

## 12-Amorphous, Imperfectly Ordered and Quasi-periodic Materials

forms of Mössbauer diffraction spectra also occur due to interference. So we suppose a possibility to separate the quadrupole doublets in the Mössbauer spectra. The only problem for realization of the method is the necessity to have a single crystal sample with quasicrystal structure, enriched in the Mossbauer isotope  $^{57}\text{Fe}$ .

### 12.02 - Disordered Materials

**DS-12.02.01** ELECTRON DIFFRACTION AND MICROSCOPY OF DISORDERED SOLIDS. By J.M. Cowley, Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287-1504, USA

For both high resolution electron microscopy and electron nanodiffraction, possibilities exist for the derivation of information of ordering in thin films when the correlation lengths are in the difficult range of 1-3nm. These possibilities may be enhanced by holographic methods but are essentially limited in that they give data only on two-dimensional projections of three-dimensional disordered structures. Nanodiffraction, using electron beams of diameter 1nm or less in a scanning transmission electron microscope, used in association with various imaging modes, has proved useful for studying many poorly ordered systems. The structures of small metal catalyst particles and their crystallographic relationship to the supporting material have been found. It has been shown that the local symmetries of quasicrystalline materials persist when the material is almost amorphous. It has been found that the multi-layer walls of carbon graphite nanotubes may be cylindrically bent or may have near planar regions and certain regions of hexagonal or rhombohedral ordering or may be heavily disordered with mutual translations and rotations of the carbon sheets.

**DS-12.02.02** MEASUREMENT OF DISPLACEMENT PAIR CORRELATIONS IN CRYSTALLINE SOLID SOLUTIONS BY ANOMALOUS DIFFUSE X-RAY SCATTERING.\*  
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The measurement of near-neighbor pair correlations in crystalline solid solutions from diffusely distributed intensity gives us a description of the local chemical order and atomic displacements. Measurements made at multiple x-ray energies provide changes in contrast to separate the chemical order and displacements into their individual values for the various chemical pairs (AA, AB, BB). Results are presented for binary alloys where anomalous scattering has been used to change the real part of the anomalous scattering factor of the constituent atoms. For binary alloys with elements of similar atomic number, sufficient change can be obtained to reverse the contrast from the first-order static displacements. X-ray energies can also be chosen to make the scattering factor difference between the two elements practically zero to provide for the effective removal of thermal scattering. Thus, the Laue scattering can be recovered and the individual pair correlations separated. Several Ni-Fe alloys have been measured from the Ni rich to the Invar composition. Insights to the magnetic behavior of these alloys are discussed in terms of the interatomic distances between atom pairs.

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**DS-12.02.03** A THREE-DIMENSIONAL (3D) MODEL FOR THE DIFFUSE SCATTERING IN CUBIC STABILIZED ZIRCONIAS. By T.R. Welberry\*, Research School of Chemistry, Australian National University, GPO Box 4, Canberra City, ACT 0200, Australia.

A position-sensitive detector (PSD) system has been used to make measurements of the diffuse X-ray scattering in a cubic  $\text{Y}_2\text{O}_3$  stabilized zirconia, ( $\text{Zr}_{0.61}\text{Y}_{0.39}\text{O}_{1.805}$ ), in far greater detail than has hitherto been reported. In addition to the fairly prominent diffuse peaks visible in [1 1 0] sections that have been the centre of discussion in many previous studies we see a number of other characteristic diffraction features.

We describe the development of a three-dimensional (3D) model which provides a simple explanation of virtually all the features that occur in the complex diffuse X-ray diffraction patterns. The model consists of two stages: a scheme for ordering the oxygen vacancies, followed by the relaxation of the cations around these vacancies. Monte Carlo simulation is used in both these stages, followed by direct computation of the diffraction patterns from the resulting lattice realisations. The model which at present best fits the observed scattering patterns is one in which the oxygen vacancies order in such a way as to avoid nearest neighbour  $\frac{1}{2}(1\ 0\ 0)$  pairs, next-nearest  $\frac{1}{2}(1\ 1\ 0)$  pairs and third-nearest  $\frac{1}{2}(1\ 1\ 1)$  pairs across empty cubes of oxygens, but allows third-nearest  $\frac{1}{2}(1\ 1\ 1)$  pairs across cubes of oxygens containing the cations. These vacancy-pairs, which essentially provide octahedral coordination of the enclosed cation, are therefore present almost entirely as either single isolated octahedra or neighbouring  $\langle 1\ 1\ 0 \rangle$  pairs of octahedra. A comparison of the diffuse patterns with those from a calcia stabilized zirconia is also made.

