Showcasing research from Reshef Tenne et al. at the Weizmann Institute of Science, Israel and co-workers at the Technische Universität Dresden, and the Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Germany.

Tubular structures from the LnS–TaS$_2$ (Ln = La, Ce, Nd, Ho, Er) and LaSe–TaSe$_2$ misfit layered compounds

Nanotubes from a new family of misfit compounds – LnX–TaX$_2$ (Ln = lanthanide atom; X = S, Se) are reported in this work. Careful structural study combined with computer simulations are used to characterize these new nanostructures.
Tubular structures from the LnS–TaS$_2$ (Ln = La, Ce, Nd, Ho, Er) and LaSe–TaSe$_2$ misfit layered compounds$^\dagger$

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Nanotubular structures from a new family of misfit compounds LnS–TaS$_2$ with (Ln = La, Ce, Nd, Ho, Er) and LaSe–TaSe$_2$ (some of them not known hitherto) are reported. Stress relaxation originating from the lattice mismatch between the alternating LnS(Se) and TaS$_2$(Se) layers, combined with seaming of the dangling bonds in the rim, leads to the formation of a variety of nanotubular structures. Their structures are studied via scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) and selected area electron diffraction (SAED). Tubules exhibiting a single folding vector for the LnS(Se) as well as TaS$_2$(Se) layers were often found. The small values of the c-axis periodicities are indicative of a strong interaction between the two constituent layers which was also supported by Raman spectroscopy and theoretical calculations.

Introduction

Misfit layered compounds

Misfit layered compounds (MLC) have a general formula of (MX)$_n$(TX$_2$)$_m$ with (M = Sn, Pb, Sb, Bi, rare earths; T = Nb, Ta, Ti, V, Cr; X = S, Se; 0.08 ≤ $y$ ≤ 0.28; $m = 1$–3).$^1,2$ The TX$_2$ and MX layers have different crystallographic structure and they are stacked periodically. TX$_2$ is a three-atom thick sandwich layer with a pseudo-hexagonal structure, in which the metal atoms are surrounded by six chalcogen atoms, either in octahedral or in trigonal prismatic coordination. Although bulk TaS$_2$ can adopt either structure,$^3$–$^6$ trigonal prismatic is the relevant coordination in MLC.$^1,2,7$ The two atom thick MX slice can be considered as a distorted NaCl structure with an orthorhombic unit cell. The value of $y$ is determined by the ratio of the projected atomic surface densities of the two subsystems. Interactions between the MX and TX$_2$ subsystems result in various types of mutual structural modulations, depending on the compounds.$^1,2,7$ For the LnS–TaS$_2$ and LaSe–TaSe$_2$ MLC that are discussed here, the mutual structural modulation results in an in-plane commensurate “$b$” and an in-plane incommensurate “$d$” direction. In particular, the $b$-axis of LnS (Fig. 1a) fits to $\sqrt{3} \times a$ of TaS$_2$, where $a$ is the in-plane lattice parameter of TaS$_2$ when indexed according to a pseudo-hexagonal unit cell (marked in brown in Fig. 1b). Therefore, it is convenient to describe the pseudo-hexagonal TaS$_2$ layer in terms of an ortho-pseudo-hexagonal unit cell that has primitive dimensions $a$ and $b = \sqrt{3} \times a$, as shown in purple in Fig. 1b. A misfit then occurs along the $a$ direction, as the ratio $a_{\text{LnS}}/a_{\text{TaS}_2}$ is an irrational number. Therefore, the superstructure lacks three dimensional periodicity and it is impossible to define one common unit cell. A complete description of the entire structure is possible in a $(3 + 1)D$ superspace$^1,2$ where an additional dimension ($D$) is inserted to reflect the incommensurate modulation of the atomic positions of the two subsystems along the $a$-axis.

It should be noticed that some of the compounds described in the present study, like HoS–TaS$_2$ and LaSe–TaSe$_2$, were not reported in the literature before even in the bulk form.

Stability of LnS–TaS$_2$ misfit compounds

The Ln atoms within LnS–TaS$_2$ MLC inherently prefer a trivalent state.$^1,8$ It has been proposed that a considerable amount of charge transfer from LnS to the partially filled TaS$_2$ $d_{z^2}$ band enhancements the Coulombic interaction between the two sublayers which is believed to be one of the stabilizing mechanisms of these compounds. The $d_{z^2}$ band is a very narrow (~1 eV wide).
The larger amount of charge transfer may result in higher Coulombic interaction between the LnS and the TaS₂ layers, shorter bond lengths between the Ln and the S atoms of the TaS₂ layer⁴ and smaller periodicity values along the c-axis of the TaX₂ and the LnX (X = S, Se) layers in many of the tubular structures from the LnX–TaX₂ MLC. (a) Single layer of LnX projected along the c-axis and oriented in such a way that its b-axis is parallel to the tube plane (blue arrow) and to the solid green arrow in (b). (b) Single layer of TaX₂ projected along the c-axis. Pseudohexagonal and ortho-pseudohexagonal unit cells are marked in brown and purple respectively. The solid green arrow represents the c-axis with respect to the ortho-pseudohexagonal unit cell, coincides with the tube axis (blue arrow). The two dashed green arrows represent crystallographically equivalent directions rotated by 60° and 120° relative to the direction marked by the solid green arrow. (c) Initiation of bending around the b-axes of the LnX and TaX₂ layers that comprise an LnX–TaX₂ slab. (d) A concentric tubule whose axis (perpendicular to the plane of the paper) coincides with the b-axis of LnX and TaX₂. (e) Representative partially unfolded sheets, demonstrating the scrolling process for the NdS–TaS₂ MLC case in particular.

