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Oligomers of the left-handed Z-DNA diffract X-rays to the highest resolution among all crystal forms of DNA. We present the crystal structure of a Z-DNA hexamer duplex d(CGCGCG)₂ determined at ultrahigh resolution of 0.55 Å. The structure has been refined to R = 6.77% in the full-matrix anisotropic mode with total absence of stereochemical restraints for DNA, according to the practice of small-molecule crystallography. This way led to very accurate, unbiased values of atomic coordinates and displacement parameters, accompanied by reliable estimates of their standard uncertainties. In consequence, we are able to present a detailed analysis of very fine features of the Z-DNA stereochemistry, not available in the existing literature. Detailed comparisons of the stereochemical library values with the present accurate Z-DNA parameters, shows in general a good agreement, but also reveals significant discrepancies in the description of guanine-sugar valence angles and in the geometry of the phosphate groups.

It should be noted that the crystal structure presented here has a nearly record-breaking resolution in the PDB, where it is surpassed only by crambin (1EJG and 3NIR) determined at 0.54 and 0.48 Å resolution. In the area of nucleic acids, it is currently the highest-resolution model.

Keywords: Z-DNA, ultra-high resolution

MS44.P01

Acta Cryst. (2011) **A67**, C518

Direct Determination of Long-period Stacking/Ordered Structures in Mg₈₁Zn₈RE₁₁

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Mg alloys containing a small amount of Zn and Y, e.g., Mg-1at.%Zn-2at.%Y alloy, reveal excellent mechanical properties with high yield strength ~600Mpa and elongation ~5% at room temperature. One of the remarkable microstructural features is formation of a novel type of long-period stacking/ordered (LPSO) structure [1], which is long-period chemical-ordered as well as stacking-ordered. There are long-period stacking polytypes denoted as 18R, 14H, 10H, 24R, (Fig.1) all of which are composed of a common structural unit represented by local ABCA stacking where B- and C-layers are significantly enriched by Zn and Y (these particular layers are denoted as B' - and C' -layers hereafter). These LPSO structures were firstly identified in Mg-Zn-Y alloys, but at present the LPSO phases have been found in several Mg-Zn-RE (RE: Rare Earth = Dy, Ho, Er, Tm, Gd, Tb) alloys [2].

Looking carefully the electron diffraction patterns taken along the stacking direction (*c*-axis), we find many weak satellite spots that suggest a further ordering within the B' - and C' -layers. In the present work, we investigate the detailed chemical order in the LPSO Mg-Zn-RE phases, using aberration-corrected scanning transmission electron microscopy (STEM). Since the reported compositions of the LPSO phases were different by the nominal compositions of the alloys, we considered that the chemical order in the LPSO phases also changes by them. Therefore we have chosen LPSO phases in the Mg₉₇Zn₁Y₂ alloy, the Mg₉₇Zn₁Er₂ alloy and the Mg₈₅Zn₆Y₉ alloy.

Using the technique of electron diffraction and direct observation by STEM, we determined the chemical order in the LPSO phases. The chemical order was formed by 6-times periodic structures within the

basal planes. From the results of direct observations, we found that there were clusters of additional elements which have ordered configurations similar to a L₁2-type structure. 6-times periodic structures within basal planes were composed by the periodic arrangements of these clusters. The difference of the nominal compositions of the alloys did not affect the configuration of the cluster, however the densities of clusters in the basal planes were seem to be changed by the nominal compositions. Finally, we constructed averaged models of the LPSO phases from the experimental results. The validity of the model was confirmed by simulations of electron diffraction and STEM image.

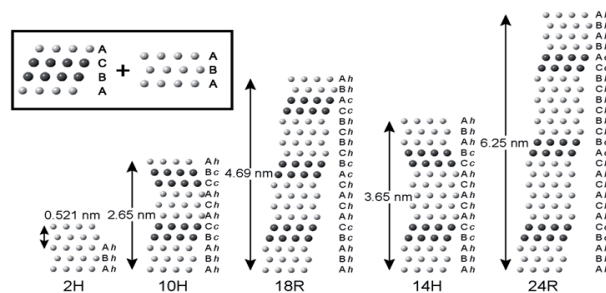


Fig. 1 Stacking polytypes of LPSO phases

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Keywords: magnesium alloys, crystal structure, electron microscopy

MS44.P02

Acta Cryst. (2011) **A67**, C518-C519

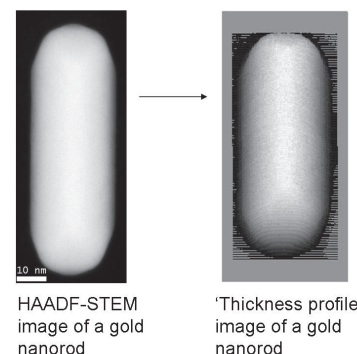
A Method to Determine the 3D Morphology and Crystallography of Nanoparticles

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Nanocrystals have unique properties which are different from the bulk material and strongly dependent on their morphology and crystallography. Characterising the morphology and crystallography is important for understanding the relationship between shape and properties and for determining the mechanism controlling nanocrystal growth.

