Commensurate and incommensurate superstructures in rare earth metal chalcogenides $\text{REX}_2-\delta$

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The structures of the chalcogenides $\text{REX}_2-\delta$ ($\text{RE} = \text{La-Nd, Sm; Gd-Lu}; X = \text{S, Se, Te}$) of trivalent rare earth metals attracted some attention as different commensurate and incommensurate superstructures are found in a quite narrow composition range $0 \leq \delta \leq 0.2$. All structures share a common structural motif of an alternating stacking of puckered $[\text{REX}]$ and planar $[X]$ layers and are closely related to the ZrSSi structure (space group $P4/nmm$), which is regarded as their common aristotype, Figure 1 (left) [1]. For electronic reasons, the planar $[X]$ layer shows distortions from a perfect square net, as dianions $X_2^{2-}$ are found for the non-deficient $\text{REX}_2$. By reducing the chalcogenide content, ordered vacancy patterns are observed within the planar layers. The different amounts of vacancies, i.e. the value of $\delta$, drives the structures towards the formation of different commensurate and incommensurate superstructures for the $\text{REX}_2-\delta$ compounds. For each single vacancy in the chalcogen layer of the sulfides and selenides, one $X_2^{2-}$ anion is found to maintain a charge balanced composition. In a chemical sense, this can be rationalised as a disproportionation reaction upon elimination of $X$. The tellurides show different ordering patterns in the planar $[\text{Te}]$ layer for the non-deficient $\text{RETe}_2$ compounds, but also a tendency to form larger anionic fragments for the deficient $\text{RETe}_2-\delta$ compounds, as seen for the commensurate structure of $\text{GdTe}_{1.8}$, e.g. [2].

La$\text{Te}_{1.94}$ and La$\text{Te}_{1.82}$ are two examples of different incommensurate crystal structures for $\text{RETe}_2-\delta$ compounds, e.g., driven by a different amount of vacancies in the planar $[\text{Te}]$ layer [3, 4]. Both compounds share an average tetragonal unit cell with $a \approx 4.50$ Å and $c \approx 9.17$ Å, reflecting the structure of their aristotype. The major difference of these compounds are their respective $q$ vectors, which are compatible with tetragonal symmetry for La$\text{Te}_{1.94}$, but indicate a loss of the fourfold rotational axis for La$\text{Te}_{1.82}$, ending up in an orthorhombic superspace group. The $[\text{Te}]$ layer of La$\text{Te}_{1.94}$ is mainly composed of single vacancies, isolated $\text{Te}^{2-}$ anions and $\text{Te}_2^{2-}$ anions. La$\text{Te}_{1.82}$ is more Te deficient and features adjacent vacancies in addition to $\text{Te}_3^{4-}$ anions to guarantee charge balance. The chemical bonding within different chalcogen layers is compared by the DFT-based ELI-D descriptor.

![Figure 1. Average structure of La$\text{Te}_{1.82}$ (left), Fourier section around Te2 atoms in the modulated structure of La$\text{Te}_{1.82}$ (centre), and section of the diffraction image of Gd$\text{Te}_{1.8}$ (right).](image-url)


