The GdPS Structure, a New PbFCl-Type Derivative

F. HULLIGER

Laboratorium für Festkörperphysik ETH, CH–8093 Zürich, Switzerland

AND

R. SCHMELCZER AND D. SCHWARZENBACH

Institut de Cristallographie, Université de Lausanne, CH–1015 Lausanne-Dorigny, Switzerland

The structure of GdPS is orthorhombic, space group *Pmnb*; $a = 5.3620(5)$, $b = 5.4079(6)$, $c = 16.742(2)$ Å, $Z = 8$. It is a distorted derivative of the tetragonal PbFCl structure (a_0, c_0) with $a \approx b \approx 2^{1/2} a_0$, $c = 2c_0$. The distortions are due to the formation of phosphorus chains. This structure type is found also in other rare-earth sulfopolyphosphides, e.g., with $Ln = La \cdots Sm$, $Tb \cdots Tm$, Y.

Introduction

Up to now neither the stoichiometry nor the structure can be predicted for line phases of a binary or ternary system. As a rule the more electronegative elements, i.e., those in the upper right corner of the periodic system, form Mooser–Pearson phases under normal conditions, particularly with the electropositive elements such as the alkali, alkaline-earth, and rare-earth elements. The probability for a phase to obey the Mooser–Pearson rules (*1, 2*), hence to be a semiconductor or possibly a semimetal but never a true metal, increases with the anion concentration. Thus all phases with more anions than would correspond to the normal valence rules are suspect of being nonmetallic polyanionic compounds. On going to analogs with heavier anions the energy-band gaps decrease and band overlap at certain parts of momentum space finally may occur. This overlap may modify the crystal structure. In alkali and alkaline-earth compounds, where no *d*-bands are involved, the crystal structure will change completely whereas with *d*-element cations the structure may remain unchanged or simply become more symmetric.

The X-ray pattern of GdPS could not be accounted for by any of the appropriate structure types, such as pyrite, marcasite, arsenopyrite, $ZrSi_2$, CaC_2, $CuAl_2$, etc. From its nonmetallic character, however, it was clear that GdPS was a true polyanionic compound. So we suspected its structure to be a distorted version of a known MX_2 or MXY type occurring in a metallic phase or in a nonmetallic one containing more anion valence electrons (*3*). The similarity of the the GdPS pattern with those of its heavy-anion analogs, the metallic PbFCl-type $LnSb_xTe_{2-x}$ phases, suggested a PbFCl derivative. This seemed all the more reasonable as meanwhile such a distorted version had been found in CeAsS (*4*). It turned out that the GdPS structure is in fact yet a second type of PbFCl derivative.

Experimental Part

Lath-shaped single crystals of GdPS up to $1 \times 5 \times 0.2$ mm^3 had been obtained by an

TABLE I

CRYSTALLOGRAPHIC DATA FOR GdPS, ORTHORHOMBIC, $Pmnb$ (No. 62), $Z = 8^a$

	x	y	z	$10^5 U_{11}$	$10^5 U_{22}$	$10^5 U_{33}$	$10^5 U_{12}$	$10^5 U_{13}$	$10^5 U_{23}{}^b$
Gd$_I$		0.0160(2)	0.1376(1)	642	686	529	0	0	11
Gd$_{II}$		−0.0152(2)	0.6469(1)	635	660	494	0	0	11
P	0.0382(5)	0.7046(4)	−0.0025(2)	1015	460	840	18	8	19
S$_I$		0.5150(5)	0.1888(3)	835	639	773	0	0	−20
S$_{II}$		0.4883(5)	0.6833(3)	857	637	756	0	0	−34

^{a} P in 8 (d): $\pm(x,y,z;\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z;\frac{1}{2}-x,y,z;x,\frac{1}{2}+y,\frac{1}{2}-z)$, Gd$_I$, Gd$_{II}$, S$_I$, and S$_{II}$ in 4 (c): $\pm(\frac{1}{4},y,z;\frac{1}{4},\frac{1}{2}+y,\frac{1}{2}-z)$. At 295°K: $a = 5.3620(5)$ Å, $b = 5.4079(6)$ Å, $c = 16.742(2)$ Å, $V = 488.1(1)$ Å^3.

^{b} The anisotropic temperature factor is defined as $\exp(-2\pi^2 \sum h_i h_j a_i^* a_j^* U_{ij})$.

iodine-transport process at temperatures around 1000°C (3). GdPS powder and single crystals are stable in air. Small undeformed crystals were selected for the precession and the intensity measurements which were carried out with Nb-filtered MoKα radiation. The intensity data were collected with an automatic four-circle diffractometer Syntex P2₁ up to $2\theta = 60°$. They were corrected for absorption using an absorption coefficient $\mu_{MoK\alpha} = 290.34$ cm^{-1}. A total of 787 reflections were collected, 726 of which had an intensity $>3\sigma$. For the data reduction and structure-solving procedure the X-ray System (5) program package was used. The structure was solved by the usual Patterson and Fourier methods. Extinction corrections were found to be important in the least-squares refinement. The final R value thus obtained was 0.046. The relevant data are listed in Table I. The setting $Pmnb$ was chosen for the space group in order to make the relationship with the tetragonal PbFCl structure evident. Interatomic distances are given in Table II.

