Zintl phases have attracted the attention of chemists and physicists due to their peculiar type of bonding: The generally accepted characteristics of Zintl phases is a unique hybrid bonding with covalent, metallic, and ionic contributions. Prototypic examples are the 7 binary alloys with NaTl-type structure [1, 2]. Recently, we observed a phase transition from the cubic face-centered structure into a tetragonal low-temperature structure at 170(10) K for LiIn [3]. This phase transition is translationengleich and characterized by an increase of $\eta = c/(a\sqrt{2})$ from 1 for the cubic phase to 1.0050(3) for the tetragonal distorted phase. Combined neutron and X-ray powder diffraction has been applied to find out if the instability of the cubic structure at low temperature is a common feature for all 7 Zintl phases with NaTl-type structure or a pecularity of LiIn. Only two other compounds, LiAl and LiCd, showed some indication for a structural transition during cooling, but the available resolution and the high neutron absorption coefficient for Cd, respectively, prevented a unique and quantitative statement. Therefore, high-resolution synchrotron powder diffraction was performed at beamline B2 [4] to clarify the low-temperature behaviour of LiAl and LiCd. The air sensitive samples were filled into 0.3 mm diameter capillaries and loaded in a closed-cycle cryostat, designed for synchrotron powder diffraction between 10 and 350 K [5]. The selected wavelength was determined to $\lambda = 1.11957(1) \text{Å}$, based on the peak positions of 6 reflections from a Si NBS 640b standard.

The reflection profiles for LiCd are well described by symmetric Lorentzian shape and appear extremely broadened as compared to the instrumental resolution function, see figure 1. Those reflections with the most pronounced splitting caused by a tetragonal distortion, i.e. (400) and (620), are much broader than those with no such splitting, i.e. (hhh) reflections. This is a strong hint for a tetragonal splitting similar to the observed low-temperature structure of LiIn.
However, two other observations are at least challenging this model or are even in contradiction to such a splitting scheme: 1. The reflections (111) and (444) are also broadened, and the ratio of their half widths cannot be explained by a particle size effect only. Therefore, at least one more mechanism for the broadening of reflections must be taken into account, e. g. inhomogeneities in the Li:Cd ratio for different crystallites resulting in a distribution of lattice parameters, or defects like stacking faults. 2. Intensities are asymmetrically distributed into the splitted reflections due to their different multiplicities; but none of the observed profiles shows any indication for an asymmetric peak shape. At present, it is still not clear whether LiCd remains cubic at low temperature or not and how to interpret the severe and highly anisotropic peak broadening.

The splitting of LiAl reflections at low temperature is shown in figure 2 for two representative ranges and is in agreement with a transition from the cubic face-centered NaTl-type structure at room temperature into a tetragonal body-centered structure. However, in contrast to the transition in LiIn, a shrinking of the c-axis is observed, i. e. $\eta$ becomes smaller than 1. A value of $\eta = 0.998$ at 10 K is estimated from the first set of experiments, but additional diffraction data are needed to support the proposed low-temperature structure and to follow the temperature dependence of $\eta$.

Figure 2: Splittings of LiAl reflections at 10 K. The figure on the left hand side corresponds to the (531) reflection of the cubic phase, the one on the right hand side to (620).

Thanks to D. Mirkovic, J. Gröbner and R. Schmid-Fetzer (Thermochemie & Mikrokinetik II at TU Clausthal) for their help in the preparation of LiAl.

References