

MS60.28.3*Acta Cryst.* (2005). **A61**, C79**Structural Studies of Nanocrystalline Metals**Radomír Kužel, *Faculty of Mathematics and Physics, Charles University, Praha, Czech Republic.* E-mail: kuzel@karlov.mff.cuni.cz

Microstructure of metals (Cu, Fe, Mg, Cu with Al₂O₃) obtained by high-pressure torsion and its evolution with post annealing was studied by conventional powder diffraction in symmetric Bragg-Brentano geometry. This included evaluation of lattice parameters and texture but mainly line profile analysis in terms of both approximate modified Williamson-Hall method and total powder pattern (or multiple line profile) fitting [1-3]. Typical line-broadening anisotropy was explained by dislocation line broadening and elastic anisotropy. Dislocation density in the order of 10¹⁵ m⁻² and crystallite size (~ 50 - 500 nm) were determined. The method was completed by X-ray film technique (area detection), diffuse scattering in the transmitted wave, transmission electron microscopy and life-time positron annihilation spectroscopy. Common features and differences for the microstructure evolution of studied metals are discussed.

Films made of small amount of colloidal Au nanoparticles prepared with pre-calculated size were investigated in parallel beam geometry. The diffraction line profile analysis also revealed strong line broadening anisotropy and indicated not only small crystallite size but also the presence of stacking faults and dislocations. The results were confirmed by conventional and high-resolution TEM and UV/vis spectroscopy

[1] Scardi P., Leoni M., *Acta Cryst.*, 2002, **A58**, 190-200. [2] Scardi P., Leoni M., Dong Y.H., *Eur. Phys. J.*, 2000, **B18**, 23-30. [3] Ribárik G., Ungár T., Gubicza J., *J. Appl. Cryst.*, 2001, **34**, 669-676.

Keywords: powder diffraction, line profile analysis, severe plastic deformation

MS60.28.4*Acta Cryst.* (2005). **A61**, C79**Size Anisotropy and Lognormal Size Distribution in the Powder Diffraction Whole Pattern Fitting**

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The approach developed by Popa and Balzar [1] to model the size broadening in powder diffraction patterns by samples with lognormal size distribution of spherical crystallites can be easily extended to include size anisotropy if the crystallite shape is approximated by an ellipsoid.

In comparison with the existing approaches using ellipsoids to describe the size anisotropy, this approach uses a peak breadth symmetrized according to the crystal Laue class.

The proposed model was tested on a zinc oxide diffraction pattern measured in a Bragg – Brentano geometry. The model is compared with the previously proposed model using spherical harmonics to describe the size anisotropy [2].

[1] Popa N. C., Balzar D., *J. Appl. Cryst.*, 2002, **35**, 338-346. [2] Popa N. C., *J. Appl. Cryst.*, 1998, **31**, 176-180.

Keywords: powder diffraction, size effect, anisotropy

MS60.28.5*Acta Cryst.* (2005). **A61**, C79**Development of a NIST SRM 1979 Nano-Crystallite Size Standard for Broadening of X-ray Line Profiles**

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The development of traceable material standards is critical in the advancement of nano-technology. A NIST nano-crystallite size Standard Reference Material (SRM) 1979 has been developed for this very purpose, assuring improvement in the measurement accuracy of the size distribution and shape of nano-crystallites from X-ray line profile analyses and electron microscopy techniques.

SRM 1979 will consist of two materials prepared with the use of flow reactor technology to permit large, 1 kg batches. Production methods were chosen to minimize the presence of structural defects that may contribute to line broadening. The first material sample is ceria (cerium (IV) oxide, CeO₂) with an (approximate) average spherical crystallite size of 20 nm over a size range of 5–35 nm. The second is zinc oxide (ZnO) with approximately cylindrical crystallite morphology of 80 nm and a size range of 60–100 nm.

The certification of the SRM has also seen the development of a Bayesian/maximum entropy method. This analysis takes full account of the form of the instrumental, background and statistical noise contributions embedded in the diffraction data. As well as providing the most probable solution, the method produces a full error analysis of the size distribution—a critical element in certifying SRM 1979.

The X-ray analysis presented here will be compared with the results of direct observations of SRM 1979 using TEM imaging, and a discussion based on this comparison will be presented.

