

08.2-21 ON THE CRYSTAL CHEMISTRY OF THE RARE-EARTH PNIGOCHALCOGENIDES LnXY . By R. Schmelzger (Institut für Angewandte Physik der ETH, CH-8093 Zürich), F. Hulliger (Laboratorium für Festkörperphysik der ETH, CH-8093 Zürich) and D. Schwarzenbach (Institut de Cristallographie, Université de Lausanne, CH-1015 Lausanne-Dorigny).

All the known LnXY phases (Ln = trivalent rare-earth cation; $\text{X} = \text{P, As, Sb}$; $\text{Y} = \text{S, Se, Te}$) adopt structures which are related to the tetragonal ZrSiS -type structure. This structure is characterised by square net layers of cations and anions, stacked along the fourfold axis:



($\text{M} = \text{Zr}$, $\text{X} = \text{Si}$, $\text{Y} = \text{S}$). All the known representatives of this structure type are metallic.

The LnXY compounds with the lighter anions (i.e. $\text{X} = \text{P, As}$ and $\text{Y} = \text{S, Se}$) crystallize in distorted versions of the ZrSiS -type structure. The distortions decrease with increasing size of the anions. The deformations mainly take place in the X layers whereas the cations and the more electronegative Y anions suffer only minor shifts from the positions in the parent ZrSiS structure.

In the orthorhombic GdPS -type structure of the LnPS phases, the relatively strong distortions lead to infinite phosphorus chains of the type "cis-trans" ($\sim \sim$) (F. Hulliger, R. Schmelzger and D. Schwarzenbach, *J. Solid State Chem.* (1977) **21**, 371). In the LnAsS phases (CeAsS -type structure) the deformations are less pronounced and result in infinite "trans-trans" ($\sim \sim$) arsenic chains (G. Sfez and C. Adolphe, *Bull. Soc. Fr. Minéral. Cristallogr.* (1972) **95**, 553). The $\text{X} - \text{X}$ bonding distances ($\text{X} = \text{P, As}$) are comparable with known single-bond lengths. Thus, stoichiometric LnPS and LnAsS are Mooser — Pearson phases. Their nonmetallic character is confirmed by resistivity measurements.

On substituting the anions in LnXY by their heavier analogs, the probability of forming Mooser — Pearson phases decreases. Although the LnAsSe compounds with $\text{Ln} = \text{Pr, Sm, Tb, \dots, Tm, Lu}$, Y crystallize in the CeAsS -type structure, they can no longer be considered as true Mooser — Pearson phases. The deformations in the arsenic layers are smaller than in the LnAsS phases and the $\text{As} - \text{As}$ distances within the resulting chains are too long to represent single bonds.

The structure of NdAsSe is isopuntal with the CeAsS type. The deviations from the parent ZrSiS type, however, are very small and insufficient to form infinite $\text{As} - \text{As}$ chains. Only As pairs can be identified. Thus, NdAsSe is certainly not a Mooser — Pearson phase. The structure of LaAsSe , finally, is the least distorted ZrSiS derivative among the structures adopted by the LnAsSe family, and is practically of the ZrSiS type (R. Schmelzger, D. Schwarzenbach and F. Hulliger, *Z. Naturforsch.* (1981) **36b**, in press).

The LnSbTe phases, which appear to be nonstoichiometric, adopt the undistorted ZrSiS -type structure and are therefore all metallic (R. Wang, H. Steinfink and A. Raman, *Inorg. Chem.* (1967) **6**, 1299).

08.2-22 $\text{Er}_{1.2}\text{Mo}_6\text{S}_8$ --STRUCTURE WITH THREE INCOMMENSURATE SUPERSTRUCTURES AND DISORDER. H. Brigitte Krause, Physics Dept., Northern Ill. U., DeKalb, IL, 60115, USA, and John M. Cowley, Physics Dept., Arizona State U., Tempe, AZ, 85281, USA.

A series of $(\text{Sn Er}_{1-x})_{1.2}\text{Mo}_6\text{S}_8$ compounds was examined with selected area electron diffraction and high resolution electron microscopy. In addition to the expected rhombohedral (approximately cubic) Chevrel phase, several different superlattices and sublattices were observed. Furthermore, for $\text{Er}_{1.2}\text{Mo}_6\text{S}_8$ a new monoclinic, or nearly monoclinic, structure type was discovered. The b -direction of the monoclinic unit cell coincided with the b -direction of the pseudocubic Chevrel phase, and the lattice constant $b_{\text{C}} = b_{\text{M}} = 6.37\text{\AA}$ is identical for both phases. The monoclinic a -axis is $a_{\text{M}} = 12.10\text{\AA}$, the c -axis is $c_{\text{M}} = 8.17\text{\AA}$, and the angle $\beta_{\text{M}} = 96.5^\circ$. The monoclinic axes are rotated with respect to the pseudocubic axes such that $[101]_{\text{M}}$ is in the direction of $[001]_{\text{C}}$ and $[10\bar{1}]_{\text{M}}$ approximately in the direction of $[100]_{\text{C}}$.

In spite of the similarities between the cubic and monoclinic geometry, there are distinct differences: the

volume ratio of $\frac{V_{\text{M}}}{V_{\text{C}}} = 2.4$ does not allow a simple interpretation in terms of an Mo_6S_8 cube arrangement as in the Chevrel phase. In addition to regular monoclinic reflections, incommensurate reflections and diffuse scattering were observed. The diffuse scattering occurred in reciprocal lattice sheets perpendicular to the b -direction. One of the incommensurate doublets occurred at $[110]_{\text{M}}$ with a splitting parallel to the b -axis and corresponding to about 100\AA in real space. Another doublet at $[010]$ had splitting in the cubic $[101]$ direction. A third series of incommensurate reflections occurred in the cubic $[110]$ direction with splittings both in the direction of $[110]_{\text{C}}$ and $[010]_{\text{C}}$. The incommensurate reflections and lattice images indicate a modulation of the structure interpretable as antiphase domains. Structure models will be proposed.