Gd_8Se_{15}—A 24-Fold Superstructure of the ZrSSi Type[**]

Enkhtsetseg Dashjav, Oliver Oeckler, Thomas Doert,*
Hansjürgen Mattausch, and Peter Böttcher

In the structures of the rare-earth polychalcogenides LnX_n (Ln = Sc, Y, La, Ce–Lu; X = S, Se, Te) homonuclear bonds are frequently observed between the chalcogen atoms for $n \geq 1.5$. All of these compounds can be derived from one common structural pattern: Puckered [LnX] double sheets sandwiched by planar-quadratic [X] layers. This principal pattern is also found in the isopointal, tetragonal compounds of the ZrSSi, PbFCl, (anti-)Fe_2As, and (anti-)Cu_2Sb types. We prefer the ZrSSi type as basic type because of its striking similarities to the LnX_2 compounds. The structures of the compounds $LnTe_{2.5}$ (=Ln_2Te_5) and $LnTe_3$ can be regarded as stacking variants of the LnX_2 structure. The LnX_2 compounds have been under studied since the mid-1950s. Hints at chalcogen-deficient phases $LnX_{2-\delta}$ ($0 \leq \delta \leq 0.5$), accompanied by the occurrence of superstructures, have since been given in a large number of contributions. Chalcogen deficiencies have only been observed in the planar quadratic [X] layers.[1]

Up to now, only one completely ordered superstructure of the type $LnX_{2-\delta}$ has been solved. The compound $CeSe_{1.9}$ is a ten-fold superstructure of the ZrSSi type ($a = \sqrt{5}a_0$, $b = \sqrt{5}a_0$, $c = 2c_0$; a_0, c_0: unit cell dimensions of the basic structure), in which one out of ten Se atoms in the [Se] layer is missing, one Se atom appears as an isolated Se^{2-} ion, and the remaining eight Se atoms form four pairs of Se_2^{2-} dumbbells, which are arranged as an eight-membered ring around the vacant site.[2]

The 24-fold supercell of the ZrSSi type observed for Gd_8Se_{15} ($a = 3a_0$, $b = 4a_0$, $c = 2c_0$, space group $Amm2$) is the second ordered superstructure of the rare-earth polychalcogenides $LnX_{2-\delta}$ which could be solved by X-ray investigations. First hints on this material were obtained by Wang and Steinfink during their investigation of the structure of $ErSe_2$ but the superstructure was not determined.[3] The same 24-fold supercell (space group $Amm2$) has been chosen to describe the superstructure of $NdTe_{1.90}$ but a certain amount of disorder remains in the structure model.[4] A closely related monoclinic 24-fold supercell (space group $A2_1/m11$) describes $DyS_{1.76}$ and Dy_6S_{11}, both with substantial disorder.[5, 6] A related 24-fold supercell was suggested for $YSe_{1.83}$ but without a structural solution.[7] Finally, the structure of $Dy_{11}Se_{20}$ has been refined in a model which is based on a 66-fold supercell.[8] The crystal structure of Gd_8Se_{15} given in this work is, therefore, the first structural refinement of the $ErSe_2$ type, in which the deficient [Se] layer can be described without disorder in the 24-fold supercell of the ZrSSi type.[9]

Figure 1 shows the structural similarities of Gd_8Se_{15} with the ZrSSi type: Slightly puckered [GdSe] double sheets are sandwiched by almost planar [Se] layers along the c axis. The Gd–Se distances are in the range 2.90–3.18 Å and occur in the [GdSe] sheets as well as between the Gd and the Se atoms of the selenium layers. These distances are in the range of the sum of the ionic radii (Gd^{3+}: 0.94–1.11 Å; Se^{2-}: 1.98 Å). Overall, there are ten crystallographically independent Gd^{3+} centers: four with coordination number (CN) nine (capped tetragonal antiprism; d_{Gd-Se}: 2.93–3.18 Å); five with CN = 8 (bicapped trigonal prism; d_{Gd-Se}: 2.91–3.05 Å); and one with CN = 7 (capped trigonal prism; d_{Gd-Se}: 2.90–3.00 Å). All Gd–Gd distances are larger than 3.94 Å; the doubled radius of Gd in the metal, $2r_{met}$, is 3.57 Å.

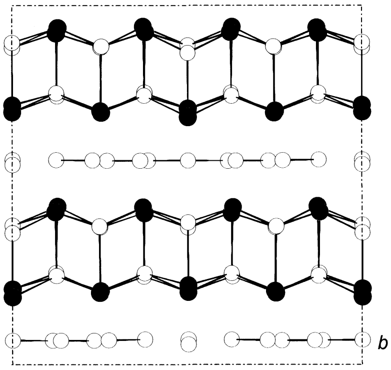

Figure 1. Projection of the crystal structure of Gd_8Se_{15} along [100]. One unit cell is depicted; Gd atoms: black; Se atoms: white.[16]

As can be seen from Figure 2, as a result of the occurrence of ordered defects in the selenium layer, only 21 out of 24 possible positions are occupied. Besides three vacancies, three isolated Se^{2-} anions, five Se_2^{2-} dumbbells, and one Se_8^{8-} ring is observed. The shortest Se–Se distances occur in the two crystallographically independent dumbbells (2.42 and

