Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Solid State Chemistry 173 (2003) 259–272
JOURNAL OF SOLID STATE CHEMISTRY
http://elsevier.com/locate/jssc

The lanthanoid polyantimonides with the ideal compositions Pr_5Sb_{12} and Nd_5Sb_{12} crystallizing with a new structure type and Ho_2Sb_5 with Dy_2Sb_5-type structure

Tobias Schmidt, Rainer O. Altmeyer, and Wolfgang Jeitschko*

Institut für Anorganische und Analytische Chemie, Universität Münster, Wilhelm-Klemm-Straße 8, D-48149 Münster, Germany

Received 16 August 2002; received in revised form 10 December 2002; accepted 19 December 2002

Abstract

The title compounds were isolated in well-crystallized form from samples with a substantial excess of antimony, annealed at temperatures slightly below the melting point of that element. Their crystal structures were determined from single-crystal diffractometer data. $Pr_{9-x}Sb_{21-y}$ and $Nd_{9-x}Sb_{21-y}$ crystallize with a new monoclinic structure type, Pearson symbol *mS*(62–5.4), space group *Cm*, $Z = 2$ with $a = 2859.1(4)$ pm, $b = 426.3(1)$ pm, $c = 1356.1(2)$ pm, $\beta = 95.52(1)^\circ$, $R = 0.034$ for 4351 structure factors and 188 variable parameters for $Pr_{9-x}Sb_{21-y}$ and $a = 2845(2)$ pm, $b = 424.7(8)$ pm, $c = 1345.9(9)$ pm, $\beta = 95.42(7)^\circ$, $R = 0.069$ for 2928 *F* values and 188 variables for $Nd_{9-x}Sb_{21-y}$. Of the 30 atomic sites, three show fractional occupancy corresponding to the compositions $Pr_{8.303(5)}Sb_{20.03(1)}$ and $Nd_{8.30(2)}Sb_{19.98(9)}$, respectively. A model for the order of occupied atomic sites with a tripled *b*-axis is proposed resulting in the ideal compositions Pr_5Sb_{12} and Nd_5Sb_{12}. The holmium compound Ho_2Sb_5 has a Dy_2Sb_5-type structure: *mP*28, $P2_1/m$, $a = 1301.8(3)$ pm, $b = 414.9(1)$ pm, $c = 1451.1(2)$ pm, $\beta = 102.14(1)^\circ$, $R = 0.028$ for 2573 *F* values and 86 variables. In both structure types most rare earth atoms have nine antimony neighbors forming tricapped trigonal prisms. The coordination polyhedra of the antimony atoms show a great variety, with a trigonal prism of rare earth atoms as one extreme case. The other extreme coordination of an antimony atom is a distorted octahedron formed by six antimony atoms. The differences and similarities of both structures are discussed. Chemical bonding within the antimony polyanions is analyzed on the basis of an extended Zintl–Klemm concept using bond-length–bond-strength relationships.

1. Introduction

The phase diagrams of the binary systems of rare earth elements with antimony have been investigated some years ago. On the antimony-rich side they contain compounds formed by peritectic reactions [1–9]. The crystal structures of several of these compounds have not been known at the time of these investigations. For that reason the compositions of these compounds are not known accurately. We have recently reported on the antimonides Ln_2Sb_5 (Ln = Sm, Gd, Tb, and Dy) and determined their crystal structure on the basis of single-crystal X-ray data of Dy_2Sb_5 [10]. Our investigations concerning the corresponding systems with the early lanthanoids resulted in the two isotypic antimonides $Pr_{9-x}Sb_{21-y}$ and $Nd_{9-x}Sb_{21-y}$, reported here. In addition, we found the new compound Ho_2Sb_5 which is isotypic with Dy_2Sb_5. The crystal structures of these three compounds were all determined from single-crystal X-ray data. Preliminary results for $Nd_{9-x}Sb_{21-y}$ have already been presented by us at a conference [11].

The least-squares refinements of the occupancy parameters of the praseodymium and neodymium compounds showed that three out of the 30 crystallographic sites have fractional occupancies. These three sites are arranged in a string parallel to the short *b*-axis of the structure. Atomic order for these sites can be achieved if the *b*-axis is tripled. This order corresponds to the composition Ln_5Sb_{12} with a Ln/Sb ratio of 29.41/70.59, which is very close to the ratios 29.31/70.69 and 29.35/70.65 resulting from the least-squares refinements for the praseodymium and neodymium compounds, respectively. However, since the weak superstructure reflections corresponding to the tripled *b*-axis have not been observed, we mostly refer to these compounds with the formula $Ln_{9-x}Sb_{21-y}$.

*Corresponding author. Fax: +49-251-8333-136.
E-mail address: jeitsch@uni-muenster.de (W. Jeitschko).