### Formation of tubular structures

The misfit in the a-b plane is the main driving force for scrolling as shown in Fig. 1c. In the MLC discussed here, such a misfit occurs along the a-axis. The tube axis is then expected to be parallel to the common b-axis and perpendicular to the a-axis along which the lattice parameters differ most as shown in Fig. 1a. Upon scrolling, the energy associated with the misfit is reduced.¹¹ Spontaneous bending is mostly expected for an asymmetric MX–TX₂ lamella, i.e. one that is bounded by MX on one side and by TX₂ on the opposite side. The formation of the nanotubes is further stimulated by the seaming of dangling bonds at the rims of the layers as reported before for binary layered compounds, like WS₂, and is shown schematically in Fig. 1c. These two independent mechanisms promote the formation of concentric tubules which may effectively decrease the minimal equilibrium radius resulting from the misfit.

### Experimental and computational section

#### Synthesis of the tubular structures

The synthesis of LnS–TaS₂ (Ln = La, Ce, Nd, Ho, Er) and LaSe–TaSe₂ MLC tubular structures was carried out in evacuated ampoules at a vacuum of ~5 × 10⁻⁵ torr. Ta, Ln, S or Se powders were taken at molar ratios of ~1:1:3. Small amounts of TaCl₅ or TaBr₅ (~0.1 of a molar amount of Ta) powder were added as a Cl/Br source. Cl/Br is believed to act as a transport agent. The powders used were purchased from the following companies and had the following purity: La, Ho, Er (Strem Chemicals 99.9%), Nd (Strem Chemicals 99.8%), Ce (Alfa Aesar 99.9%), Ta (Alfa Aesar 99.9%), S (Sigma Aldrich 99.98%), Se (Fluka 99.9%), TaCl₅ (Alfa Aesar 99.9%), TaBr₅ (Strem Chemicals 99.9%). The materials were inserted into the ampoule in a glove box at a nitrogen atmosphere to prevent oxidation. After sealing, the ampoules were inserted into a preheated vertical furnace and two annealing steps were performed. First, the ampoules were held in a temperature gradient of 400 °C at the bottom (with the precursors) and 850 °C at the upper part for 1 h. In the second
step, the temperatures were tuned to 850 °C at the bottom (with the precursors) and 50 °C at the upper part. This step lasted for 4–16 h. Afterwards the ampoules were removed rapidly from the furnace and were cooled at plain air. Most of the product remained at the hot edge of the ampoules and the amount of the substance transported to the cold edge was negligible. It should be emphasized that the nanotubes are obtained in appreciable yields under a narrow window of conditions, only. Otherwise, micron-size platelets of the same compounds or the binary compounds predominate in the reaction product.

Electron microscopy, XRD, Raman spectroscopy

After the ampoules were opened, the powder products from the hot zone were examined by SEM, HRTEM, STEM, XRD, and Raman spectroscopy.

X-ray diffraction (XRD) patterns were recorded with a Rigaku TTRAXIII diffractometer (Cu-Kα radiation, 1.54 Å) operating in the Bragg-Brentano (θ–2θ) mode. For SEM analysis, a small amount of the powder was placed on carbon tape stuck to an aluminum stub. The resulting samples were examined using an Zeiss Ultra model 55 SEM and a LEO model Supra 55VP SEM equipped with an EDS detector (Oxford model INCA).

For high-resolution transmission electron microscopy (HRTEM) a solution of the product in ethanol was dripped onto a lacey/holey carbon/collodion-coated Cu grids. The resulting samples were examined by Philips CM120 TEM, operating at 120 kV equipped with EDS detector (EDAX-Phoenix Microanalyzer); JEOL JEM2100 operating at 200 kV and FEI Tecnai F30-UT HRTEM operating at 300 kV. High-resolution scanning transmission electron microscopy (STEM) images and EDS chemical maps were taken on a probe-corrected FEI Titan 80-200 G2 ChemiSTEM instrument equipped with a Bruker Super-X detector at 200 kV.

For Raman spectroscopy measurements, droplets of an ethanol solution containing the product were dripped on Si wafers. Raman measurements were carried out using a Renishaw Micro Raman InVia Imaging Microscope equipped with a CCD device. Tubes with diameters of 0.2–1 μm could easily be discerned using the light microscope. A He–Ne laser (λ = 633 nm) was used for excitation.