TABLE II

INTERATOMIC DISTANCES IN GdPS

Gd$_I$	4 P at 3.103(2×) and 3.128 Å (2×)
	3 S$_I$ at 2.831, 2.842, and 2.906 Å
	2 S$_{II}$ at 2.788 Å
	4 Gd$_{II}$ at 3.808(2×) and 3.814 Å (2×)
Gd$_{II}$	4 P at 2.924(2×) and 3.113 Å (2×)
	2 S$_I$ at 2.771 Å
	3 S$_{II}$ at 2.753, 2.790, and 2.843 Å
P	2 P at 2.252 and 2.271 Å
	2 Gd$_I$ at 3.103 and 3.128 Å
	2 Gd$_{II}$ at 2.924 and 3.113 Å
	4 P at 3.091, 3.222, and 3.477 Å (2×)
	2 S$_I$ at 3.549 and 3.678 Å
	2 S$_{II}$ at 3.579 and 3.850 Å
S$_I$	3 Gd$_I$ at 2.831, 2.842, and 2.906 Å
	2 Gd$_{II}$ at 2.771 Å
	2 S$_I$ at 3.393 Å
	2 S$_{II}$ at 3.431 Å
	4 P at 3.549(2×) and 3.678 Å (2×)
S$_{II}$	2 Gd$_I$ at 2.788 Å
	3 Gd$_{II}$ at 2.753, 2.790, and 2.843 Å
	2 S$_I$ at 3.431 Å
	2 S$_{II}$ at 3.507 Å
	2 P at 3.579 Å

Discussion

The GdPS structure is a distorted version of the PbFCl structure with $a \approx b \approx 2^{1/2} a_0$, $c = 2c_0$. The basic tetragonal PbFCl structure can be described by the stacking of square layers Cl$_n$–Pb$_n$–F$_{2n}$–Pb$_n$–Cl$_n$. The cations are thus located between an F square and a Cl square which is twice as large and rotated relative to the former. Whether the Cl atom of the adjacent sheet, which is located above the center of the Cl square, should be regarded as a ninth neighbor depends upon the free parameters. In BiOF the distances are Bi–4O = 2.79 Å, Bi–1O = 2.75 Å, whereas in EuOBr, Eu–4Br = 3.18 Å, Eu–1Br = 4.46 Å, and in ZrSiTe (6) Zr–4Te = 2.93 Å, Zr–1Te = 3.90 Å. This structure type thus comprises
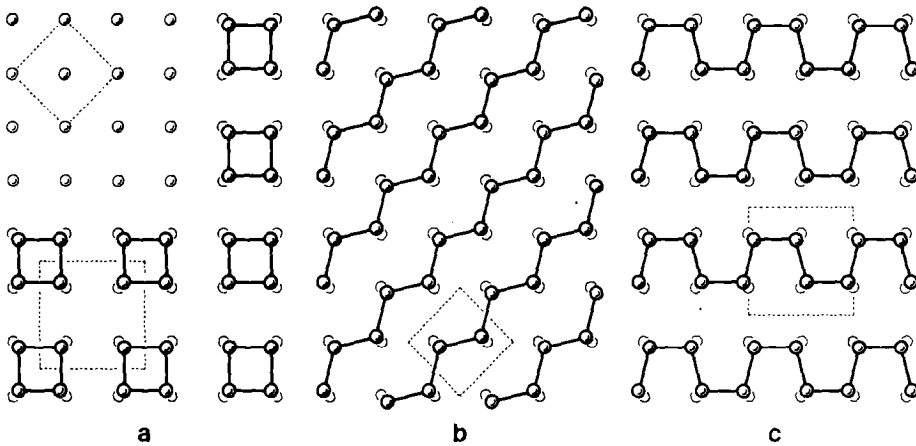
FIG. 1. Three possibilities for the formation of P^{-1} polyanions by distorting a planar square P net as present in the PbFCl-type structure. (a) Above: the undistorted square net of the PbFCl-type structure; below: hypothetical. (b) The As net present in the CeAsS. (c) The P net of the GdPS type.

