PS-12.01.37
THE STRUCTURE OF THE DOUBLE PEROVSKITE PB_2COWO_6 IN ITS INCOMMENSURATE PHASE

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This perovskite exhibits a sequence of phase transitions from cubic (T > 300K) to orthorhombic symmetry (T < 230K) including an incommensurate monoclinic phase in the range 300K > T > 230K. The satellites observed in this temperature range seem to be exceptional and therefore, a structural study of this particular phase has been initiated.

Up to now, only the structure of the cubic phase is known. The attempt to solve the orthorhombic phase and understand the reasons for its stability seems to be only possible through the knowledge of the monoclinic incommensurate phase. The results of the incommensurate structure analysis of Pb_2CoWO_6 is presented here from crystals prepared by the group of H. Schmid at the University of Geneva. All the specimens exhibit multiple domains and although their presence seems to handicap seriously the process of structure analysis, it appears that they play a key role in the resolution of the structure. The main reflections originating from the various domains are all superimposed ($\beta_{mono} \approx 90°$) whereas the satellites associated with each domain are well resolved.

Based on electron microscopy observations which assign a unique pair of satellites to each single reflection, X-ray diffraction intensities have been collected on a specimen exhibiting four domains. The unique monoclinic axis could thus be identified from the refinement based on main and satellite reflections. In addition, an anti-parallel displacement of the Pb atoms could be detected from the analysis of the incommensurate structure.

PS-12.01.38 CRYSTALLOGRAPHIC APPLICATIONS OF GENERALIZED BESSEL FUNCTIONS

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Recently a theory of Generalized Bessel Functions (GBF) has been developed. The number of theoretical results and applications derived from this new field is increasing rapidly. Numerical properties and algorithms to calculate GBF are being studied. Basic properties will be discussed and two possible applications in crystallographic computing will be presented. The analysis of incommensurate (IC) structures is computationally more difficult than of ordinary ones. This is mainly due to the structure factor expressions involving numerical integration or infinite series of ordinary Bessel Functions. Compact analytical expressions are known for special cases only. A possible application of the GBF in IC structure analysis is proposed. These functions can be used to derive analytical expressions for structure factors and their partial derivatives for a wide class of IC structures. The existing programs can be improved by taking into account some interesting numerical properties of these functions (e.g. recurrence relations, analytical expressions for derivatives, generating functions etc.). Bessel Functions are also widely used in crystallographic statistics to derive both exact and approximate probabilistic formulae in direct methods theory and applications. Recently, some novel expressions for joint probability density functions of several structure factors have been derived using exact random-walk techniques. Unit cell heterogenicity has also been taken into account in this new approach. Again, Bessel Functions have been the primary analytical tool. GBF can be used to derive new exact expressions for some joint probability density functions. The Σ_1 relationship in the space group $P\bar{1}$ is the first example. The classical approximate formulae can be derived using asymptotic properties of these new functions. We conclude that there exists a new class of special functions suitable for dealing with several crystallographic computing problems.

PS-12.01.39 NEW CONFORMATIONAL ASPECTS OF THE ODD-EVEN EFFECT IN THE STRUCTURE OF THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS BY X-RAY DIFFRACTION ANALYSIS

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It was observed that the structure and the thermal behaviour of thermotropic liquid crystalline polymers comprising a rigid core segment and a flexible spacer group in a repeating unit are strongly related to the odd-even number of methylene groups. In this paper, we propose a model of the molecular packing in the smectic phases, in correlation with the odd-even effect, for the two following series of polyesters:

C5Cn

BB-n
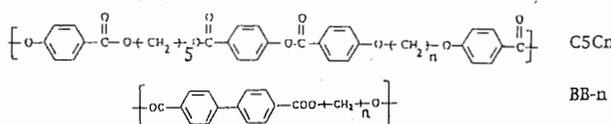
where n indicates the number of methylene groups. X-ray diffraction patterns of oriented fiber samples show that while the terms BB-n, with n even, exhibit a smectic A mesophase in which molecular chains are aligned normally to the smectic layers, all the other terms exhibit smectic C mesophases where the molecular chains are tilted of an angle $\cong 25°$ with respect to the layer normal.

The structural analyses of the polyesters were performed by using a computer program to fit the observed X-ray diffraction intensity data, the smectic layer thicknesses and molecular chain tilt angles starting from various theoretical molecular chain conformations. According to the results obtained , it can be concluded that:
1) the most likely conformation of methylene groups is of the TGT$\bar{G}$ type. Based on the nature of this conformation, the even number methylene groups dispose in line with mosogenic groups perpendicularly to the smectic layers and consequently exhibit a smectic A phase. Differently, in the odd number methylene terms, an angle of about 120° is formed between two adjacent mosogenic groups, hence the molecular chain gives rise to a zig-zag line along the smectic layer normal, thus resulting in a smectic C like structure.
2) For C5Cn , a shift of half the length of the repeating unit is present between two adjacent moleculear chains along the normal to the smectic layers.

This result gives a clear explanation of the reason why all the even membered terms form a smectic A like structure and odd membered series polyester form a smectic C like structure.

(1) B.YANG, X-ray diffraction study structure of thermotropic liquid crystals, Ph.D Thesis (1991)
(2) E. CHIELLINI et al., Mol. Liq. Cryst. 125, 279 (1992)
(3) W. R. KRIGBAUM et al., Macromolecules 16, 1271 (1983)

PS-12.01.40 ON THE POSSIBILITIES OF MÖSSBAUEROGRAPHIC STUDIES OF QUASICRYSTAL STRUCTURES.

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The Mössbauer spectroscopy studies, carried out for quasicrystals Al-Fe-Me (Me-Cu, Ni, etc.) have shown, that the spectra are a superposition of poorly resolved quadrupole doublets with very close parameters, corresponding to several nonequivalent positions of Fe nuclei. A problem of these doublets separation still exists. The Mössbauerography method (Mössbauer diffraction) can be useful for its decision. It was shown in our studies, that the interference of Mössbauer radiation scattering by nonequivalent Fe atoms leads to the specific forms of Mössbauer energy spectra. The line forms for constructive and destructive interference were calculated for the different distances between the resonances (P. P. Kovalenko et al., JETP, 1985, 88, 1336-1347). The interference effects were observed experimentally both for the magnetic (I. G. Tolpekin et al., JETP, 1988, 94, 329-343) and the quadrupole (I. G. Tolpekin et al., Phys. Lett. A, 1990, 147, 323-325) hyperfine structures in the diffraction scattering by the single crystal Fe_3BO_6. It has allowed to determine the only possible structures, composed by the magnetic fields and the Electric Field Gradients in the crystal. If a number of nonequivalent Fe positions will be more than two, the specific

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 Mössbauer isotope Fe^{57}.

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.

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 Y_2O_3 stabilized zirconia, $(Zr_{0.61} Y_{0.39} O_{1.805})$, 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 $\frac{1}{2}\langle 1\,0\,0\rangle$ pairs, next-nearest $\frac{1}{2}\langle 1\,1\,0\rangle$ pairs and third-nearest $\frac{1}{2}\langle 1\,1\,1\rangle$ pairs across empty cubes of oxygens, but allows third-nearest $\frac{1}{2}\langle 1\,1\,1\rangle$ 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: ZrO_2, CeO_2, $LiNbO_3$. 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, ZrO_2 doped with various amounts of oxides like CaO, Y_2O_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 $(Zr_{1-x}Ca_xO_{2-x}, 0.07 \le x \le 0.15)$ 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 Φ_1-phase develop, i.e. the