s3.m11.p5 **Structure of the incommensurate phase of ammonium tetrafluoroberyllate and the mechanism of the phase transition.** Lukás Palatinus[a] and Sander van Smaalen[b], [a]*Institute of Physics of the Academy of Sciences, Prag, Czech Republic, and* [b]*Laboratory of Crystallography, University of Bayreuth, 95440 Bayreuth, Germany. E-mail: palat@fzu.cz*

Keywords: Ammonium tetrafluoroberyllate; Modulated structure; Ferroelectric phase transition

Ammonium tetrafluoroberyllate $(NH_4)_2BeF_4$ has the β-K_2SO_4 type structure at room temperature. Below 175K a two-fold superstructure has been found [1]. Between 175 and 182K $(NH_4)_2BeF_4$ is incommensurate with a modulation vector of $q=(1/2-\delta, 0, 0)$, $\delta\cong0.02$ [2].

We have determined the incommensurately modulated structure of $(NH_4)_2BeF_4$ at T=176.5K [3]. Single crystal X-ray diffraction with synchrotron radiation was measured at HASYLAB (Hamburg). Structure refinements were performed in 3+1-dimensional superspace. The Maximum Entropy Method (MEM) was used to obtain a model-independent estimate of the modulation functions [3,4]. Furthermore the MEM was employed to study the electron density in the chemical bonds.

The modulation results in translations and rotations of the NH_4^+ and BeF_4^{2-} ions. These movements cause a shortening of the N-F and H-F distances. This indicates stronger interactions in the N-H…F hydrogen bonds compared to the non-modulated structure. This observation is in agreement with the low-temperature two-fold superstructure [5].

The low-temperature superstructure is ferroelectric. A model was proposed for the mechanism of the phase transition [2], stating that a modulated microscopic polarization is present in the incommensurate phase, while the macroscopic polarization develops at the lock-in transition to the ferroelectric phase. We show that the polarization corresponds to the second harmonic of the modulation functions, both in the commensurate and incommensurate phases. The microscopic polarization in the incommensurate phase then would give rise to observable second-order satellites. However, we have not found any observed second-order satellites in our experiment. Thus, our results indicate that the incommensurate phase contains no or extremely small microscopic polarization, in variance with the model in [2].

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s3.m11.p6 **Mechanism of Incommensurate Modulation in 4, 4'-Dichlorobiphenyl Sulfone.** Yuansheng Pan,[a] David Brown,[b] F. J. Zuniga[c] and Gervais Chapuis[a], [a]*Ecole Polytechnique Fédérale de Lausanne, Laboratoire de Cristallographie, BSP, 1015 Lausanne, Switzerland,* [b]*Laboratoire des Matériaux Organiques a Propriétés Spécifiques, UMR CNRS 5041, Université de Savoie, 73376 Le Bourget du Lac, France, and* [c]*Departamento de Fisica de la Materia Condensada, Facultad de Ciencias, Universidad del Pais Vasco, Apdo. 644, Bilbao, Spain. E-mail: Yuansheng.Pan@epfl.ch*

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The molecular solid 4, 4'-dichlorobiphenyl sulfone is a van der Waals crystal. It has been extensively studied by X-ray diffraction, neutron scattering, NMR, NQR and Raman spectroscopy owing to a phase transition from a commensurate to an incommensurately modulated phase occurring at 150 K. A molecular dynamics simulation was carried out with the MD program *ddgmq* and a consistent force field.

The MD simulation is able to reproduce the incommensurate phase in this compound. Diffraction patterns of simulated structures clearly show the same features as the experimental one with satellites up to higher order. In the incommensurate phase, the simulation results reveal a new structural mechanism which essentially consists of two displacive modulation waves acting on the molecules. The modulated waves consists of x- and z-displacements of the molecule position with wavelengths 10.6 resp. 5.3 times larger than the b axis. The combination of the two modulated waves can exactly reproduce all satellites as experiment.

The z-component of the modulated wave originates from interactions between O and H atoms from two neighboring molecules along z. The interactions between two terminal Cl and H atoms from two neighboring molecules induces the modulation with x-displacement along b. The two intermolecular interactions modify the bending angle resp. torsion angle of the two carbon rings. The two modulations derived from the MD simulation are in good agreement with the experimental data. Our simulation is not only able to reproduce well all the experimental details, it also provides structural details and mechanism of the dynamics of the incommensurate modulation.

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