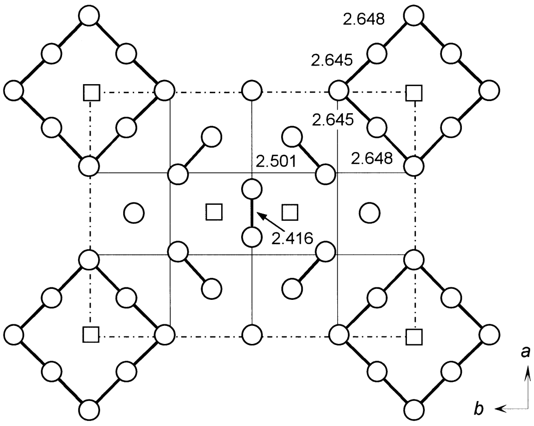

Figure 2. Projection of one of the selenium layers onto (001); the supercell is depicted as a dash-dot line, subcells indicated; vacancies: white squares, Se atoms: white circles. Selected Se–Se distances are given [Å].[16]

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[*] Dr. T. Doert, Dipl.-Chem. E. Dashjav, Prof. Dr. P. Böttcher
Institut für Anorganische Chemie der Technischen Universität
Mommsenstrasse 13, 01062 Dresden (Germany)
Fax: (+49) 351-4637287
E-mail: thomas.doert@chemie.tu-dresden.de

Dipl.-Chem. Dipl.-Min. O. Oeckler, Dr. H. Mattausch
Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1, 70569 Stuttgart (Germany)

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2.50 Å). They are considerably larger than the sum of the covalent radii (2.34 Å), nevertheless this is often observed for such dimers (M_2Se_2 (M = Na, K): 2.40–2.43 Å;[10] MSe_2 (M = Ba, La, Ce, Eu): 2.40–2.47 Å;[11] $LnSe_{1.9}$ (Ln = La, Ce, Pr, Nd, Sm): 2.49 Å).[2, 12] The Se–Se distances in the almost planar eight-membered ring (torsion angles 174.9(1)° and 175.1(1)°) are already 2.65 Å. Additionally, two relatively short Se ⋯ Se contacts of 2.94 and 3.05 Å are observed between the Se^{2-} anions and the longer $Se_2{}^{2-}$ dumbbells (sum of the van der Waals radii of selenium is 3.80 Å).

Considering the charge on the rare-earth metal as Gd^{3+} and the selenium atoms in the puckered double sheets as Se^{2-}, the overall charge in the unit cell is +24 per [GdSe] double sheet. Thus, 21 selenium atoms of the former square layer must carry 24 negative charges. This requirement is fulfilled by three vacancies, three isolated Se^{2-} anions, five $Se_2{}^{2-}$ dumbbells and one eight-membered selenium ring, represented as $Se_8{}^{8-}$. Upon counting electronic charges in this way, the Se atoms on the corners of the eight-membered ring carry two lone pairs, whereas the ones on the middles of the edges carry three lone pairs (hypervalence). These selenium atoms show slightly elongated displacement parameters along the edges compared to those of the corners. This displacement parameter should at least be additionally twice as large, if the eight-membered ring was built of statistically disordered $Se_2{}^{2-}$ dumbbells with Se–Se distances of 2.50 Å. We therefore compare the linear triatomic Se units of the Se_8 ring with molecular anions like $I_3{}^-$ or with the linear triatomic tellurium units in NaTe or Tl_2Te_3.[13] All of these groups can be symmetrical or slightly asymmetrical. In every case, even in the eight-membered Se ring in Gd_8Se_{15}, one calculates (Pauling[14]) bond orders of about 0.30 ± 0.05 ($d_n = d_1 - 0.6\log n$; d_n = observed bond distance, d_1 = covalent single-bond distance).

To our knowledge, such isolated Se_8 units with eight nearly equivalent Se–Se distances have never been observed before, although a certain similarity to the arrangement of the four $Se_2{}^{2-}$ dumbbells of the $CeSe_{1.9}$ type exists.[2, 12]

Experimental Section

All preparations were carried out under an argon atmosphere. Mixtures of gadolinium and selenium (molar ratios Gd:Se = 8:15) were heated to 950 °C in an evacuated and sealed quartz ampoule for seven days. After cooling, a chemical transport reaction (850 °C–650 °C, I_2 as carrier) was performed. Dark-metallic, almost tetragonal platelets of Gd_8Se_{15} grow on the cooler site of the ampoule. X-ray diffraction patterns of the powder can be indexed completely and unambiguously with the results of the single crystal-structure determination of the superstructure. Striking differences occur, however, compared to calculated diagrams based on a structure model in the substructure (ZrSSi type). The composition of several crystals was checked by energy-dispersive X-ray microanalysis (EDX); no deviation from the composition found by X-ray structure determination was found.

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[9] Crystal structure analysis of Gd_8Se_{15}: crystal dimensions: 0.09 × 0.05 × 0.02 mm^3; data collection at ambient temperature; STOE IPDS-Diffractometer, $Mo_{K\alpha}$ radiation, dynamic reflection profiles, $2\theta_{max} = 60°$, 23906 reflections (4878 independent); orthorhombic, space group *Amm*2 (No. 38), $a = 12.172(1)$, $b = 16.212(1)$, $c = 16.624(1)$ Å, $V = 3280.4(4)$ Å^3, $Z = 6$; $F(000)$: 6132. Correction for Lorentz and polarization effects, numerical absorption correction (STOE X-SHAPE and X-RED, $\mu = 48.844$, $T_{min} = 0.3058$, $T_{max} = 0.9458$); structure solved by direct methods.[15] The structure model was refined as an inversion twin (Flack parameter: 0.55(8)) with 188 parameters and converged at $R_1 = 0.035$ and $wR_2 = 0.063$ for 3418 observed reflections ($I > 2\sigma(I)$), and $R_1 = 0.059$ and $wR_2 = 0.069$ for all reflections (SHELXL-97). Min./max. residual electron density $-1.895/+2.212$ e Å^{-2}; weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0270P)^2]$ with $P = (F_o^2 + 2F_c^2)/3$.[15] Further details on the crystal structure may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-411069.

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