Computational details

The present calculations were based on the density-functional tight-binding (DFTB) method. For these calculations, rectangular periodic boundary conditions were applied. The effective one-electron potential in the Kohn–Sham Hamiltonian is approximated as a superposition of the potentials of the neutral atoms. Furthermore, only one- and two-center integrals are calculated to set-up a scalar relativistic Hamilton matrix. The valence basis included the 6s, 6p, and 5d orbitals for La; 3s and 3p orbitals for S and the 5s, 5p, and 4d orbitals for Ta. The states below these levels were treated within a frozen-core approximation. For a detailed description of the calculations, see Section S7.1 in the ESI.

Results and discussion

Here nanotubes from a new family of LnS-TaS₂ (LaSe-TaSe₃) MLC, are reported. The tubular phase constituted ~50% of the total product for the LaS-TaS₂ case, ~20% for NdS-TaS₂ and ErS-TaS₂, ~5% for HoS-TaS₂ and LaSe-TaSe₂ and merely 1% for the CeS-TaS₂ case. Syntheses were carried out in fused silica tubes under vacuum. The tubular structures were produced in the hot zone of the ampoules among other by-products, in contrast to e.g. MS-TaS₂ with M = Sn, Pb, Bi, Sb that condensed at the cold end of a temperature gradient. The addition of a small amount of TaCl₅ or TaBr₅ powders was essential for nanotube growth. The use of TaBr₅ instead of TaCl₅ resulted in a higher yield in the case of LaSe-TaSe₂ nanotubes. For the sake of comparison, iodine was used as a transport agent for the growth of LnS-TaS₂ MLC single crystals which were obtained at the cold zone of the tube within several days. Also, the ampoules were subjected to a very fine temperature gradient of 850–950 °C between the edges. Typically, a deviation of only a few degrees from the prescribed procedure leads to an appreciably smaller yield of the nanotubes in the product.

Chemical analysis of the LnS-TaS₂ with (Ln = La, Ce, Nd) tubular structures using both EDS within the SEM and TEM (of individual nanotubes) indicated the presence of 1–2 at% of Cl or Br in the case of LaSe-TaSe₂. Indeed, peaks of Cl (Br) are clearly seen on the EDS spectra recorded from these compounds as shown in Fig. S2 in the ESI. However, no clear peak of Cl could be detected for (Ln = Ho and Er). Nevertheless, in all cases (of LnS-TaS₂ with Ln = La, Ce, Nd, Ho, Er and LaSe-TaSe₂) tubular structures could not be produced without the addition of TaCl₅ (TaBr₅) powder to the ampoules.

Representative SEM images of the products are shown in Fig. 2 and Fig. S3 in the ESI. Table 1 summarizes the typical range of outer diameters of the tubules as well as their yields of production.

The ratio between the inner and outer diameters varied between the limiting cases of 0 and 1 for all of the LnS(Se)–TaS₂(Se) MLC tubular structures that are described here. Partially unrolled LnS–TaS₂ MLC sheets, as well as pristine TaS₂, LnS, and metallic Ln and Ta residuals (identified from XRD spectra; see Fig. 5 and Section S4 in the ESI†) were always present in the powder. It is suggested that in several cases after the initial tube is produced, further layers can form within the preformed core which serves as an “internal template”. Presumably also, the growth of the nanotubes did not start at once with some nanotubes starting to grow earlier and others later-on. Hence some of the nanotubes stayed longer in the reaction zone giving rise to the possibility for a secondary growth (templating effect) on the outer as well as the inner-most surface layer of the nanotube. Therefore, nanotubes of different internal and external diameters and length were obtained. That might explain the large variety of the internal diameters within the tubes. Furthermore, the seaming of the dangling bonds provides additional driving force for the formation of concentric tubes with small internal diameter. Energy-wise, templated growth is not as demanding and may lead to scrolling, as is often observed.
for the outermost layers of the tubular structures. Therefore, in such cases part of the layers have a tube-like morphology and part (mostly the outermost layers) show a scroll like structure.

**Structural analysis of the tubular structures**

In many of the tubes from all of the LnS(Se)–TaS2(Se) MLC that are discussed here, the classical behavior of one common \( b \)-axis coinciding with the tubule axis (as presented in Fig. 1) was observed. In this case both the TaS2(Se) and the LnS(Se) layers had a single folding vector. Tubules exhibiting two folding vectors of the TaS2 layers with one two or three folding vectors of the LnS layers were encountered as well (see Section S1.1 in the ESI†). The latter configuration of the layers is very common in nanotubes from the PbS–NbS2\(^{14}\) and PbS–TaS2\(^{7}\) MLC which were widely described by us in the past.

