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Preparation and Crystal Structure of $RESe_{1.9}$ (RE = Ce, Pr)

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Vapor phase transport technique with I_2 yielded single crystals of $CeSe_{1.9}$ and $PrSe_{1.9}$, respectively. The isostructural title compounds are tetragonal, space group $P4_2/n$ with $Z = 20$. Lattice parameters $a = 9.3598(9)$ and $c = 16.938(2)$ Å for $CeSe_{1.9}$; $a = 9.296(2)$ and $c = 16.860(4)$ Å for $PrSe_{1.9}$. The structure determinations result in a formulation of $RESe_{1.9}$ as $RE_{20}(Se(I)_2)_8Se(I)_2\square_2Se(II)_{20}$, in accordance with the magnetic measurements, where the layer built up by the $Se(I)_2^{2-}$ pairs, $Se(I)^{2-}$ ions, and the vacancies corresponds to the F layer in the PbFCl substructure.

Introduction

Much experimental work has been done on rare-earth (RE) selenides (*1*). From the collected publications it can be seen that the given compositions and structures of the polyselenides are controversial. Physical properties have often been investigated on compounds not clearly defined (*2*). Thus it seemed necessary to start a reinvestigation of the polyselenides with more detailed analytical and structural studies.

Experimental

Preparation

Metallic chips of the rare-earth metals (Ce-, Pr-metal, Alfa Products, 99.9%) were mixed together with selenium shot (Alfa products, 99.999%) in the ratio Ce : Se = 2 : 3 and Pr : Se = 1 : 2, respectively. After sealing in evacuated quartz glass tubes the mixtures were heated at 400°C for 2 days. Then the temperature was raised to 900°C and maintained for 3 days. Finally the products were air quenched. X-ray powder diffraction phase analysis of the polycrystalline products confirmed in one case the composition Ce_2Se_3 considering published powder data (*3*) and in the other case the composition $PrSe_2$ as deduced by comparison with the known powder pattern of $CeSe_2$ (*4*).

Single crystals of $RESe_{1.9}$ (RE = Ce, Pr) were grown ($CeSe_{1.9}$, 1 week; $PrSe_{1.9}$, 4 weeks) by chemical vapor phase transport with iodine (*5*). A typical procedure of the preparation of single crystals is the following. The rare-earth selenides (1.0 g) together with iodine (0.040 g) were sealed in evacuated quartz glass tubes (length 170 mm, inner diameter 15.5 mm), which then were placed in a horizontal two-section furnace. One side of the tubes was kept at 950 to 1000°C and the other side at 700°C. The

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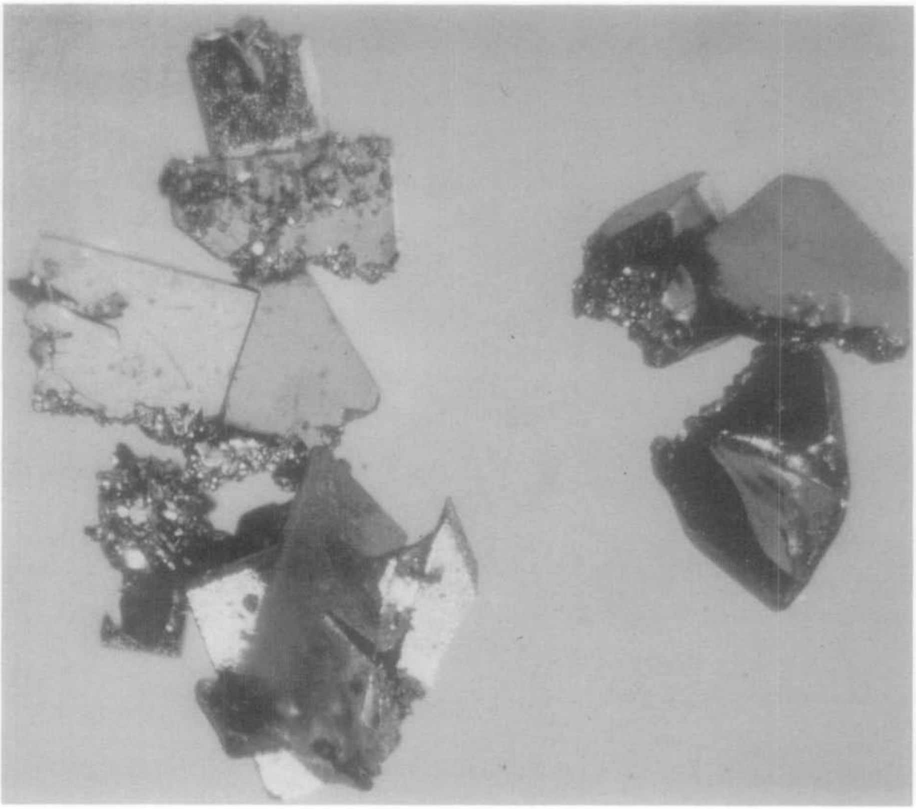

