Modulation functions of incommensurate Rb$_2$ZnCl$_4$
include modulated anharmonic ADPs

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Rubidium tetrachlorozincate, Rb$_2$ZnCl$_4$, belongs to the class of A$_2$BX$_4$ ferroelectric compounds with the $\beta$-K$_2$SO$_4$ structure type at high temperatures. A phase transition from a periodic to an incommensurately modulated phase occurs at $T_{\text{inc}} = 303$ K with a modulation wave vector of $q = (0, 0, 1/3 - \delta)$ ($\delta \approx 0.02$). A lock-in transition towards a threefold superstructure ($\delta = 0$) takes place at $T_{\text{lock-in}} = 192$ K [1]. In first approximation, the modulation of Rb$_2$ZnCl$_4$ can be described by sinusoidal displacement waves [2]. On approaching the lock-in transition, the modulation increasingly deviates from this shape, as it has been evidenced by the growth of the intensities of higher-order satellite reflections in the X-ray diffraction of this compound on cooling toward $T_{\text{lock-in}}$. Anharmonic displacement modulation functions close to the lock-in transition have been studied by X-ray diffraction by Aramburu et al. [1].

We have re-analyzed the incommensurate structure of Rb$_2$ZnCl$_4$ close to the lock-in transition, with the purpose of investigating the nature of the modulations by means of the maximum entropy method (MEM) [3]. Based on a combination of structure refinements and the analysis of MEM-densities and difference Fourier maps, we have shown that modulations of atomic displacement parameters (ADPs) and modulations of anharmonic ADPs form an intrinsic and important part of the modulation of Rb$_2$ZnCl$_4$ at $T = 196$ K, close to the lock-in transition [4].

X-ray diffraction experiments were performed at beamline F1 of Hasylab, DESY, Hamburg, employing radiation of a wavelength of 0.5000 Å and a MAR-CCD area detector. A large crystal-to-detector distance of 225 mm was chosen, in order to be able to resolve closely-spaced reflections. Multiple runs with different off-sets were required, in order to obtain a complete data set up to $[\sin(\theta)/\lambda]_{\text{max}} = 0.86$ Å$^{-1}$. The effective dynamic range of the experiment was increased by measuring with three exposure times of 2, 8 and 64 seconds per image, respectively. Integrated intensities of Bragg reflections were extracted from the measured images by the software EVAL15 [5]; absorption correction was performed with SADABS [6]. The resulting data set of intensities of Bragg reflections—including satellite reflections up to fifth order—was used for structure refinements with JANA2006 [7] and maximum entropy calculations with BAYMEM [3]. Diffraction images with the longest exposures contain heavily overexposed main reflections. Nevertheless, only 237 out of 3549 fifth-order satellite reflections were larger than 3 times their standard uncertainties (‘observed’). More increased overexposure does not seem feasible with CCD detectors. Therefore, future beamlines at PETRA equipped with PILATUS detectors will give the opportunity of measuring such weak scattering effects, maybe even including satellites of still higher orders, then providing conclusive evidence for the true nature of modulation functions.

Structure models in the present analysis always included basic-structure coordinates and harmonic atomic displacement parameters (ADPs) for each of the six crystallographically independent atoms. Model A included all Fourier coefficients up to fifth order for the displacement modulation functions. This model corresponds to the model published in [1]. The best structure model was denoted as $D_r$. It included modulated ADPs and modulation functions for anharmonic ADPs of third order as well as basic-structure anharmonic ADPs of fourth order.

Evidence for modulated anharmonic ADPs of odd orders comes from the MEM electron density maps. Figure 1 shows the difference between the location of a local maximum in the MEM map
Figure 1: Selected modulation functions, $u_y$[Cl1] and $u_x$[Rb1]. Filled circles are the trace of local maxima in the MEM electron-density map; open circles are the trace of the corresponding center-of-charge. The displacement modulation functions are represented by full lines for model $A$, and by dashed lines for model $D_r$. Reprinted from [4].

and the average position of the atom in the model. This trace (filled circles) may vary wildly around the trace (open circles) corresponding to the center of charge around each local maximum. It is known that the center-of-charge does not coincide with the maximum of the density in case of odd-order anharmonic displacements. Therefore, we have taken the observed signature of the MEM densities as evidence for modulated anharmonic ADPs, as it was subsequently confirmed by structure refinements. Figure 1 also compares the modulations obtained from the MEM with the displacive modulations of the models. In model $D_r$, the displacive modulation function coincides with the trace of the center-of-charge in the MEM-map, thus confirming the above interpretation. The missing modulations of ADPs in model $A$ apparently are compensated by additional, unphysical displacement modulations of the atoms (compare left and middle panels).

These results should be compared to those in Ref. [1]. Aramburu et al. [1] have measured satellite reflections up to fifth order with a point detector, employing the four-circle diffractometer at beamline D3 of Hasylab. They measured only a limited number of reflections, which were selected by choosing those reflections that were expected to be strong satellites on the basis of a soliton model. The resulting data set (Aramburu data) consists of much fewer reflections than available in the present data. Based on a refinement like model $A$, it was concluded that the data were in agreement with a soliton model for the modulation [1]. The present analysis could not confirm this interpretation, probably because (i) the present data includes observed reflections not measured in [1], and (ii) the introduction of modulated (an)harmonic ADPs has lead to a different model for the displacive modulation than that used in Ref. [1].

References