TEM images of LnS–TaS2 with (Ln = La, Ce, Nd, Ho, Er) and LaSe2–TaSe2 tubular structures are shown in Fig. 3 and Fig. S5–S8 in the ESI.† The SAED patterns of the shown tubular structures indicate that there is a single folding vector for both the TaS2(Se) and the LnS(Se) layers, consistent with the structure shown in Fig. 1d. Such patterns were commonly encountered for LnS–TaS2 (Ln = La, Er) as shown in Fig. 3a and b and more rarely for (Ln = Ce, Nd, Ho) and LaSe–TaSe2 as shown in Fig. S7a, S6a, S6b and S5, respectively, in the ESI.† Fig. 3a shows the structure of a LaS–TaS2 nanotube. Here, the LaS and TaS2 layers are stacked in an alternating sequence along their common \( c \)-axis with a 1.15 nm periodicity, as determined from line profiles and from the distance between basal reflections in diffraction patterns. In Fig. 3a, six pairs of spots with interplanar spacings of 1.64 Å and 2.83 Å are equally-azimuthally distributed on a circle and are marked by small red...
circles. These spots are attributed to the (11.0) and (10.0) planes of TaS₂ (200) and (020) in the ortho-pseudohexagonal indexing system. The multiplicity factor for these planes is six. This observation suggests the presence of a single folding vector for the TaS₂ layers. Four pairs of spots belonging to the LaS₀₂₀ spots of TaS₂ and the 020 spots of ErS. This shift is indicative of away from the red dashed circles that correspond to the 10.0 (marked by segmented green ellipses) are ‘shifted’ slightly shown in Fig. 3b, it is apparent that the 200 spots of ErS from those of their LaS–TaS₂ counterpart (see Table 2 and the lattice periodicities of the latter MLC nanotubes are differ-
ent from those of their LaS–TaS₂ counterpart (see Table 2 and the SAED patterns. Fig. 4 shows representative high-resolution STEM images of a LaS–TaS₂ nanotube. The high-angle-scattered intensity is stronger for the TaS₂ layers owing to their greater projected cation density. Therefore, the TaS₂ layers appear brighter in high-angle annular dark field (HAADF) images and dark in bright-field (BF) STEM images. A perfectly alternating sequence of layers with a single folding vector is observed for all LaS–TaS₂ periods of the nanotube shell. The structure overlay in Fig. 4b shows that the folding of the tube is along the incommensurate a-axis, while the tube axis is parallel to the commensurate b-axis, as shown in Fig. 1d. Notwithstanding the fact that Fig. 4 was taken with full atomic resolution, the

<table>
<thead>
<tr>
<th>Compound</th>
<th>TaS₂ d(11.0) = d(200)* = a/2 [Å]</th>
<th>TaS₂ d(10.0) = d(020)* = b/2 [Å]</th>
<th>LnS(110) [Å]</th>
<th>LnS(220) [Å]</th>
<th>LnS(200) = a/2 [Å]</th>
<th>LnS(020) = b/2 [Å]</th>
<th>Difference between a and b of LnS [%]</th>
<th>Mean c-axis periodicity ED/XRD [Å]</th>
<th>The value of y within the ESI†</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaS–TaS₂</td>
<td>1.64</td>
<td>2.83</td>
<td>3.99</td>
<td>2.01</td>
<td>2.86</td>
<td>2.83</td>
<td>1</td>
<td>11.5/11.45</td>
<td>0.145</td>
</tr>
<tr>
<td>CeS–TaS₂</td>
<td>1.64</td>
<td>2.84</td>
<td>4.00</td>
<td>2.01</td>
<td>2.845</td>
<td>2.84</td>
<td>0.17</td>
<td>11.4/11.28</td>
<td>0.17</td>
</tr>
<tr>
<td>NdS–TaS₂</td>
<td>1.63</td>
<td>2.82</td>
<td>3.86</td>
<td>1.98</td>
<td>2.78</td>
<td>2.82</td>
<td>1.4</td>
<td>11.1/11.11</td>
<td>0.23</td>
</tr>
<tr>
<td>HoS–TaS₂</td>
<td>1.61</td>
<td>2.8</td>
<td>3.8</td>
<td>1.91</td>
<td>2.61</td>
<td>2.8</td>
<td>7.3</td>
<td>11.1/11.11</td>
<td>0.25</td>
</tr>
<tr>
<td>ErS–TaS₂</td>
<td>1.62</td>
<td>2.8</td>
<td>3.8</td>
<td>1.9</td>
<td>2.59</td>
<td>2.8</td>
<td>8</td>
<td>11.1/11.11/11.25</td>
<td>0.25</td>
</tr>
<tr>
<td>LaSe–TaSe₂</td>
<td>1.71</td>
<td>2.98</td>
<td>4.22</td>
<td>2.12</td>
<td>3.02</td>
<td>2.98</td>
<td>1.2</td>
<td>12</td>
<td>0.13</td>
</tr>
</tbody>
</table>
intrinsic tubular structure imposed a severe restriction on the visibility of sulfur. In fact, the tantalum and lanthanum atoms overlap with sulfur in projection owing to the bending of the nanotube shells and hence the sulfur signal is not detected against the background of the heavy atom signal. Consequently, no effort was undertaken for structure refinement in this analysis.