FIG. 1. Crystals of $PrSe_{1.9}$.

starting material was placed at the high-temperature end. Single crystals of $CeSe_{1.9}$ have a coffin lid appearance; $PrSe_{1.9}$ forms thin platelets. Both selenides are deeply colored and have a shiny luster (Fig. 1).

Analyses

The composition of the samples was determined by ICP-methods giving $CeSe_{1.89\pm0.01}$ and $PrSe_{1.90\pm0.01}$, respectively. A significant amount of hydrogen and oxygen could not be found. Possible silicon and iodine contamination could not be detected by microprobe analysis.

Crystallographic Work

Precession photographs (Mo$K\alpha$ radiation) of single crystals yielded almost the same diffraction pattern for both compounds. In addition to strong reflections indicating a tetragonal subcell with PbFCl or anti-Cu_2Sb-type structure we found weak reflections enlarging the cell dimensions:

$$\mathbf{a}' = \mathbf{a} + 2\mathbf{b}, \quad \mathbf{b}' = -2\mathbf{a} + \mathbf{b}, \quad \mathbf{c}' = 2\mathbf{c}$$

$$a' = b' = \sqrt{5}a, \quad c' = 2c.$$

The Laue symmetry is reduced to $4/m$. With the systematically absent reflections ($hk0$ for $h + k = 2n$ only, $00l$ for $l = 2n$ only) the space group $P4_2/n$ could be derived unambiguously. Details of the X-ray data collections and information about the structure determinations are given in Table I. Atomic scattering factors for neutral atoms were taken from "International Tables of X-Ray Crystallography" (*6*). The program

TABLE I

EXPERIMENTAL INFORMATION AND STRUCTURE DETERMINATION DETAILS

Compound	$CeSe_{1.9}$	$PrSe_{1.9}$
Crystal shape	Coffin lid like	Platelet
Crystal volume (mm^3)	0.0204	0.00124
Diffractometer	Siemens AED 2, graphite monochr., Mo$K\alpha$ radiation	
Determination of cell parameters		
No. of reflections used (θ-range)	50 (7.7–30.0)	37 (7.8–30.0)
Cell parameters at 293 K (Å)	$a = 9.3598(9)$	$a = 9.296(2)$
	$c = 16.938(2)$	$c = 16.860(4)$
Space group	$P4_2/n$	$P4_2/n$
Z	20	20
Calculated density (g cm^{-3})	6.317	6.452
Intensity data collection		
Max. sin θ/λ ($Å^{-1}$)	0.7567	0.756
Range of h, k, l	$\overline{14}, \overline{14}, \overline{26}$ to 14, 14, 9	$\overline{14}, \overline{14}, \overline{26}$ to 14, 14, 10
Scan mode	ω	ω
Min. scan angle (°)	1.05	1.05
Max. scan time (sec)	31.5	31.5
Standard reflections	126, $\bar{1}\bar{2}\bar{6}$, $24\bar{6}$	126, $\bar{1}\bar{2}\bar{6}$, $24\bar{6}$
Intensity variation	<1%	<1%
Measured reflections	16,222	15,938
Unique reflections	2,703	2,633
Observed reflections ($F > 3\sigma(F)$)	2,044	1,825
R_{int}	0.0855	0.1055
Absorption correction		
Min.–max. transmission	0.0049–0.0459	0.0124–0.6366
μ (cm^{-1})	357.43	375.76
Structure determination technique	Deduced from PbFCl-type by plausibility	
Structure refinement (based on F)		
R^a, $R_w{}^a$, ($w = 1/\sigma^2(F_o)$), S^a	0.038, 0.029, 2.52	0.058, 0.044, 3.74
No. of parameters refined	68	68
Max. final $\lvert\Delta\rvert/\sigma$	0.00	0.00
Max. and min. $\Delta\rho$ ($eÅ^{-3}$)	2.0, −2.9	3.9, −6.7