In this paper we describe a rapid method to measure the thickness profile of a nanoparticle from a single annular dark field scanning transmission electron microscope (ADF-STEM) image [1]. This method deliberately uses ADF-STEM images just below lattice resolution, to enable relatively fast image quantification and measurement but at the expense of spatial resolution. Our focus here is on speed, to provide scientists working on nanocrystals a route to make a meaningful statistical comparison of the shape and properties of a large number of particles in a practical timeframe.

We have applied this



method to determine the surface crystallography of single crystal gold nanorods grown in the presence of Ag and found that, contrary to the current consensus, the surface facets are sparsely packed atomic planes [2]. This result has profound implications for understanding nanocrystal growth and morphology and forces a reconsideration of established theoretical models of nanoparticle growth.

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Keywords: quantitative scanning transmission electron microscopy, thickness profile determination, gold nanorods morphology.

MS44.P03

Acta Cryst. (2011) **A67**, C519

Real space charge density mapping by quantitative convergent beam electron diffraction (QCBED)

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Quantitative energy-filtered convergent beam electron diffraction (QCBED) can be used to measure the low order structure factor amplitudes and phases of microcrystals of known structure very accurately. This TEM-based technique uses a small electron probe of nanometer dimensions, so that a perfect crystal region can be selected for electron diffraction. It refines structure factors, absorption and specimen thickness using multiple scattering calculations, and measures the structure factors on absolute scale. Thus, extinction corrections, absorption corrections and scaling problems are avoided in electron diffraction. For non-centrosymmetric crystals, the refinement of charge density maps requires highly accurate measurements of structure factor phases, which can now also be measured using the QCBED method [1-3]. Electron diffraction is much more sensitive to ionicity at low scattering angles than X-ray diffraction [3], making it more suitable for charge-density mapping and the imaging of bonds. The accuracy is equivalent to that of the X-ray Pendulösung method [4-5], allowing the covalent and ionic contributions to be separately visualised.

Accurate structure factors of Cu, GaN and AlN have been measured by QCBED. The measurement standard deviations are normally less than 0.2% for both amplitudes and phases of low order structure factors. Accurate charge density maps have been obtained and the bonding character has been studied. Multipole refinement on Cu supports a free electron model [5]. Polar covalent bonds in Ga-N and Al-N are observed in experimental charge density maps, using multipole refinement of combined measurements of structure factor magnitudes and phases [1-2].

Supported by DOE award DE-FG03-02ER45996

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Keywords: quantitative convergent beam electron diffraction (QCBED), real space charge density, bonding

MS44.P04

Acta Cryst. (2011) **A67**, C519

Direct measurements of lattice distortion and mapping of point defects

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Recent advances in transmission electron microscopes (TEM) have enabled detection of light atoms, even the lightest hydrogen atomic columns, which have scattering strength too weak to be detected by non-aberration corrected TEM.[1] The detection limit of the state-of-the-art TEM/scanning TEM (STEM) has been tested in diverse systems; for example, identifying single light atom such as nitrogen and boron, and probing charge redistribution by chemical bonding [2-3]. Image simulations in those reports were essential to verify the experimental results. In fact, low signal to noise ratio in extreme measurements often requires substantial data processing as well as significant amount of experimental data.

Here, we present image and diffraction simulations to access the feasibility of detecting structural defects in a crystal such as point defects and static displacements. It is well known that local strain fields by structural defects enhance contrast in images. We exploited first-principles calculations to find relaxed structures of a crystal with point vacancies as well as a crystal with a structural distortion caused by strain in complex oxides. The multislice method was employed to simulate STEM images and convergent beam electron diffraction patterns of both the relaxed structures and non-relaxed structures. Adjusted parameters include convergence angles, focal depths, and scattering angles. Furthermore, the contribution of bonding charges to the images was examined by comparing simulation results using projected potentials from the first-principles calculations and using conventionally used atomic potentials.

Image simulations on strained oxide materials with tetragonal distortion, such as NdNiO₃, were applied for structural analysis. We used an aberration corrected microscope for atomic-resolution STEM images, and performed quantitative analysis of the image to extract structural parameters. The results were compared with the first-principles calculations, which indicated reliability of this approach.

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Keywords: aberration correction, atomic resolution imaging, multislice simulations

MS45.P01

Acta Cryst. (2011) **A67**, C519-C520

Vapour induced transformations investigated by powder diffraction analysis

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Solvent vapour exposure on the organic crystalline materials often induces pseudo-polymorphic transformations (solvation, solvent exchange and desolvation). Such transformations have potential to improve and/or control the solid-state properties of the target materials and are important phenomena in the field of material science. However, such transformations have not been completely understood because of