Stacking disorder of the LnS (with Ln = La, Ce, Nd, Ho, Er) and TaS2 layers along the c-axis was also observed, as shown for a NdS–TaS2 MLC in Fig. S8 in the ESI.† As a result, the basal reflections (marked by a blue bracket in Fig. S8c, ESI†) are smeared. Also, part of the Ta–Ce–S tubules were found to exhibit a periodicity of 2.43 nm along the c-axis, as shown in Fig. S7b in the ESI.† This periodicity is more than twice the regular periodicity of 1.145 nm, which corresponds to the CeS/TaS2 (1 : 1) periodic stacking. The structure of these Ta–Ce–S nanotubes could not be fully interpreted at this point.

X-ray diffraction (XRD) patterns recorded from the total products obtained during the attempts to synthesize LaS–TaS2, NdS–TaS2 and ErS–TaS2 tubular structures are shown in Fig. 5 and Fig. S4 in the ESI.† A series of different diffraction orders 00n (basal reflections similar to the reflections marked by small blue arrows in the SAED patterns), corresponding to the LnS–TaS2 MLC (superstructures) with LnS and TaS2 layers stacked periodically along the c-axis, can be clearly identified. For the 001 (first order) superstructure peaks, corresponding values of 11.45 Å, 11.28 Å and 11.11 Å were obtained for LaS–TaS2, NdS–TaS2 and ErS–TaS2 MLC, respectively. The line profiles generated from (HRTEM) images yielded quite similar values of 11.5 Å, 11.4 Å and 11.1 Å.

Other XRD peaks were assigned to the non-basal reflections arising from the structurally modulated LnS and TaS2 layers. The (11.0), (10.0) planes of TaS2 (or 200 and 020 respectively according to the ortho-pseudohexagonal system of labeling) as well as (110) and (220) planes of LnS within the LnS–TaS2 MLC are marked on the patterns (the 020 peaks of LnS coincide and 200 roughly coincide with that of 10.0 of TaS2). These diffraction peaks correspond to the SAED peaks marked by the red and green markers respectively in Fig. 3a, b and Fig. S6a in the ESI.†

It is known from the literature that for most of the MLC in their planar form a shift of b/2 along the b-axis between two consequent layers of the same type is observed leading by that to a “doubling” of the periodicity along the stacking direction for that specific subsystem. The stacking is named C-centered when its periodicity is 11–12 Å (with no b/2 shift) and F-centered when the periodicity is twice that distance, i.e. 22–24 Å (i.e. including the b/2 shift). These configurations were actually determined from the intensity-ratio of the TX2 and the MX peaks of the XRD patterns (in some cases with the assistance of SAED patterns of planar sheets). It is possible that the periodicity of one of the subsystems, e.g. TX2 would be twofold of MX or vice versa. (Four possibilities are possible CC, CF, FC and FF, the first letter corresponds to MX and the second to TX2). However, in the tubular structures described above the situation is even more complex. The successive layers of the same type might also be slightly shifted one with respect to the other due to the folding of each layer into a tube of a slightly different diameter. As stated earlier, many tubes reported here possess a single folding vector of the LnS(Se) and the TaS2(Se) layers with one common b-axis coinciding with the tube axis. However, a fraction of the analyzed LnS(Se)–TaS2(Se) nanotubes exhibited different rotational variants of the LnS(Se) and the TaS2(Se) layers with two different mutual orientations (between the LnS(Se) and TaS2(Se)) and orientations relative to the tubule axis as detailed in Section S1.1 in the ESI.† This situation is completely analogous to the case of the PbS–TaS2 and PbS–NbS2 nanotubes described before. Therefore the consequent layers of the same type are not only “shifted” but also rotated one relative to the other. Since XRD is obtained from the whole product the ratios of the peak’s intensities can not be directly related with the type of centering (the b/2 movement of the consequent layers of the same type related to planar crystals). Also, it was shown previously from SAED data that the b/2 shifts deduced from XRD are not a general feature and often occur non-systematically even for planar crystallites.²²

It is well established that, in contrast to planar crystals, the Bragg conditions for diffractions from the basal as well as from...
non-basal planes can be potentially fulfilled simultaneously within the same tubule (for different incidence θ angles). For a tubule lying on a plane surface (parallel to the sample plane) the basal (XRD) reflections are obtained from the upper and the bottom part of the tubule. However the diffraction from the \(hk0\) planes of LnS and the \(TaS_2\) are obtained from the side walls of the tubule. Therefore, in the case of nanotubes, diffraction peaks can be produced from both, for the correct incident angles according to the Bragg’s law. Therefore the difference between the intensities of the basal and the non basal reflections cannot be attributed to preferred orientation (texture). XRD patterns representing texture are well documented in the literature for the case of planar (non-tubular) crystallites (see p. 14 in ref. 1).

Peaks arising from the residual by-products, such as pristine LnS (Ln = La, Nd, Er), (and also 1T-TaS\(_2\) in Fig. S4a and b, [ESI\(^{†}\)]) and excess unreacted metallic Ln or Ta were also observed however for simplicity reasons they are not marked in the XRD patterns.

