

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  $180^\circ$ .

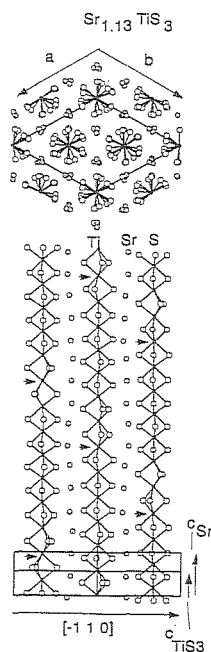
The origin of the incommensurability is most probably caused by the incompatible intrinsic packing of hexamine and acid molecules. In this hypothesis, the acid molecules must reorient themselves in order to fit in the extremely stable layers of hexamines. Molecular mechanic methods have been performed 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!

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**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 7th 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.