12-Amorphous, Imperfectly Ordered and Quasi-periodic Materials

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THE STRUCTURE OF THE DOUBLE PEROVSKITE Pb₂CoWO₆ IN ITS INCOMMENSURATE PHASE

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The perovskite exhibits a sequence of phase transitions from cubic (T > 300K) to tetragonal (T < 280K) 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 and to 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 Pb₂CoWO₆ are presented here from crystals prepared by the group of H. Scherdel 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 (θₘ₀ₐₙ=9°) 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.

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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 polyesters comprising a liquid core segment and a flexible spacer group is 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 phase, in correlation with the odd-even effect, for the following series of polyesters:

\[ \text{C}_n \text{H}_{2n+2} \text{O} \cdot \text{C}_6 \text{H}_{26} \text{O} \cdot \text{C}_n \text{H}_{2n+2} \text{O} \cdot \text{C}_6 \text{H}_{26} \text{O} \cdot \text{C}_n \text{H}_{2n+2} \text{O} \]

where n indicates the number of methylene groups. X-ray diffraction patterns of orientated fiber samples show that with the terms C₃, with an even, exhibit a smectic A phase in which molecular chains are aligned normally to the smectic layers, all the other terms exhibit smectic C mesophases whereas the molecules of the same length are tilted of an angle 25° 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 T₀ type. Based on the nature of this conformation, the even number methylene groups dispose in line with monomeric group essentially in the smectic A phase and consequently exhibit a smectic A phase. Differently, in the odd number methylene films, at an angle of about 12° in front of the plane between two adjacent monomeric groups, the molecular chain gives rise to a zig-zag line along the smectic layer normal, thus resulting in a smectic C mesophase group.

2. For CₙCₙCₙCₙCₙ, 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 numbered terms form a smectic A like structure and odd numbered members polymer form a smectic C like structure.


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ON 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 solving. 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, 85, 1336-1347). The interference effects were observed experimentally both for the magnetic (I. G. Tolpekin et al., JETP, 1988, 84, 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 Fe₃B₆C₆. It has allowed to determine the only possible structures, compared with the magnetic fields and the Electric Field Gradient in the crystal. If a number of nonequivalent Fe positions will be more than two, the specific