[a] Definitions given in *Acta Crystallogr. Sect. B* **38**, 699 (1982).

used was STRUCSY from the diffractometer software package.[1]

Magnetic Measurements

The magnetic behavior of $PrSe_{1.9}$ was measured in the temperature range 3–250 K by the Faraday method (Fig. 2). The magnetic data were interpreted using a model (*7*) developed previously in which the influence of the crystal field is theoretically described by the angular overlap model (*8*). The procedure of calculation corresponds to the one given in (*9*). The values for the angular overlap parameters e_σ and e_π are taken from inelastic neutron scattering measurements on PrSe (*10*). The calculations agree well (Fig. 2) with the observed ones. Thus it can be concluded that the va-

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[1] Additional material to this paper (lists of observed structure factors, anisotropic thermal parameters) can be ordered from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, FRG. Please quote Reference CSD53368, the names of the authors, and the title of the paper.

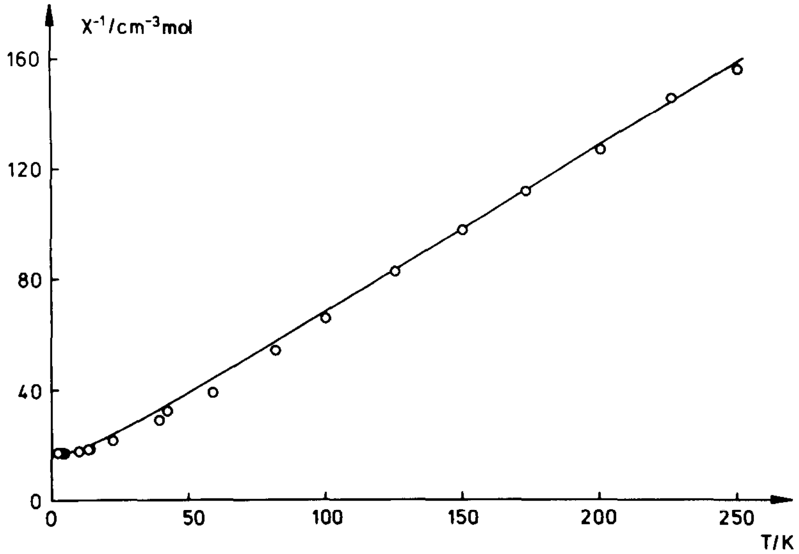

FIG. 2. Inverse magnetic susceptibility vs temperature for $PrSe_{1.9}$ (the solid curve represents the calculated values).

lency of Pr is +3, and therefore Se_2^{2-} units have to be assumed in $PrSe_{1.9}$.

