

the size-property correlation in these MoS₂ nanosheets. Our results imply that nanostructured films with a high density of edge spins can give rise to magnetism even though the bulk material is nonmagnetic. For the first time, we show that Arsenic(ii) sulfide nanocrystal could be fabricated by a wet process of cluster-mediated nucleation method from the bulk material. Arsenic sulfide nanocrystals can show size-dependent fluorescences ranging from 287nm to 450 nm as well as two-photon upconversion. In China, realgar was also reported to be used as a drug in traditional Chinese medicine for more than 1500 years although arsenic is well known to be a highly toxic material. Preliminary pharmacokinetic studies showed that arsenic sulfide quantum dots may afford good potential in anti-cancer treatment.

Keywords: nanocrystals, arsenic sulfide, molybdenum sulfide

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***In-situ* transmission electron microscopy and theoretical studies on the coalescence of nanoparticles**

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The production of low-cost nanoparticulate devices based on a bottom-up approach is subject of current research activities. One of the important questions on the way to sustainable devices concerns the question of their mechanical, thermal or electrical stability. Several routes of bottom-up integration of nanoparticulate systems are under investigation, including chemical linking, hybrid integration in a stable matrix and thermal processing. This presentation will focus on aspects of the thermal processing of nanoparticulate films and demonstrate a variety of different processes, which are directly related to the chemical bonding of the material. The thermally activated densification and sintering processes have been studied using time resolved *in-situ* hot-stage transmission electron microscopy of self-supporting films. The experiments were documented as live stream with a TV-rate CCD camera on a hard disc recorder. Varying mechanisms were found for the different materials: a) for ionic ITO particles, an adjustment of the crystal orientation prior to the coalescence is observed at temperatures well below of half the melting temperature; b) for covalent silicon, a melting and subsequent wetting process of the nanoparticles is observed; c) metallic silver particles form area defects during their coalescence, which migrate out of the particles afterwards. These observed mechanisms go clearly beyond the models of classical sintering theory. Our experiments clearly demonstrate that a more sophisticated treatment is necessary in order to understand the sintering processes in nanoparticles, which needs to take into account the chemical bonding and crystallographic orientation. DFT and KMC and MD Simulations support and substantiate the presented experimental results.

Keywords: nanoparticles, sintering / coalescence, *in-situ* transmission electron microscopy

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Structural and magnetic properties of MBE grown MnSb layers

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We present results, which open the way towards generating novel materials utilizing the electron spin. We propose to create such materials, by producing the appropriate inclusions in a semiconductor matrix. Bulk MnSb has a TC of 587 K, being therefore a good candidate to form ferromagnetic nano-inclusions in the semiconductor. To establish the best growing condition for MnSb layers and for multiphase materials, we present results of a characterization of MnSb layers grown on GaAs (100) or GaAs (111) substrates by the MBE method. To determine the crystallographic orientation and the local atomic order of the layers, w -2q scans and x-ray absorption studies of the Mn K- edge were performed at DESY-HASYLAB. The phase analysis of the near surface region was performed in glancing incidence geometry (2q scan). In the layer grown on (100) GaAs the existence of two hexagonal MnSb domains with 10.1 and 11.0 orientations and polycrystalline inclusions of zinc-blende GaSb and hexagonal MnSb was detected. The diffraction peaks, observed for a layer grown on (111) GaAs, were indexed as 00.1 MnSb and 111 GaSb. No diffraction peaks originating from polycrystalline inclusions were found. The EXAFS analyze has shown that MnSb layers grown on (100) and (111) substrates have slightly different stoichiometries and/or the number of defects. The magnetic properties were examined by x-ray magnetic circular dichroism at MAX-lab (beamline D-1011). The spin magnetic moment per Mn atom was found to be 1.5 μ_B for both layers but large differences between layers were observed in x-ray reflectivity data, probably produced by a different morphology of these layers. This work was partially supported by a national grant of the Polish Ministry of Science and High Education N202-052-32/1189.

Keywords: synchrotron diffraction, ferromagnetic semiconductor, X-ray absorption spectroscopy

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Leverage analysis: A statistical tool to enhance the control on the crystal structure refinement

