

**MS10.04.02 OBSERVING AND UNDERSTANDING ARCS OF DIFFUSE SCATTERING FROM QUASICRYSTALS.**

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Localized arcs of diffuse scattering are caused by particular short-range correlations between bonded icosahedral clusters. They were observed in AlMn, the first quasicrystal discovered, after annealing. They were observed in the TiMnSi quasicrystal on the day of its discovery; in that material they appear with high contrast and their shapes and locations in reciprocal space were mapped in detail. Electron diffraction in the TEM, on selected planes in reciprocal space, produces two-dimensional images from which the full three-dimensional structure of the arcs can be inferred. X-ray diffraction has also been useful in observing the arcs, especially in materials in which their contrast is not as great as in TiMnSi. TEM investigations demonstrated that the disorder producing the arcs in TiMnSi is topological rather than chemical. Simulations of the scattering of waves from icosahedral glass models and from random canonical-cell tiling models contain arcs very similar to those observed. They can be traced to the contribution of nearest-neighbor icosahedral clusters to the pair correlation function. Improving the quality of the glasses (as assessed by the widths of the simulated diffraction peaks) with constraints that force a uniform, high density of clusters increases the contrast of the arcs in the simulations. In the best glasses weak diffraction peaks can be resolved within the arcs, like those sometimes seen in the measurements. Too-tight constraints produce a crystal structure, the 1/1 1.3-nm cubic approximant (a bcc cell with icosahedral clusters at the corner and body center sites). Local correlations in the glass like those in the 1/1 crystal phase are strongly suggested as the source of the arcs. Modeling of these quasicrystals as canonical-cell tilings has led to the same conclusion; indeed, a highly constrained glass is structurally identical to a random canonical-cell tiling. This role of local correlations has been confirmed in a pleasingly direct way in a simulation of the diffraction from polycrystalline 1/1 structure, in which only grain orientations for which the icosahedral clusters in the bcc phase could connect coherently across grain boundaries were allowed. With grain sizes of 1.3 nm, excellent agreement with the data was obtained.

**MS10.04.03 METHODS FOR AB INITIO STRUCTURE SOLUTION OF DECAGONAL QUASICRYSTALS**

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N-dimensional Patterson methods have been combined with the maximum entropy method for ab initio phase determination of decagonal structures [1].

To unravel the n-dimensional Patterson function the symmetry minimum function has been extended to the embedding dimensions. Given the n-dimensional space group this Patterson superposition method allows the positions of the hyperatoms to be located and a first crude structure model to be derived.

To retrieve the shape and chemical composition of the acceptance domain of each hyperatom, this procedure is combined with the maximum entropy method. This method is exclusively constrained by the positions of the hyperatoms in the n-dimensional unit cell and result of the symmetry minimum function in physical space. These constraints enforce quasiperiodicity and correct atomic distances can be easily implemented.

Applying the maximum entropy method in perpendicular space allows a detailed idealised decagonal structure model to be derived, as only solutions within the planes of the acceptance domains are possible. The physical space approach, however, provides the capability to determine more complex non-periodic structures as well as to introduce deviations from the ideal

quasiperiodic structures.

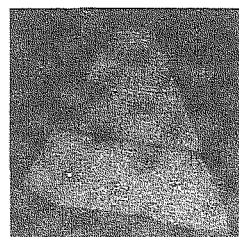
The combined algorithm has been tested on decagonal Al<sub>70</sub>Co<sub>15</sub>Ni<sub>15</sub>, where the existing structure model could be improved. The structure models of decagonal Al<sub>71</sub>Fe<sub>5</sub>Ni<sub>24</sub>, Al<sub>70.5</sub>Mn<sub>16.5</sub>Pd<sub>13</sub> (using multiple anomalous dispersion data) and Al<sub>80</sub>Os<sub>10</sub>Pd<sub>10</sub> will be presented.

- [1] Haibach, T, Steurer, W.: Five-dimensional Symmetry Minimum Function and Maximum Entropy Method for ab initio Solution of Decagonal Structures. Acta Crystallogr. A (1995) in press.