0022-4596/03/$ - see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0022-4596(03)00054-9

2. Sample preparation, properties, and lattice constants

The samples were prepared by reaction of the elemental components at high temperatures. The rare earth elements were purchased in the form of ingots with nominal purities of 99.9%. Filings of these elements were prepared under dry (Na) paraffin oil. Adhering iron particles were removed by a magnet. The paraffin oil was washed out by dry hexane. The filings were stored under vacuum and only briefly exposed to air prior to the reactions. The antimony powder had a stated purity of 99.99%.

Because of the suspected peritectic formation of the compounds, we prepared the samples with compositions of high antimony content. The elements were mixed in the atomic ratios varying between 1:6 and 1:8. The mixtures were cold-pressed to pellets, sealed in evacuated silica tubes, and slowly heated (10°C/h) to temperatures between 750°C and 800°C. After annealing for one week, the samples were slowly cooled (2°C/h) to 550°C and held at that temperature for two weeks, followed by quenching in air.

The samples tubes were opened in air, and characterized by the Guinier technique with monochromated Cu$K\alpha_1$ radiation using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. The patterns were indexed with monoclinic cells as obtained from the single-crystal investigations using the calculated patterns [12] as guides. The lattice constants (Table 1) were obtained from least-squares fits of the data. The consistency of the data may be judged from the plot of the average atomic volumes (Fig. 1).

The products are stable on air for long periods of time. The binary rare earth antimonides crystallize in the form of needles (the monoclinic *b*-axes corresponding to the needle axes) with metallic luster. They can clearly be distinguished from the excess antimony in a stereo microscope. Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope, suited for detecting elements heavier than sodium, did not reveal such elements.

3. Single-crystal investigations

Single crystals, suited for structure determinations were isolated from the samples and selected for further investigations on the basis of Laue diffractograms. A complete set of Weissenberg diagrams was recorded for the neodymium compound, which revealed the *C*-centered monoclinic cell. Intensity data for the structure determinations were measured on a four-circle diffractometer (Enraf-Nonius) with graphite-monochromated

Table 1
Lattice constants of binary monoclinic antimonides as determined from Guinier powder data[a]

Compound	*a* (pm)	*b* (pm)	*c* (pm)	β (°)	*V* (nm^3)
$Pr_{9-x}Sb_{21-y}$	2856.9(4)	426.0(1)	1354.6(2)	95.55(1)	1.6409
$Nd_{9-x}Sb_{21-y}$	2849.3(4)	424.8(1)	1349.7(2)	95.48(1)	1.6262
Ho_2Sb_5	1301.8(2)	415.4(1)	1452.9(2)	102.11(1)	0.7682

[a] Standard deviations in the place values of the least-significant digits are given in parentheses throughout the paper.

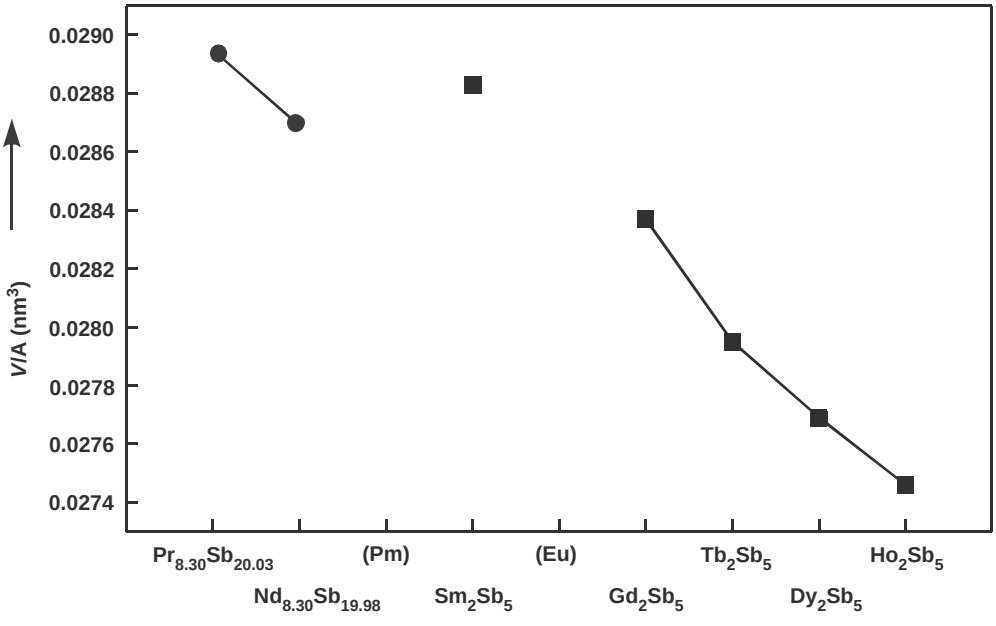

Fig. 1. Average atomic volumes V/A for antimonides with $Nd_{9-x}Sb_{21-y}$ and Dy_2Sb_5-type structure.