Keywords: nanocrystallites, standard reference material, line profile analysis

MS61 STRUCTURES PHASE TRANSITIONS AND PROPERTIES AT HIGH PRESSURE

Chairpersons: Mohammed Mezouar, Nozomu Hamaya

MS61.28.1*Acta Cryst.* (2005). **A61**, C79**Single Crystal Studies of the Incommensurate Composite Structure of Rb-IV**

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A number of elements have recently been shown to have a composite incommensurate high pressure phase. This phase has a so called 'host-guest' structure type comprising a tetragonal 'host' framework with channels along the fourfold c axis. Within these channels are 1D chains of atoms that form a 'guest' structure that is incommensurate with the host. We have observed host-guest structures in the alkali and alkaline-earth metals Rb, Sr, Ba, and in the group Va elements Bi, Sb and As [1]. Among these elements Rb is unique in having a 16-atom host structure, and transition to a disordered phase comprising liquid-like guest chains [2].

The 1D guest chains in Rb-IV are more than 7 Å apart [3], and this raises the question as to the nature of the host-chain and chain-chain interactions in the ordered phase, and how this interaction weakens or vanishes at the transition to the disordered phase. The strength of the host-chain interaction can be inferred from the intensity of the *hk*lm modulation reflections. Although these extremely weak reflections could not be detected with the powder techniques used previously to determine the structure of Rb-IV [3], they should be detectable using single crystal methods. In this talk I will present new results on the full modulated structure of Rb-IV using x-ray diffraction data collected from high quality single crystals of Rb-IV at ~18GPa.

[1] McMahon M.I., Nelmes R.J., *Z. Kristallogr.*, 2004, **219**, 742-748. [2] McMahon M.I., Nelmes R.J., *Phys. Rev. Lett.*, 2004, **93** (5), 055501. [3] McMahon M.I., Rekhi S., Nelmes R.J., *Phys. Rev. Lett.*, 2001, **87** (5), 055501.

Keywords: rubidium, incommensurate composite structure, high-pressure crystallography

MS61.28.2*Acta Cryst.* (2005). **A61**, C79-C80**Structural and Vibrational Studies of Solid Ammonia to 120 GPa**

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Like water, ammonia is a major member of the group of simple hydrogen-bonded molecular ices. The study of its high-pressure properties is first of natural interest due to its abundance in the solar system, like in the Jovian planets. Ammonia also presents a fundamental interest in condensed-matter physics as an H-bonded solid. Hydrogen bonds are weaker in ammonia than in water since 3 H atoms share a single lone pair. Whereas the symmetric state of water ice has been observed experimentally, the symmetrization path in ammonia appears more complicated. Actually, the phase diagram is barely known above 10 GPa. The solid transforms to the orthorhombic phase IV above 4 GPa; the presence of new phases has been suggested by Raman [1], Brillouin [2] and IR [3] experiments. But these results are confusing — what are the transition pressures ?, and incomplete — what is the nature of these new phases ?

We have conducted X-ray diffraction experiments up to 120 GPa and polarized Raman scattering on single crystals up to 70 GPa at low temperature. The use of single crystals allowed us to observe for the first time both very weak diffraction peaks and Raman modes and follow their evolution with pressure. Comparison between NH_3 and ND_3 showed significant isotopic effects.

[1] Gauthier, et al, *Phys. Rev. B*, 1988, **37**, 2102-2115. [2] Gauthier, et al., *Sol. State Comm.*, 1988, **68**, 149. [3] Sakashita, et al, *Rev. High Pres. Sc. Tech.*, 1998, **7**, 796-798.

Keywords: ammonia, high-pressure XRD, raman spectroscopy

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Phase Transitions in Transition Metal Monooxides: Interplay Between Structural, Magnetic, and Electronic Properties