**MS10.04.04 DYNAMICAL X-RAY DIFFRACTION IN ICOSAHEDRAL Al-Pd-Mn QUASICRYSTAL.**

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Large size crystals of Al<sub>70</sub>Pd<sub>21.5</sub>Mn<sub>8.5</sub> were grown by the Bridgman method. Berg-Barrett topographs of a thick specimen showed three large grains approximately equal in size. Regions extending several mm<sup>2</sup> in size could be identified, over which the diffracted intensity was uniform, an indication of crystal perfection. The integrated intensity of several reflections was measured on an absolute basis with  $\lambda = 1.54 \text{ \AA}$  and the structure factor was extracted from the experimental value of the integrated intensity by making use of dynamical theory. Such procedure is justified by the fact that the rocking curves were extremely sharp ( $\approx 30$  arcseconds) and that anomalous transmission has been observed in similar samples (S.W. Kycia *et al.*, Phys. Rev. B48, 3544 (1993)). While good agreement is found between theory and experiment for the strong reflections, large discrepancies are observed for the weak reflections, which are more sensitive to the details of the atomic surfaces in 6D space.



Berg-Barrett topographic photo. Symmetric Bragg geometry;  $\lambda = 1.54 \text{ \AA}$ . Reflection excited:  $(0\ 2\ 4\ 0\ \bar{2}\ 4)$  on a two-fold axis, normal to the specimen surface. The dark circle is due to surface stain. The white lines are regions of strain.

**MS10.04.05 THE INCOMMENSURATELY MODULATED PHASES OF HEXAMINE DERIVATIVES.**

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Hexamine suberate, azelate and sebacate form layer structures with alternating sheets of hexamine and alkanedioic acid linked by H-bonds between N and O atoms. The acid molecules are totally extended with 6, 7 and 8 carbon atoms and an acid group at each end. They form a two-dimensional array with their axis inclined by 30° with respect to the layer normal.

At room temperature, hexamine suberate and sebacate (even number of carbons) are strongly modulated, as witnessed by satellite reflections up to the fourth, respectively sixth order. The modulations are very stable between 120 and 300K. Hexamine azelate (odd number of carbons) is commensurate. However, strong diffuse scattering observed on precession photographs reveals some disorder in the structure.

The two incommensurate compounds have been refined using the superspace group formalism. Displacive atomic modulations including up to eight harmonics lead to satisfactory models. The analysis of the refinements indicates that in a layer, the zig-zag

planes of the acid chains take essentially two orientations, forming an angle of approximately  $60^\circ$ . In addition, intermediate orientations lying within the two extremes are also observed. In the commensurate structure, the disorder originates from the acid chains which can take two possible orientations, with zig-zag planes forming an angle of  $180^\circ$ .

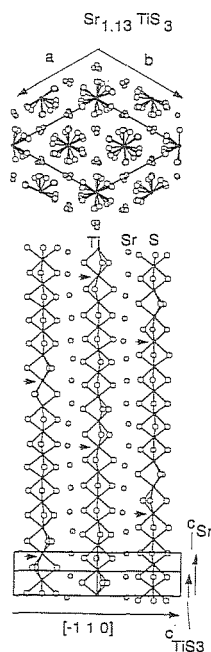
The origin of the incommensurability is most probably caused by the incompatible intrinsic packing of hexamine and acid molecules. In this hypothesis, the acid molecules must reorient themselves in order to fit in the extremely stable layers of hexamines. Molecular mechanic methods have been performed in a rigid framework of hexamines. A layer of suberic acid composed of parallel chains has been placed within this frame. The optimisation of the system leads to the features observed in the incommensurate structures. Simulations with a layer of azelaic acid molecules generates, however, a single set of orientations of the chains which are all parallel. This strongly support our hypothesis on the origin of the incommensurability.

**MS10.04.06 RIETVELD ANALYSIS OF INCOMMENSURATE COMPOSITE CRYSTALS  $Sr_xTiS_3$  ( $x=1.1-1.2$ ).** M. Onoda, M. Saeki, A. Yamamoto and K. Kato National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305, Japan

The structures of incommensurate composite crystals  $Sr_xTiS_3$  ( $x=1.1-1.2$ ) have been analyzed on the basis of a four-dimensional superspace group  $pR3_1m_s$  using the powder X-ray diffraction data and the Rietveld analysis process.

The trigonal composite crystal  $Sr_xTiS_3$  has the existence range of  $x=1.1-1.2$  according to the starting ratio of Sr/Ti in the synthesis process. All reflections including weak satellites could be indexed by four integers  $h, k, l$  and  $m$  with the reflection conditions  $-h+k+l=3n$  for  $hklm$  and  $m=2n$  for  $Oklm$ . Cell constants are approximately  $a_1=a_2=11.5$ ,  $a_3=c_{TiS_3}=3.0\text{\AA}$  and  $\sigma=(0\ 0\ c_{TiS_3}/c_{Sr})=(0\ 0\ 0.57)$ , and  $Z=3$ . The agreement of each Rietveld analysis was fairly good.

