

12-Amorphous, Imperfectly Ordered and Quasi-periodic Materials

345

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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 ($\beta_{mono}=90^\circ$) 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 heterogeneity 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 $P1$ 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.

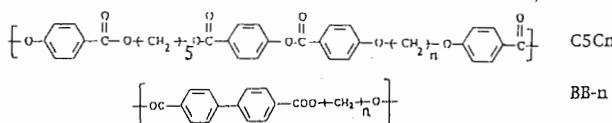
PS-12.01.39 NEW CONFORMATIONAL ASPECTS OF THE ODD-EVEN EFFECT IN THE STRUCTURE OF THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS BY X-RAY DIFFRACTION ANALYSIS

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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:



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 $\approx 25^\circ$ with respect 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 mesogenic 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 mesogenic 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 molecular 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. CHIPELLINI et al., Mol. Liq. Cryst. 125, 279 (1992)

(3) W. R. KRIGBAUM et al., Macromolecules 16, 1271 (1983)

PS-12.01.400N THE POSSIBILITIES OF MOSSBAUEROGRAPHIC 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_3B_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