**DS-12.02.04** DISORDER IN NON-STOICHIOMETRIC OXIDES:  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{LiNbO}_3$ . By F. Frey and H. Boysen\*, Institut f. Kristallographie, Universität München, Germany.

Many technologically important properties of oxide materials such as ionic conductivity, mechanical strength, ageing behaviour etc. are strongly influenced by deviations from stoichiometry and the underlying disorder. Although the most direct information about the defects and their correlations is obtained from diffuse scattering valuable information may be obtained from Bragg scattering too. From a careful analysis of site occupations and temperature factors, including anharmonic terms, and the corresponding probability density functions (pdf) the atoms involved in the disorder may be identified and their (average) displacements be determined. The temperature dependence of the B-factors helps to distinguish between static and dynamic disorder.

Zirconia,  $\text{ZrO}_2$  doped with various amounts of oxides like  $\text{CaO}$ ,  $\text{Y}_2\text{O}_3$  etc. is a particularly interesting example due to its wide range of applications. The doping leads to the stabilization of the (high temperature) cubic (fluorite) and tetragonal (distorted fluorite) polymorphs, the creation of vacancies on the oxygen lattice and an enhanced anionic (oxygen) conductivity. A quantitative analysis of the diffuse scattering in single crystals of (cubic) CSZ ( $\text{Zr}_{1-x}\text{Ca}_x\text{O}_{2-x}$ ,  $0.07 \leq x \leq 0.15$ ) up to 1750 K revealed two types of correlated microclusters based on single and double O-vacancies with relaxed neighbours. These clusters lead to an immobilization of the oxygens and in turn a reduced conductivity. Around 1300 K the number of clusters decreases (without dramatic changes in the correlation) in agreement with an increasing conductivity in this temperature range. A similar behaviour was observed in powders with additional weak and broadened superlattice peaks indicating the distortion of a sublattice with correlation length of about 30 Å. After annealing for several weeks precipitates of the so called  $\Phi_1$ -phase develop, i.e. the

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defect structures are only metastable which is important for the long time use of these materials.

In spite of a lower concentration of vacancies (tetragonal) Y-TZP ( $Zr_{1-2x}Y_{2x}O_{2-x}$  with  $x \approx 0.03$ ) shows superior conductivity at temperatures below 1000 K, roughly. This is related to a more random distribution of the defects. In addition, the diffusion pathways as determined from pdf-maps differ appreciably in both materials being slightly more favourable in TZP (where they are restricted to certain double layers) mainly due to the more favourable arrangement of the atoms in the tetragonal structure. The conductivity can be further enhanced by alloying with Ti or Ce which may again be related to an increasing "tetragonality" (c/a ratio, z(O) parameter).

Although similarities with zirconia are present in ceria ( $Ce_{1-2x}Y_{2x}O_{2+x}$ ,  $0 \leq x \leq 0.1$ ) the disorder is more complex as evidenced by additional weak superlattice peaks which may be assigned to certain substoichiometric phases  $CeO_{2-y}$ . Moreover, the disorder depends on preparation conditions and changes with temperature.

In  $LiNbO_3$  (and isotopic  $LiTaO_3$ ) deviations from stoichiometry occur without alloying with other atom species. New structure refinements disagree with previously reported disorder models: no vacancies on the Nb lattice, excess Nb on Li sites with corresponding Li vacancies. At high temperatures Li becomes mobile leading to an order-disorder phase transition at 1480 K. Diffuse planes perpendicular to (-221) are assigned to uncorrelated Nb-O-Nb chains as identified from a static contribution to the corresponding temperature factors. Intensity concentrations at low temperatures (25 K) indicate the onset of short range order correlations.

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### DS-12.02.05 Diffuse Scattering from the Organic Conductor $C_1TET - TTF.(AuI_2)_{2/3}$ .