both three-dimensional and layer-type representatives. In all known PbFCl-type chalcogenopnictides the interlayer bond and the four intralayer bonds are of comparable strength so that these phases are in fact built up of three-dimensional networks (7, 8). In the structure of GdPS, P takes the positions of F and S those of Cl. The interlayer Gd–S distances Gd_I-S_I and $Gd_{II}-S_{II}$ are slightly larger than the intralayer Gd–S distances. The Gd and the S atoms suffer only minor shifts from the positions in the tetragonal PbFCl structure. The essential change takes place in the P square layer. The nonmetallic properties of GdPS require the occurrence of one anion–anion bond per formula. Since no P–S units similar to the anion pairs in the arsenopyrite (FeAsS) and gersdorffite (NiSbS) structure can form, the only alternative is the deformation of the phosphorus square net. In Fig. 1 we have indicated three possibilities for satisfying the bond requirements: (a) discrete squares as met in the skutterudite-type structure of CoP_3, (b) simple zigzag chains as found in CeAsS (4), and (c) the truncated chains actually realized in the GdPS structure. The four P–P distances, which are equal (2.70 Å) in the PbFCl-type structure, transform to 2.252, 2.271, and 3.222, 3.091 Å in GdPS. The
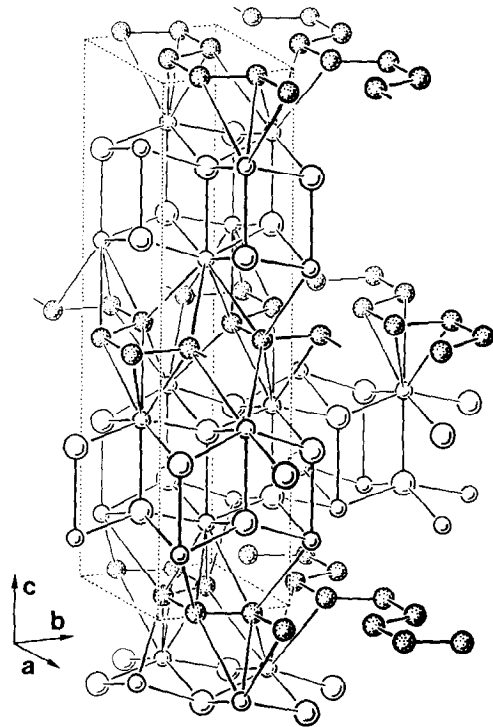

FIG. 2. The structure of orthorhombic GdPS. Smallest spheres: Gd, largest spheres: S, stippled spheres: P. Certain bonds are omitted.

P–P–P bond angle is increased from 90 to 100.5°. The bonding P–P contacts are within the range observed for P–P single bonds in similar P chains, such as 2.22 and 2.31 Å in LaP_2 (9), 2.201 and 2.224 Å (P–P–P = 102.0°) in PdP_2 (10), 2.17 and 2.21 Å (bond angles 107.1 and 109.2°) in red tetragonal α-ZnP_2 (11) and 2.17 and 2.20 Å in α-CeP_2 (12). The GdPS structure is represented in Fig. 2 where the phosphorus chains are emphasized.

From X-ray powder patterns we deduce that this structure type occurs also in other LnPS phases. In Table III we have listed some lattice constants derived from Guinier patterns taken with silicon as calibration standard. On plotting lattice constants versus Ln^{3+} ionic radii we obtain smooth, slightly concave curves.

One might expect the LnAsSe phases, at least those with the larger Ln atoms, to be isostructural with GdPS. However, our powder patterns point to a close similarity with the monoclinic LnAsS phases. In ZrSiS (6), HfSiS (13), ThSiS (14), and USiS (15) no nonmetallic modification was observed up to now. Although these phases and their analogs could display the same valence–electron configuration as LaPS, etc., they were found to crystallize either in the undistorted PbFCl

or in the UGeTe (anti-Ti_2Bi) structure. Possibly a GdPS- or a CeAsS-type HfSiS or ThSiS phase might exist as a nonmetallic low-temperature modification.

Acknowledgments

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TABLE III

LATTICE CONSTANTS OF GdPS-TYPE LnPS PHASES (295°K)^a

Ln	a (Å)	b (Å)	c (Å)
La	5.5974(8)	5.6882(7)	17.265(4)
Ce	5.5408(8)	5.6219(8)	17.112(3)
Pr	5.5042(8)	5.5750(8)	17.033(4)
Nd	5.4700(8)	5.5340(8)	16.960(4)
Sm	5.4125(8)	5.4667(8)	16.834(3)
Gd	5.3620(5)	5.4079(6)	16.742(2)
Tb	5.3307(6)	5.3721(6)	16.678(3)
Dy	5.3103(5)	5.3475(6)	16.624(3)
Ho	5.2897(7)	5.3224(6)	16.570(4)
Er	5.2654(6)	5.2973(6)	16.519(2)
Tm	5.2466(7)	5.2740(7)	16.481(4)
Y	5.309(2)	5.344(2)	16.64(4)

^{a} The estimated error of the last digit is given in parentheses.