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The least-squares crystallographic refinement can be a non-trivial task because of the occurring of some statistical outliers in the data set. This is due to a number of causes: intrinsic noise in the experimental data, not suitable weighting schemes, not valid refinement strategies, problems in the crystallographic model employed and so on. In order to adjust the refinement protocol, a suitable detection of the actually influent outliers is needed. The

improvement of the refinement can be obtained by eliminating the badly fitted reflections and/or by correcting the model, which could be too inaccurate or involve too subtle features to be modelled depending on the quality of the observations processed. A successfully recognition of the actually influencing reflections is represented by some statistical estimators based on leverage analysis (Belsey et al., 1980, Merli, 2005). Among several exploitable estimators, there are some of them that seem to be particularly suitable in crystallographic calculations: i) Cook distance (Cook, 1977), ii) DFFITIS and iii) DFBETAS_{ij} (Belsey et al., 1980). In particular, estimator i) can be used to recognize an actual outlier of the refinement, whereas estimator ii) is useful to investigate the effects when a reflection is eliminated from the data set and iii) is able to recognize the variables that are mostly influenced by each reflection. The combined analysis of these diagnostics will be presented. It will be shown how successfully it yields to the recognition of a dangerous reflection and/or the inaccurate estimate of any particular variable.

Belsey, Kuth & Welsh (1980) *Regression diagnostics*. J. Wiley & Sons

Cook (1977) *Technometrics*, 19, 15-18

Merli (2005) *Acta Cryst.* A61, 471-477

Keywords: crystallographic refinement, crystallographic statistics, leverage analysis

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Small-molecule refinement using the computational crystallographic toolbox (cctbx) with Olex2

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In recent years, the cctbx[1] (including the macromolecular toolbox, mmtbx) has firmly established itself as a highly flexible, comprehensive and all-encompassing programming tool for macromolecular structure solution and refinement. The program suite PHENIX[2] is based on this framework, and is the most visible part of this long-standing and well-managed framework. As part of an effort to modernise computational tools for small-molecule crystallography, we have been working in collaboration with the cctbx. Our aim is to extend the functionality currently offered by the cctbx to include small molecule solution and refinement. This has resulted in the creation of the Small Molecule Toolbox (smtbx) which is now included with the cctbx framework. In order to make these tools accessible to those chemists and crystallographers who are working with small molecules, the cctbx/smtbx functionality can be accessed via Olex2[2] - a modern Graphical User Interface which is designed to make working with crystal structures as easy as possible for all groups of users. In this presentation we shall elaborate on the areas of the cctbx where modifications and extensions were necessary to achieve 'small-molecule functionality' and will outline how we manage the collaboration between the various contributors (in the hope that many may join!). We will also demonstrate how this functionality is accessed from the end-user's point of view. Examples of how structure solution/refinements achieved using the smtbx compare to other solution/refinement programs will be presented. We gratefully acknowledge the support of EPSRC grant No. EP/C536274/1.

[1] cctbx: <http://cctbx.sourceforge.net/>

[2] PHENIX: <http://www.phenix-online.org/>

[3] Olex2 <http://sourceforge.net/projects/olex2> and <http://www.olex2.org>

Keywords: small molecules, cctbx crystallographic refinement, graphical user interface

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Anisotropic displacement parameters for molecular crystals from periodic HF and DFT calculations

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Accurate X-ray diffraction experiments give information about the thermally averaged charge density in the unit cell. Investigations of the static charge density requires a proper deconvolution of thermal motion and static density. Complementary information about the thermal motion in molecular crystals is seldom available. We present an approach based on periodic HF and DFT calculations using the CRYSTAL06 code [1,2] to estimate both intramolecular and intermolecular vibrational contributions to the anisotropic displacement parameters as applied to molecular crystals. Crystalline urea has been used as case system. We investigate the role of the basis-set and the adopted DFT functional: LDA, GGA and hybrid. The effect of including an empirical dispersion-force correction to B3LYP calculations has also been considered [3]. Finally, at the B3LYP/6-31G(d,p) level, the dispersion of acoustic phonons has been estimated and included through a supercell approach. The results are compared with experimental data from spectroscopy, X-ray and neutron diffraction experiments. On the basis of previous results, work has been extended to urotropine and benzene crystals and preliminary data are reported. These estimates of atomic and molecular motion are especially important for hydrogen atoms because of their low scattering power and intense thermal motion. Recent attempts to estimate hydrogen atom motion show promising results, and we compare the CRYSTAL06 approach with the SHADE [4] procedure.

[1] R. Dovesi et al. *CRYSTAL06 User's Manual*, University of Torino, 2006. (<http://www.crystal.unito.it>).

[2] F. Pascale et al. *J. Comput. Chem.* 25 888 (2004).

[3] B. Civalleri et al. *CrysEngComm* 10 405 (2008).

[4] A. O. Madsen, *J. Appl. Cryst.* 39 757 (2006) (<http://shade.ki.ku.dk>).

Keywords: molecular motion, *ab-initio* calculations, X-ray charge-density analysis

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Joint refinement of single crystal and powder data from X-ray and neutron sources

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The last version of the crystallographic software Jana – a well known tool for structure determination of aperiodic structures - has introduced the generalized data input. In the program Jana2006 data