Temperature Dependent X-Ray Diffraction of Iron-Deficient $TlFe_{2-x}Se_2$ Single Crystals

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$TlFe_{2-x}Se_2$ belongs to the group of Fe-deficient 122-superconductors with $ThCr_2Si_2$ structure [1]. Non Fe-deficient $TlFe_2Se_2$ was originally described by Klepp and Boller in space group *I*4/*mmm* [2]. *Häggström* et. al. suggested a $\sqrt{5}\times\sqrt{5}$ superstructure with ordered vacancies in *I*4/*m* for the Fe-deficient phase $TlFe_{1.6}Se_2$ based on X-ray powder diffraction data [3].

We prepared single crystals of $TlFe_{2-x}Se_2$ with nearly the same composition ($x \approx 0.4$) but two different structures – due to different ordering patterns of vacancies in the iron layers – by variation of the cooling rates. Crystals of type A exhibit a complete statistical distribution of Fe and vacancies, their diffraction images show only Bragg spots according to a $ThCr_2Si_2$ type unit cell. The occupancy of the only crystallographic Fe position was computed to 81 %. For type B crystals, however, additional reflections are observed corresponding to *Häggströms* $\sqrt{5}\times\sqrt{5}$ superstructure. According to [3], the body-centred $\sqrt{5}\times\sqrt{5}$ superstructure in *I*4/*m* should contain one fully (16*i*) and one unoccupied iron position (4*d*). We found, however, partial occupation of both iron positions in type B crystals, although to a quite different amount: The iron site at the face centre (4*d*) has an occupancy of about 31 % whereas the 16*i*-position is occupied to 93 %, Figure 1. These findings correspond to the results presented in [4]. Additionally, all crystals of type B were found to be twinned.

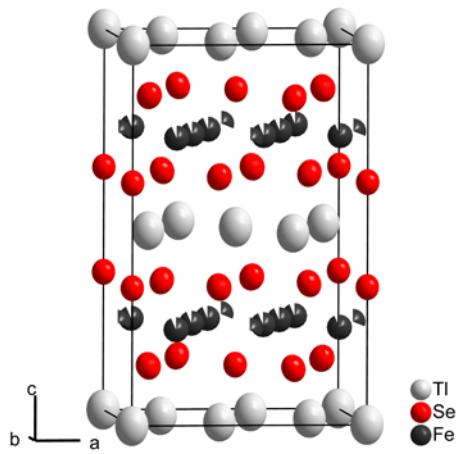

Figure 1: Structure of a type B crystal of $TlFe_{2-x}Se_2$ with partially ordered vacancies.

Temperature dependent X-ray diffraction investigations on different $TlFe_{2-x}Se_2$ single crystals were performed at the D3 beamline at HAYSLAB. Crystals of type B – partially ordered vacancy pattern in the $\sqrt{5}\times\sqrt{5}$ superstructure – were found to undergo a reversible phase transition. Upon heating, the superstructure reflections vanish at $T \approx 200$ °C but regain intensity upon cooling below the transition temperature, Figure 2. The high-temperature phase corresponds to a $ThCr_2Si_2$ type like structure with complete statistical distribution of vacancies in the Fe layers (and is thus identical to the type A structure). Upon cooling the intensities of the superstructure reflections shift slightly indicating different fractions of the twin domains before and after the phase transition. A de-twinning of the crystals by multiple heating-cooling cycles was not observed, however.

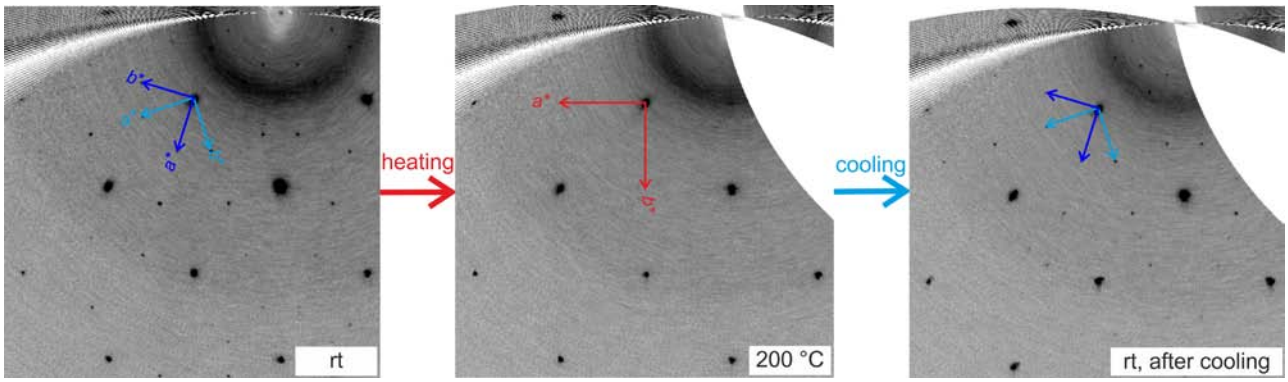

Figure 2: Section of the diffraction images of $TlFe_{2-x}Se_2$ at rt before heating, 200°C and rt after cooling.

References

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