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The iron monoxide Fe_{1-x}O (wüstite) is an important member of the highly correlated transition metal monoxide group which includes NiO , CoO , and MnO , and is also an end-member component of the $(\text{Mg,Fe})\text{O}$ solid solution, the most abundant non-silicate oxide in the Earth. At ambient conditions wüstite exists in a cubic fcc-based rock-salt structure with a nonstoichiometric formula Fe_{1-x}O . At low temperatures a rhombohedral distortion of the cubic cell is known to occur as believed to be driven by antiferromagnetic ordering. A strong C_{44} elastic constant softening is also observed in the same temperature range. At high pressures the cubic-to-rhombohedral phase transformation occurs in FeO , and C_{44} mode softening also exists at high pressures. Elastic mode softening was assigned to a strong magneto-elastic coupling in FeO . We conducted combined high-pressure and low- and high-temperature X-ray and neutron diffraction, Mössbauer spectroscopy, and ultrasonic interferometry study of FeO , FeO-MgO solid solutions, and MnO . We revealed decoupling of magnetic ordering and structural distortion in nonstoichiometric FeO in a wide temperature (up to 1100 K) and pressure (over 100 GPa) range. For MnO we observed strong correlation between magnetic ordering and structural transition at ambient pressure and could not distinguish Neel (TN) and structural transition (TS) temperatures within experimental uncertainties. The pressure dependence of TN and TS in MnO , however, is different at elevated pressures, like in the case of FeO . Cubic-to-rhombohedral phase transition was observed for ferropericlase $\text{Mg}_0.8\text{Fe}_0.2\text{O}$ at about 40 GPa and no transformation was observed in $\text{Mg}_0.95\text{Fe}_0.05\text{O}$ at pressures up to 80 GPa. The existence of a rhombohedral distortion in ferropericlase with mantle composition at high pressures coupled with the absence of magnetic ordering has important implications for the interpretation of seismological data with respect to Earth lower mantle inhomogeneity.

Keywords: high-pressure, magnesiowüstite, phase transitions

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Successive Alternation of the Propagation Direction of the Inner Shell ordering by Pressure in a Cd-Yb 1/1 Approximant Crystal

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Cd_6Yb crystal, an approximant crystal of a binary quasicrystal of a Cd-Yb alloy, consists of a new type of atomic clusters that lack a partial icosahedral symmetry [1, 2]. The first inner shell of Cd_4 , which has a tetrahedral shape instead of the typical icosahedral symmetry, is orientationally disordered at ambient pressure and temperature [2]. Single crystal synchrotron X-ray diffraction measurements revealed that the Cd tetrahedron exhibits various types of structural ordering sensitive to pressure and temperature. Four ordered phases appear in a P - T span up to 5.2 GPa and down to 10 K. The propagation direction of ordering alternates from [110] to [111] near 1.0 GPa and again to [110] at 3.5-4.0 GPa. The primarily ordered structures that appear between 210-250 K over a pressure span of 1-5.2 GPa further transform to finely ordered ones by cooling to 120-155 K. Super lattice reflection intensity measurements show that the structural transitions to primarily and finely ordered phases are driven by long and short-range interactions, respectively.

[1] Tsai A. P., Guo J. Q., Abe E., Takakura H., Sato T. J., *Nature*, 2000, **408**, 537. [2] Takakura H., Guo J. Q., Tsai A. P., *Philos. Mag. Lett.*, 2001, **81**, 411.

Keywords: high-pressure phase transformations, quasicrystals, synchrotron X-ray diffraction

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Combining Laue Diffraction with White-beam Single-crystal EXAFS

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Polychromatic radiation has been used in high pressure x-ray diffraction studies for almost two decades, but has never been demonstrated to be competitive with monochromatic experiments in terms of applicability of its results in full structure determination. This presentation will summarize the outcomes of new development efforts located at the HPCAT 16BMB beamline of APS. It will be shown that by combining the experience and ideas from such fields as high-pressure crystallography, protein Laue crystallography, microdiffraction, and EXAFS, new crystallographic methods, offering unique advantages and optimized for high pressure applications, can be developed.

Transition elements control the oxidation-reduction process and magnetism of the Earth. The theoretically predicted and observed magnetic collapse in Fe_2O_3 and other Fe-containing oxides are usually associated with distortive structural transitions that can be definitively understood only by high-pressure SXD. Moreover, since conventional XRD techniques are not sensitive enough to detect continuous electronic transformations, such as spin crossover, complementary information from techniques such as conventional and synchrotron Mossbauer spectroscopy, X-ray emission spectroscopy or EXAFS, is needed. In our white beam SDX experiments diffraction data are obtained at the same time as x-ray absorption near-edge information, providing additional information about the local environment of individual ions as well as their spin state. As examples, data obtained for Cr_2O_3 and $(\text{Fe,Mg})\text{O}$ will be demonstrated.

Keywords: phase transitions, spin crossover, polychromatic diffraction