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The sample is electrochemically prepared with a constant current of  $25 \mu A$  at  $25^\circ C$  in a 1,1,1-trichloroethane/ acetonitrile solution of  $C_1TET - TTF$  (Bis(methylthio)ethylenedithio-TTF, a hybrid molecule between  $BEDT - TTF$  and  $TTC_1 - TTF$ ) and tetrabutylammoniumdiiodoaurate. The crystals are very brittle little black bars.

X-ray diffraction intensity data of a single crystal of  $C_1TET - TTF.(AuI_2)_{2/3}$  were collected with graphite monochromatized radiation on an Enraf Nonius CAD4F diffractometer, all reflections with  $h$  odd being weak. The spacegroup is  $P2_1/c$  with  $a = 7.54 \text{ \AA}$ ,  $b = 22.45 \text{ \AA}$ ,  $c = 11.67 \text{ \AA}$ ,  $\beta = 100.14^\circ$ ,  $V = 1945.2 \text{ \AA}^3$  and  $Z = 4$ , one unit being  $C_{10}H_{10}S_8(AuI_2)_{2/3}$ . The structure was solved and refined with DIRDIF and Xtal 3.0 software packages. Final conventional refinement gives  $R = 0.065$ ,  $wR = 0.055$  and  $S = 2.988$ .

The structure consists of ordered organic residuals forming zigzag layers parallel (100), leaving channels along [100] and disordered gold-iodine chains within these channels. In the average structure the disorder shows up as very large temperature factor parameters of gold and iodine in the chain direction, fractional occupation numbers and unphysical distances between peak positions ( $\approx 1 \text{ \AA}$ ). Rotation photographs on a Weissenberg camera show diffuse planes perpendicular to the a-axis with h-indices 0.8, 1.6, 2.4 and 3.2. The planes consist of diffuse peaks superimposed on slowly varying greyness. The diffuse scattering can be explained by a tentative model with independent chains of four  $(AuI_2^-)$ -ions per five times the a-axis length. More results will be presented in detail.

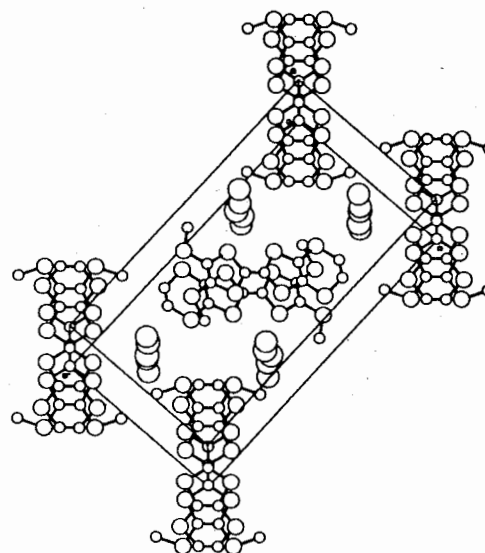


Fig. 1. The structure of  $C_1TET - TTF.(AuI_2)_{2/3}$ .

### DS-12.02.06 X-RAY DIFFUSE SCATTERING STUDY OF DISORDERS IN ORGANIC CONDUCTORS AND SUPERCONDUCTORS by J.P. Pouget\*, Laboratoire de Physique des Solides (CNRS UA2), Université de Paris Sud, 91405 ORSAY, France

Electronic and structural properties as well as instabilities exhibited by quasi one dimensional (1D) conductors are very sensitive to disorders such as those created by irradiation or substitution. Disorder in particular induces electronic localization, suppresses the superconductivity and pins the  $2k_F$  spin and charge density wave (SDW and CDW respectively) modulations ( $k_F$  is the Fermi wave vector of the 1D electron gas). In spite of these dramatic effects there is only very few detailed studies of the structural modifications induced by the disorders in the different families of low dimensional organic conductors and superconductors.

Substitutional and orientational disorders present in the family of quasi-1D organic superconductors  $(TMTSF)_2X$  based on the tetramethyltetraselenafulvalene molecule and where X is monovalent anion like  $PF_6$ ,  $ReO_4$  have been characterized by simulations of their X-ray diffuse scattering