The 00N XRD peaks are rather broad (full width at half maximum \(\sim 0.3\ \AA\) for the 001 first order reflection). This suggests the presence of a statistical distribution for the interlayer spacing along the c-axis of the LnS/\(TaS_2\) (1:1) superstructure. This observation was also confirmed by statistical analysis of electron diffraction data. Furthermore, a spreading of \(\sim 3\%\) in the (10.0) and (11.0) in-plane interplanar spacing for \(TaS_2\) and (110) and (220) in-plane interplanar spacing for LnS was observed in the analysis of the SAED patterns recorded from multiple (20–30) tubes. For every compound, average values for the mentioned spacings were calculated and tubes fitting these values were chosen for presentation. The mentioned spreading of 3% refers to the maximum difference between the upper and the lower measured values of the mentioned interplanar spacings for every compound individually.

The values of the interplanar spacing obtained from the SAED/XRD patterns are comparable to published values for the bulk MLC materials (see Table S1, [ESI\(^{†}\)]). No XRD patterns were recorded from CeS–\(TaS_2\), HoS–\(TaS_2\) or LaSe–\(TaSe_2\) due to the low yield of nanotubes in the products. In these compounds, the periodicity was determined solely from SAED patterns, as summarized in Table 2.

All the LnS compounds that are discussed here are stable in bulk form, with NaCl crystal structures and space group \(Fmm\overline{3}m\). However, as a result of the mutual structural modulation that occurs in MLC, the structures of bilayers are distorted slightly when compared to the pristine bulk phase. The interplanar spacings of \(TaS_2\) and LnS (with \(Ln = La, Ce, Nd, Er\)) within bulk LnS–\(TaS_2\) MLC, as well as their values in pristine bulk form, are given in Table S1 in the ESI\(^{†}\). To the best of our knowledge, bulk HoS–\(TaS_2\) and LaSe–\(TaSe_2\) MLC have not been reported previously. Therefore, in these cases only values for bulk HoS, LaSe, \(TaS_2\) and \(TaSe_2\) are given in this table.

The in-plane and c-axis lattice constants of tubular structures of the LnS–\(TaS_2\) MLC are smaller than those of their MS–\(TaS_2\) (M = Sn, Pb) counterparts. Since the Ln atoms prefer a trivalent state, while Pb and Sn are divalent, charge transfer from the LnS layers to the \(TaS_2\) layers is expected to be greater than for PbS or SnS\(^{7,8,10}\). BiS–\(TaS_2\) and SbS–\(TaS_2\) can be considered as an intermediate case\(^{1,7,8,17,18}\). Most of the Sb and Bi atoms in SbS and BiS are believed to be trivalent just as in their well known bulk compounds Sb\(_2\)S\(_3\) and Bi\(_2\)S\(_3\) respectively.\(^{19}\) Strong charge transfer may result in a stronger electrostatic interaction between the LnS and \(TaS_2\) layers, and consequently shorter bond lengths between the Ln and S atoms of the \(TaS_2\) layer\(^{4}\), \(i.e.,\) smaller periodicity values along the c-axis (see Fig. 6).

Presumably, charge transfer between the two sublattices is responsible for the abundance of LnS–\(TaS_2\) tubules that have a single folding vector in these samples. Despite the crystallographic equivalence of the 60° rotation of the LnS relative to the \(TaS_2\) layer (see Fig. S1 in the ESI\(^{†}\)), their orientations relative to the tubule axis are different. Obviously, only one (out of the three equivalent) common b axes between the LnS and \(TaS_2\) of the LnS–\(TaS_2\) slab can coincide with the nanotube axis (see Fig. S1 in the ESI\(^{†}\)). Therefore, the b-axis of only one LnS layer (out of three) will coincide with the tubule axis. The energy associated with folding is believed to be minimal for the LnS layer, whose b-axis coincides with the tubule axis. Since the coupling between the layers is strong, it is believed that LnS–\(TaS_2\) slabs without these rotational variants can be transformed more easily into nanotubes. This situation is obviously not the case for, \(e.g.,\) MS–\(TS_2\) (M = Pb; T = Nb, Ta) tubules, in which the interlayer interaction is not as strong and tubules with three folding vectors for the MS layers and two folding vectors for the \(TS_2\) layers are produced.\(^{7,14}\)

Table 2 and Fig. 6 show that both the average interplanar periodicity along the c-axis corresponding to the LnS–\(TaS_2\) (1:1) superstructure and the in-plane interplanar spacings decrease with increasing atomic number of Ln \((i.e.,\) La, Ce, Nd, Ho, Er) in MLC, as well as their values in pristine bulk form, are given in Table S1 in the ESI\(^{†}\). To the best of our knowledge, bulk HoS–\(TaS_2\) and LaSe–\(TaSe_2\) MLC have not been reported previously. Therefore, in these cases only values for bulk HoS, LaSe, \(TaS_2\) and \(TaSe_2\) are given in this table.