Results and Discussion

The structure of *RE*$Se_{1.9}$ (*RE* = Ce, Pr) is a distorted variation of the PbFCl-type structure with vacancies. PbFCl crystallizes in a tetragonal structure which can be characterized by stacking slabs. In turn the slabs consist of Cl, Pb, F, Pb, Cl layers with a doubled occupation of the fluorine layer (Fig. 3). Whether the Cl atom of the adjacent slab should be regarded as a ninth atom, coordinating the cation and leading to a three-dimensional structure, depends on the values of the free parameters. The structure determinations (Table II) result in a formulation of *RE*$Se_{1.9}$ as $RE_{20}(Se(I)_2)_8Se(I)_2\square_2Se(II)_{20}$, in accordance with the magnetic measurements, where the layer built up by the $Se(I)_2^{2-}$ pairs and $Se(I)^{2-}$ ions corresponds to the fluorine layer and the layer formed by the $Se(II)^{2-}$ ions to the chlorine layer. The vacancies are ordered in the Se(I) layer (Fig. 4) giving a different coordination geometry for the *RE* atoms with coordination number 9 for *RE*(1) and *RE*(3) and 8 for *RE*(2) (Fig. 5). Selected interatomic distances are given in Table III. Se–Se pairs as found here have already been observed in the corresponding compounds $CeSe_2$ and $PrSe_2$. $CeSe_2$ (*4*) and $PrSe_2$ (*11*), which have to be formulated as

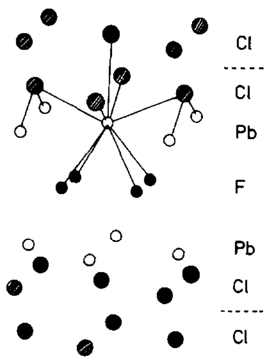

FIG. 3. The sequence of layers in the structure of PbFCl.

TABLE II

Fractional Atomic Coordinates and Equivalent Isotropic Displacement Factors (Å^2), Calculated as One-Third Trace U, for CeSe$_{1.9}$ and PrSe$_{1.9}$

Atom	Position	x	y	z	U_{eqv}
Ce(1)	8g	0.95706(3)	0.65221(4)	0.12003(2)	0.0093(2)
Ce(2)	8g	0.14732(4)	0.05398(4)	0.10446(2)	0.0093(2)
Ce(3)	4e	$\frac{3}{4}$	$\frac{1}{4}$	0.11522(4)	0.0086(2)
Se(I1)	8g	0.06866(6)	0.88190(7)	0.24929(4)	0.0129(3)
Se(I2)	8g	0.31850(7)	0.97176(7)	0.25024(4)	0.0146(3)
Se(I3)	2b	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	0.0123(4)
Se(II1)	8g	0.54888(6)	0.84779(7)	0.42711(4)	0.0089(4)
Se(II2)	8g	0.14880(6)	0.05211(6)	0.43661(4)	0.0090(4)
Se(II3)	4e	$\frac{3}{4}$	$\frac{1}{4}$	0.43426(7)	0.0087(4)
Pr(1)	8g	0.95673(6)	0.65198(7)	0.11968(4)	0.0098(4)
Pr(2)	8g	0.14745(8)	0.05352(7)	0.10486(4)	0.0097(4)
Pr(3)	4e	$\frac{3}{4}$	$\frac{1}{4}$	0.11542(8)	0.0085(5)
Se(I1)	8g	0.06763(12)	0.88078(12)	0.24935(9)	0.0153(6)
Se(I2)	8g	0.31998(13)	0.97145(12)	0.25003(10)	0.0166(6)
Se(I3)	2b	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	0.0129(8)
Se(II1)	8g	0.54900(12)	0.84789(13)	0.42765(7)	0.0095(7)
Se(II2)	8g	0.14905(13)	0.05217(11)	0.43652(7)	0.0096(7)
Se(II3)	4e	$\frac{3}{4}$	$\frac{1}{4}$	0.43451(15)	0.0087(9)

$RE_4(Se_2)_2Se_4$, crystallize in a monoclinic distorted PbFCl structure with a coordination number for the RE metal of 9. For the mentioned compounds the Se(I)–Se(I) distances are comparable (CeSe$_{1.9}$, 2.485 Å; CeSe$_2$, 2.464 Å; PrSe$_{1.9}$, 2.493 Å; PrSe$_2$, 2.475 Å). The reduction of the coordination number of some RE atoms from 9 to 8 going