Fig. 1. Projections of the modulated structure.



**MS10.04.07 COMPOSITE MODULATED STRUCTURES IN ANION EXCESS FLUORITES.** Siegbert Schmid, Klaus Fütterer, John G. Thompson and Ray L. Withers, Research School of Chemistry, The Australian National University, Canberra ACT 0200, Australia

Wide range anion-excess, fluorite related solid solutions exist in the yttrium oxide fluoride, zirconium nitride oxide fluoride, zirconium niobium oxide and zirconium tantalum oxide systems, *i.e.*  $YO_{1-\Delta}F_{1+2\Delta}$ ,  $0.12 \leq \Delta \leq 0.22$ ,  $(ZrN_{1-\Delta/2-z}F_{\Delta/2-z}O_{2z})F_{1+\Delta}$ ,  $0.12 \leq \Delta \leq 0.25$ , and  $M_2Zr_{x-2}O_{2x+1}$  ( $M = Nb, Ta$ ),  $7.1 \leq x \leq 10.3$ . All of the above systems can be described as inorganic incommensurate intergrowth compounds or more precisely inorganic misfit layer compounds. Each consists of two chemically different layers that are stacked alternately. In every case one of the layers contains the metals or metals and anions whereas the second layer contains anions

only. The widths of these solid solutions are achieved by compressing the anion-only-substructure relative to the other when adding additional anions. It has been shown that such systems are best described as composite modulated structures with a continuously varying primary modulation wave vector of the more strongly scattering metal containing substructure that is linearly dependent on composition (metal to anion ratio). It is this structural flexibility which distinguishes the above systems from other misfit layer compounds that exist as line phases.

It will be shown that the refined atomic modulation functions (AMFs) which are used to describe these systems are remarkably similar despite the variability in composition. Furthermore it will be demonstrated that the attempt to refine structures in these systems as superstructures often leads to an order of magnitude increase in the number of refined parameters and a rather worse final R-value!

Bevan, D. J. M., Mohyla, J., Hoskins, B. F. & Steen, R. J. (1990). *Eur. J. Solid State Inorg. Chem.* **27**, 451 - 465.

Schmid, S. & Withers, R. L. (1996). *Aust. J. Chem.* (in press).

Thompson, J. G., Withers, R. L., Sellar, J., Barlow, P.J. & Hyde, B. G. (1990). *J. Solid State Chem.* **88**, 465 - 475.

**PS10.04.08 SIMULATION OF THE TEMPERATURE DEPENDENCE OF THE  $Rb_2ZnCl_4$  INCOMMENSURATE PHASE DIFFRACTION PATTERN.** I. Aramburu, G. Madariaga\*, J. M. Pérez-Mato\*, Dpto. Física Aplicada I. Escuela Técnica Superior de Ingenieros Industriales y de Telecomunicación, Universidad del País Vasco, Alameda de Urquijo s/n, 48013 Bilbao, Spain, \*Dpto. Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain

The temperature variation of the intensity of 1935 main reflections and 6991 satellites up to the 7<sup>th</sup> order within the incommensurate phase of  $Rb_2ZnCl_4$  has been simulated. The static structural modulation has been varied through the changes in 3 structural parameters: the amplitude of the primary mode, the soliton density and the amplitude of a third harmonic modulation. Contrary to what it is usually expected, the temperature dependence of main reflections shows a great variety of behaviours, due to the strong influence of the modulation first harmonic on some of them. In the case of satellites, the temperature variation of their intensities has been described through the "effective exponents"  $\beta_n(T)$ :  $I_n \approx t\beta_n(T)$ , where  $t = T - T_1$ . At every temperature, a great dispersion of values for the effective exponents of the satellites of the same order is obtained. This clearly prevents to obtain a direct information of the structural changes from the only knowledge of the  $\beta_n(T)$  for some selected reflections, as it has been sometimes assumed. Besides, the average values obtained for these effective exponents at every temperature and for each satellite order do not satisfy the simple relation  $\langle \beta_n \rangle \approx n \langle \beta_1 \rangle$ , either. Finally, the influence of the different distortions present in the static modulation on a standard refinement of the structure at a fixed temperature has been analyzed. In particular, it will be shown that the common assumption of taking as many harmonics in the structural modulation as the maximum order of satellites systematically measured may not always be the most appropriate.