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LnS–CrS$_2$.\textsuperscript{20} This trend can be attributed to a decrease in the size of the Ln$^{3+}$ ion with increasing atomic number. Similarly, the greater values of $c$-axis periodicity in LaSe–TaSe$_2$, when compared to that in isostructural LaS–TaS$_2$, can be attributed to the larger ionic radius of Se and the more covalent nature of its bonding with the metal atoms. For the sake of comparison, the interlayer spacing of nanotubes of the MS–TaS$_2$ compounds with M = Sb, Sn, Bi and Pb are shown on the left side of the graph. Noticeably, the interlayer spacing of the MLC with stable Sn$^{2+}$ and Pb$^{2+}$ is larger than that of the MLC with Sb$^{3+}$ and Bi$^{3+}$ and the trivalent lanthanides. This observation suggests that the stability of the stable MLC with M$^{3+}$ is attained by a significant degree of charge transfer from the metal M to the Ta atom.

**Electronic structure**

The density-functional tight-binding (DFTB)\textsuperscript{21,22} method was used to calculate the electronic structure of bulk LaS–TaS$_2$ as shown in Fig. 7. (The electronic structures obtained by the DFTB method are comparable to the full density functional theory (DFT) method as shown in Fig. S9 (ESI†). Therefore the use of the DFTB method for the calculations is justified.) The electronic structure including local densities of states, atom-resolved charges and the resulting charge transfer of this specific family of MLC were not reported before. Since the lattice structure is incommensurate along the $a$-direction ($a_{\text{LaS}}/a_{\text{TaS}_2}$ is an irrational number), a supercell approximation which is identical to that of previous publications,\textsuperscript{23} i.e. $4\times a_{\text{LaS}} \approx 7 \times a_{\text{TaS}_2}$ was used. This cell (see Fig. 7a) contains four sublayers (2 LaS and 2 TaS$_2$) due to the fact, that this compound forms a so called CF structure (see Fig. 4 in ref. S7) with an inversion center between the two TaS$_2$ sublayers.

From the isolated LaS and TaS$_2$ sublayers, one would expect electron transfer from La to Ta in the combined system (see the DOS curves of LaS and TaS$_2$ in Fig. S10 in the ESI†). The calculated DOS of the LaS–TaS$_2$ compound is shown in Fig. 7b–e (solid black curve). An analysis of the integrated local density of states (LDOS) as well as a Mulliken population analysis show an increase of the electron density on the Ta atom.

![Fig. 7](image-url) (a) The changes in the atomic charges ($\Delta Q$) of the atoms in the compound, compared to the charges of the atoms of the isolated LaS and TaS$_2$ layers. The structure is shown in a view along the normal to the (020) plane of a LaS–TaS$_2$ unit cell (labeled according to the ortho-pseudohexagonal system for TaS$_2$). The individual atoms are colored according to the $\Delta Q$ values in the left diagram with a color code shown on the right side. The “−” and “+” signs represent gained and donated (depleted) electronic charges, respectively. The La atoms (small spheres) are shown in different hues of gray to pink, depending on their positions relative to the TaS$_2$ sublayer and subsequent $\Delta Q$. The Ta atoms (small spheres) are colored in blue and the S (large spheres) atoms in pink in the TaS$_2$ sublayer and in grey in the LaS sublayer. (b–e) Show the total and local density of states for the LaS–TaS$_2$ compound. The solid black lines correspond to total DOS curves. The local densities of states of the atom types are shown in grey: (b) S atoms and (c) Ta atoms in the TaS$_2$ sublayer, (d) S atoms and (e) La atoms in the LaS sublattice. The energy is given relative to the Fermi energy of the LaS–TaS$_2$ compound.
atoms and a decrease of the electron density on the La atoms in the LaS–TaS$_2$ system compared to the isolated LaS/TaS$_2$ layers. Different values of the transferred charges $\Delta Q$ (relative to their charges in the pristine LaS and TaS$_2$ layers) were obtained for the different La atoms (see Fig. 7a). This results from the different lattices of the subsystems and consequently from different positions of the La atoms relative to the atoms in the TaS$_2$ sublayers. The variation in charge transfer to the Ta atoms in the unit cell is much smaller (see Fig. 7a) due to the shielding of the Ta atoms by the sulfur atoms. The smallest spreading of the charge transfer was found for the sulfur atoms within the two sublayers. On average every La atom has lost 0.28 electrons, while every Ta atom has gained 0.69 electrons, compared to the isolated monolayers (see Fig. 7a and Table S2 in the ESI†). *I.e.* the electron transfer from the La d-states to the Ta d-states is compensated to some extent by corresponding changes in the S charges in each subsystem (see Table S2, ESI†) which is opposed in sign relative to the metal atoms.

Consequently, a relatively small net electron transfer between the TaS$_2$ and LaS layers (~0.2 electrons per formula unit) occurs. The charge transfer from the La to the Ta atom is dominated by the states near the Fermi level and results in a filled d$_{z^2}$ band of the Ta atoms in the combined system (Fig. 7c). Whereas both isolated monolayers have pronounced metallic character (Fig. S10, ESI†), the LaS-TaS$_2$ compound has an overall semimetallic behavior, in which the TaS$_2$ layers are almost semimetallic and the LaS layers are effectively nonmetallic. A more detailed discussion of the electronic structure will be given in a separate publication.

