from applications to surface x-ray diffraction (SXRD) [1] and low energy electron diffraction (LEED) [2].

[1] Lyman P.F., Shneerson V.L., Fung R., Harder R.J., Lu E.D., Parihar S.S., Saldin D.K., *Phys. Rev. B*, 2005, **74**, 081402(R0). [2] Saldin D.K., Seubert A., Heinz K., *Phys. Rev. Lett.*, 2002, **88**, 115507.

Keywords: holography, surfaces, structure

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X-Ray Diffraction from Semiconductor Nanostructures

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Self-organized nanostructures are of great interest in semiconductor technology due to the enhancement they introduce for device design. Quantum confinement effects and the combination of different materials lead to electronic states that cannot be realized using bulk materials or planar heterostructures. Key properties of nanostructures, such as chemical composition, shape, size, and strain state, depend sensitively on growth conditions.

X-ray diffraction techniques have been successfully used for the characterization of such nanostructures, both after growth as well as in situ during fabrication [1]. The main advantages of x-ray techniques are that they can be applied to capped structures, that they provide statistically well averaged results, and the high sensitivity to lattice strain.

In this presentation, the techniques used for the structural characterization of nanostructures will be discussed, together with recent results in particular on SiGe islands embedded in Si samples. The composition and strain distribution within the nanostructures is derived from reciprocal space maps recorded in coplanar or grazing incidence diffraction (GID) geometry. Anomalous scattering is used to obtain material sensitivity even in the case of GID.

[1] for a review see: Stangl J., Holy V., Bauer G., *Rev. Mod. Phys.*, 2004, **76**, 725, and references therein.

Keywords: Nanostructure, composition, diffraction

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Interaction of NO and CO with Surface of Pd Nanoclusters studied by XRD

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The developed recently technique of monitoring in situ a position, width and intensity of XRD profile during chemisorption or a surface reaction [1,2,3] was used to study interaction of NO and CO with Pd nanocrystal surface. The peaks evolution was interpreted via atomistic simulation. Additional insight into the surface morphology is provided by measuring time required for a transition of the Pd nanocrystals into beta hydride phase in hydrogen atmosphere. The adsorption of both gases hinders hydride transition slowing down the rate of hydrogen dissociation.

The study is an attempt to shed light on a possible surface reconstruction of the nanocrystals occurring on chemisorption. Up to date evidence for a similar phenomena could be only collected with surface science techniques on single crystals under very low gaseous pressure.

[1] Kaszukur Z., *J. Appl. Cryst.*, 2000, **33**, 87. [2] Kaszukur Z., *J. Appl. Cryst.*, 2000, **33**, 1262. [3] Kaszukur Z., *Phys. Chem. Chem. Phys.*, 2004, **6**, 193.

Keywords: nanocrystals, palladium, surface reconstruction

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Three Dimensional Charge Density Measurements at Surfaces

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Charge density measurements in bulk materials using primarily x-ray diffraction but in some cases transmission electron diffraction is a very well established field. In principle, being able to directly measure the charge density at a surface is at least as scientifically interesting if not more so; one could start to directly probe numerous important processes such as bond formation at a surface. Until very recently it has not been possible to achieve this due to experimental problems. The first work reported was with transmission electron diffraction for the MgO (111) $\sqrt{3}\times\sqrt{3}$ R30 surface where significant charge transfer was measured, but only in two dimensions. We will describe here results using surface x-ray diffraction for the Si (001) 2x1-H surface where a charge density analysis has been done in three-dimensions.

Keywords: surfaces, charge density, X-ray diffraction

MS76 NEW ALGORITHMS FOR STRUCTURE PREDICTION

Chairpersons: Peter Erk, Sam Motherwell

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Assessing Lattice Energy Minimisation for Crystal Structure Prediction

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The goal of reliable crystal structure prediction has been a driving force for the development of methodologies in modelling molecular organic crystals. The first step in crystal structure prediction involves a search for all low energy structures on the potential energy surface. Such searches usually generate far more energetically feasible structures than are known or are likely to be observed and the energy differences between possible structures are typically very small. Therefore, the ordering of energetic stability requires a high quality model for the lattice energy.

Several options for modelling the energies of predicted crystal structures are examined: empirical atom-atom potentials with atomic charges and multipoles; the recently developed semiclassical density sums (SCDS or "Pixel") method [1]; and periodic density functional theory calculations. The models are assessed on a test set of small organic molecules [2] and results of the most recent (third) blind test of crystal structure prediction are also examined. Advantages and shortcomings of the various methods are discussed.

[1] a) Gavezzotti A., *J. Phys. Chem. B*, 2002, **106**, 4145-4154; b) Gavezzotti A., *J. Phys. Chem. B*, 2003, **107**, 2344-2353. [2] a) Day G. M., Chisholm J., Shan N., Motherwell W. D. S., Jones W., *Crystal Growth & Design*, 2004, **4**, 1327-1340; b) Day G. M., Motherwell W. D. S., Jones W., *Crystal Growth & Design*, 2005, *in press*.

Keywords: molecular modelling, crystal structure prediction, energy minimization

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A Hybrid Method for the Accurate Energy Ranking of Molecular Crystals

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