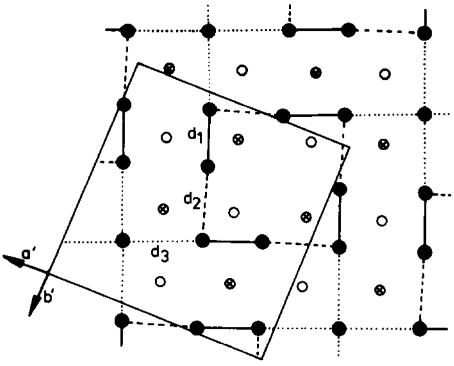

Fig. 4. The Se(I) layer in the crystal structure of RESe$_{1.9}$ (RE = Ce, Pr). In addition to the Se(I) atoms (●) the figure shows the RE atoms above (⊗) and below (O) the layer. Values for the interatomic distances d_1, d_2, and d_3 are given in Table III. The unit cell is lined out.

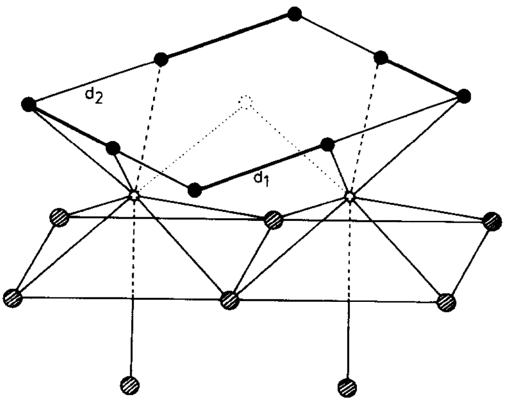

Fig. 5. The coordination geometry for the RE atoms (O) with the coordination number 8 (Se(I) = ●, Se(II) = ◍).

TABLE III

INTERATOMIC DISTANCES (Å) FOR $\mathrm{CeSe}_{1.9}$ AND $\mathrm{PrSe}_{1.9}$

			$\mathrm{CeSe}_{1.9}$	$\mathrm{PrSe}_{1.9}$
RE(1)	2	Se(I1)	3.110(1), 3.242(1)	3.089(1), 3.219(1)
		Se(I2)	3.259(1)	3.233(2)
		Se(I3)	3.073(1)	3.057(1)
	2	Se(II1)	3.084(1), 3.108(1)	3.064(1), 3.090(1)
	2	Se(II2)	3.106(1), 3.117(1)	3.085(1), 3.094(1)
		Se(II3)	3.033(1)	3.016(1)
RE(2)		Se(I1)	3.025(1)	3.009(1)
	2	Se(I2)	3.041(1), 3.190(1)	3.023(1), 3.169(1)
	2	Se(II1)	3.005(1), 3.012(1)	2.988(1), 2.994(2)
	2	Se(II2)	3.003(1), 3.031(1)	2.986(1), 3.012(1)
		Se(II3)	3.074(1)	3.051(1)
RE(3)	2	Se(I1)	3.110(1) (2×)	3.091(1) (2×)
	2	Se(I2)	3.149(1) (2×)	3.133(2) (2×)
	2	Se(II1)	3.030(1) (2×)	3.014(1) (2×)
	2	Se(II2)	3.108(1) (2×)	3.088(1) (2×)
		Se(II3)	3.064(2)	3.050(2)
Se(I1)	3	Se(I2)	d_1 = 2.485(1), d_2 = 2.947(1), 3.475(1)	d_1 = 2.493(1), d_2 = 2.921(1), 3.438(1)
		Se(I3)	d_3 = 3.228(1)	d_3 = 3.193(1)

from $RE\mathrm{Se}_2$ to $RE\mathrm{Se}_{1.9}$ is completed in $RE_2\mathrm{Se}_3$ which crystallizes in a defect $\mathrm{Th}_3\mathrm{P}_4$-type structure (powder work (*12*), single-crystal work (*11*)). The successive reduction of the coordination number from 9 to 8 is confirmed by preliminary structural work on $\mathrm{PrSe}_{1.8}$ (*11, 13*) which shows an incommensurate superstructure of PbFCl.

Acknowledgments

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