Raman spectroscopy

Raman spectroscopy measurements were carried-out on single LaS–TaS$_2$ and NdS–TaS$_2$ tubular crystals of 200–500 nm thickness (see Fig. 8). The differences between the Raman modes of pristine bulk LnS$^{24}$ and 2H–TaS$_2$$^{25}$ and the modes observed in the corresponding MLC can be interpreted in terms of charge transfer from the LnS to the TaS$_2$ layers.$^{25}$ Charge transfer increases both the intralayer and the interlayer interaction between the layers, thereby affecting the Raman frequencies. In addition, the Raman spectra are expected to be affected by the mutual structural modulation. Recall that the structure of the LnS layers (and to a lesser extent that of the TaS$_2$ layers) within the MLC is slightly different from bulk LnS with a NaCl structure.

Representative Raman spectra recorded from single tubular nanocrystals of LaS–TaS$_2$ and NdS–TaS$_2$ are shown in Fig. 8. A spectrum of a 2H–TaS$_2$ platelet was measured for comparison as well. The spectra recorded from LaS–TaS$_2$ MLC tubular crystals are in excellent agreement with the results published previously for a bulk single crystal of LaS–TaS$_2$ MLC.$^{25}$

The mode at 400 cm$^{-1}$ is in perfect agreement with the A$_{1g}$ (intralayer out-of-plane vibration) mode of 2H–TaS$_2$. The mode at 327 cm$^{-1}$ is attributed to the E$_{2g}$ (intralayer in-plane vibration) mode, which occurs at 286 cm$^{-1}$ in bulk 2H–TaS$_2$. The large upshift of the intralayer E$_{2g}$ mode of the TaS$_2$ (41 cm$^{-1}$ in this case) has been reported for various intercalation compounds of 2H–TaS$_2$ (and 2H–NbS$_2$), including the misfit compounds$^{25–27}$ and is attributed to charge transfer from the LnS to the TaS$_2$ layers. The mode at ~149 cm$^{-1}$ matches the A$_{1g}$ (intralayer out-of-plane vibration) mode at 148 cm$^{-1}$ of LaS in a LaS–TaS$_2$ MLC single crystal. An additional A$_{1g}$ mode at 122 cm$^{-1}$ was observed by Kishoda *et al.*$^{25}$ but was not observed here due to experimental limitations at lower wavenumbers. As mentioned previously, the observed Raman modes of the LaS layers within LaS–TaS$_2$ MLC are different from the modes observed in LaS bulk single crystals with NaCl structure.$^{24}$ The broad band between ~240 and 303 cm$^{-1}$ is attributed to the two-phonon band as detailed elsewhere.$^{25}$

The spectra recorded from NdS–TaS$_2$ tubular crystals are quite similar to their LaS–TaS$_2$ counterparts. However, no previous literature data could be found for bulk NdS–TaS$_2$ MLC. Inasmuch as spectra recorded from bulk LnS–TaS$_2$ MLC with (Ln = La, Ce, Sm and Gd) were found to be similar,$^{25}$ the similarity of NdS–TaS$_2$ is not surprising.

Conclusions

Nanotubular structures were formed from LnS–TaS$_2$ (Ln = La, Ce, Nd, Ho, Er) and LaSe–TaSe$_2$ MLC in evacuated silica tubes when subjected to appropriate temperature profiles and growth times. The compounds were found to be commensurate along the $b$-axis and incommensurate along the $a$-axis. SAED patterns of the tubes suggest a single folding vector for the LnS(Se) and TaS$_2$(Se) layers in many cases. As expected, the commensurate $b$-axes of the LnS(Se) and TaS$_2$(Se) layers coincide with the tubule axis.

The mutual structural modulation of the TaS$_2$(Se) and LnS(Se) lattices results in an orthorhombic distortion of the rocksalt LnS(Se) lattice, while the TaS$_2$(Se) is barely modified. The difference between the in-plane lattice parameters ($a$ and $b$) of LnS in LnS–TaS$_2$ MLC became more significant for HoS and
ErS than for LaS, LaSe, CeS and NdS. Both the c-axis periodicity of the LnS-TaS$_2$ superstructure and the in-plane lattice periodicities of the LnS and TaS$_2$ layers decrease with increasing atomic number of Ln. The periodicity is greater for selenides than for corresponding sulfides.

The smaller periodicities in the LnS-TaS$_2$ tubules relative to their SnS-TaS$_2$ and PbS-TaS$_2$ counterparts indicate a stronger interaction between the two subsystems for the former. Such an observation is supported by a high upshift in the E$_{2g}$ Raman mode of TaS$_2$ in these compounds. Theoretical calculations for LaS-TaS$_2$ indicate a small net charge transfer from the LaS layer to the hexagonal sublattice. But on the other hand, also larger changes of the metal atom’s charges and consequently of the occupations of their electronic states can be observed. This results in a nearly full occupied d$_{z^2}$ band in the TaS$_2$ subsystem. Hence, the electronic structure of the TaS$_2$ part is comparable to that of MoS$_2$ or WS$_2$.

Competing financial interest

The authors declare no competing financial interest.

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