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Commensurate and Incommensurate Superstructures in Rare Earth Metal Tellurides $RETe_{2-\delta}$

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Abstract

The structures of the rare earth metal polychalcogenides $REX_{2-\delta}$ ($RE = \text{La-Nd, Sm; Gd-Lu}$; $X = \text{S, Se, Te}$; $0 \leq \delta \leq 0.2$) attracted some attention due to their distorted square planar chalcogenide layer and the motives observed within these layers. All structures share a common structural pattern, namely an alternating stacking of puckered $[REX]$ and planar $[X]$ layers, and are closely related to the $ZrSSi$ structure (space group $P4/nmm$), which is regarded as their common aristotype [1].

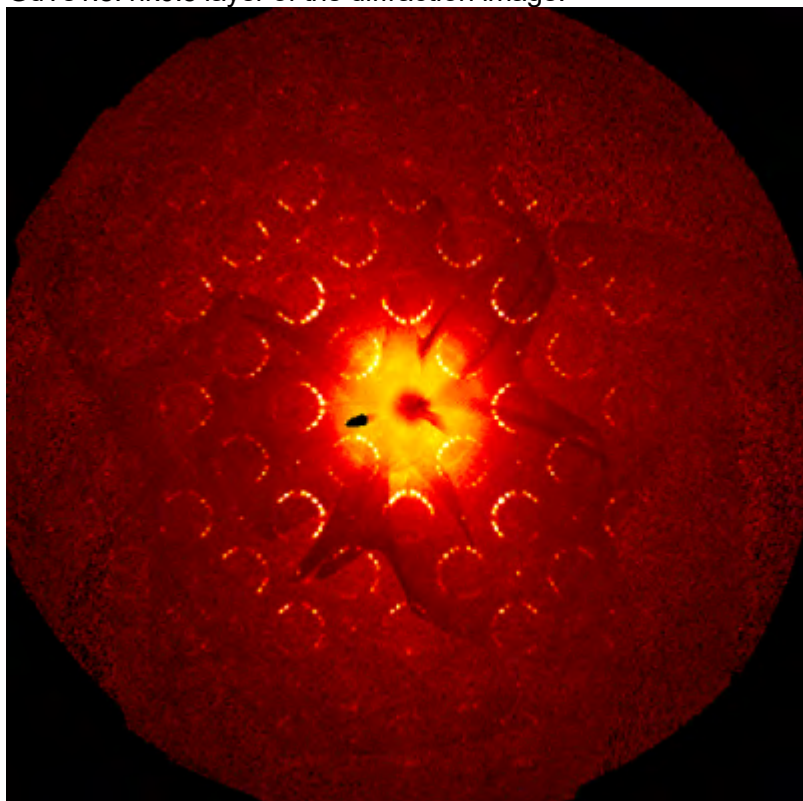
For electronic reasons, the planar $[X]$ layer shows distortions from a perfect square net, forming dianions X_2^{2-} for the non-deficient REX_2 compounds. By reducing the chalcogenide content, vacancies are observed within the planar layers, resulting in different commensurate or incommensurate superstructures for the $REX_{2-\delta}$ compounds depending on the vacancy concentration. The $[REX]$ slabs are not involved in the internal charge re-balancing associated with the vacancy formation and, hence, merely change. For the sulfides and selenides we find additional X^{2-} anions along the vacancies to maintain a charge balanced $[X]$ layer in $REX_{2-\delta}$. Tellurides, however, show different ordering patterns in the planar $[Te]$ layer for the non-deficient $RETe_2$ compounds, but also a tendency to form larger anionic fragments for the deficient $RETe_{2-\delta}$ compounds, as seen for the commensurate structure of $GdTe_{1.8}$, e.g. [2].

$LaTe_{1.94}$ and $LaTe_{1.82}$ are two distinct examples of incommensurate crystal structures for $RETe_{2-\delta}$ compounds, differing in the number of vacancies in their planar $[Te]$ layers [3, 4]. Both compounds share an average tetragonal unit cell with $a \approx 4.50 \text{ \AA}$ and $c \approx 9.17 \text{ \AA}$, i.e. the structure of their common aristotype. The major difference between these compounds are their respective q vectors, which are compatible with tetragonal symmetry for $LaTe_{1.94}$, but indicate a loss of the fourfold rotational axis for $LaTe_{1.82}$, ending up in an orthorhombic superspace group. The $[Te]$ layer of $LaTe_{1.94}$ is mainly composed of single vacancies (point defects), isolated Te^{2-} anions and Te_2^{2-} anions. $LaTe_{1.82}$ is more Te deficient and features adjacent vacancies in addition to linear Te_3^{4-} anions to guarantee charge balance.

References

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- [3] Poddig, H., Finzel, K., Doert, T. (2020) Acta Crystallogr. Sect. C 76, 530–540.
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GdTe1.8: hk0.5 layer of the diffraction image.



LaTe1.82: de Wolff sections through Te(2)