Table 2
Crystallographic data of $Pr_{9-x}Sb_{21-y}$, $Nd_{9-x}Sb_{21-y}$, and Ho_2Sb_5

Compound	$Pr_{9-x}Sb_{21-y}$	$Nd_{9-x}Sb_{21-y}$	Ho_2Sb_5
Space group	*Cm* (No. 8)	*Cm* (No. 8)	$P2_1/m$ (No. 11)
a (pm)	2859.1(4)	2845.2(16)	1301.8(3)
b (pm)	426.3(1)	424.7(8)	414.9(1)
c (pm)	1356.1(2)	1345.9(9)	1451.1(2)
β (°)	95.52(1)	95.42(7)	102.14(1)
V (nm^3)	1.6452(4)	1.619(2)	0.7662(2)
Pearson symbol[a]	*mS*(62–5.33)	*mS*(62–5.44)	*mP*28
Formula units/cell (*Z*)	2	2	4
Composition	$Pr_{8.303(5)}Sb_{20.03(1)}$	$Nd_{8.30(2)}Sb_{19.98(9)}$	Ho_2Sb_5
Formula mass	3608.6	3629.8	938.6
Calculated density (g/cm^3)	7.28	7.45	8.14
Crystal dimensions (μm)	$100 \times 10 \times 10$	$67 \times 10 \times 10$	$200 \times 20 \times 20$
$\theta/2\theta$ Scans up to 2θ (°)	65	60	70
Range in h, k, l	± 42, ± 6, ± 20	± 40, 0–5, ± 18	± 20, ± 6, ± 23
Total no. of reflections	16743	5269	13396
Unique reflections	6658	5266	3728
Internal residual R_i	0.065 (*I*)	—	0.068 (*I*)
Reflections with $I_0 > 2\sigma$ (I_0)	4351	2928	2573
No. of variables	188	188	86
Conventional residual R ($F > 2\sigma$)	0.034	0.069	0.028
Weighted residual R_w (all F^2)	0.072	0.158	0.075
Flack parameter	–0.0003(618)	0.0006(3712)	–
Largest diffraction peak/hole ($e/Å^3$)	4.3/–3.6	4.4/–5.3	3.6/–3.6

[a] Pearson symbol is given in the form as suggested by Parthé et al. [13].

Mo$K\alpha$ radiation and a scintillation counter with pulse-height discrimination. The scans were along the Laue streaks ($\theta/2\theta$) with background counts at both ends of each scan. Absorption corrections were applied using psi scan data. Further details of the data collections are summarized in Table 2.

The structure of the neodymium compound was solved by interpretation of the Patterson function and subsequent difference Fourier analyses. The holmium compound had been recognized to be isotypic with Dy_2Sb_5 [10] already from its powder pattern. The structures were refined by a full-matrix least-squares program [14] using atomic scattering factors, corrected for anomalous dispension as supplied by the program software. Weights were based on the counting statistics and a parameter accounting for secondary extinction was refined as a least-squares variable.

As checks for the composition we refined occupancy parameters for each structure. For Ho_2Sb_5, no significant deviations from the ideal occupancy parameters were observed: these parameters varied between the values of 0.993(5) for the Sb10 atom and 1.007(5) for Sb6. In contrast, for both $Pr_{9-x}Sb_{21-y}$ and $Nd_{9-x}Sb_{21-y}$ significant deviations from the ideal occupancy parameters were found for the positions of the Pr1(Nd1), Sb1, and Sb12 atoms, while the occupancy parameters for all other atomic positions were rather close to the ideal values: they varied between 0.988(6) for the Pr7 position and 1.018(7) for the Sb21 position of $Pr_{9-x}Sb_{21-y}$ and between 0.94(2) and 1.06(2) for the Sb14 and Sb18 positions, respectively, for $Nd_{9-x}Sb_{21-y}$. Therefore, in the final refinement cycles only the occupancy parameters for the Pr1(Nd1), Sb1, and Sb12 positions were varied, while all other occupancy parameters were held at the ideal values. The results of the three structure refinements are summarized in Tables 2–6. The crystal structures of $Pr_{9-x}Sb_{21-y}$ and Ho_2Sb_5, their relationship, their coordination polyhedra and antimony polyanions are shown in Figs. 2–7. The positional and the anisotropic displacement parameters for all refinements have been deposited.[1]

We should mention that the structure refinements of $Pr_{9-x}Sb_{21-y}$ and $Nd_{9-x}Sb_{21-y}$ in the noncentrosymmetric space group *Cm* were not straightforward. The structure of these isotypic compounds is nearly centrosymmetric. Structure refinements in the corresponding centrosymmetric space group *C*2/*m* led to conventional residuals of nearly 10% with half as many variable parameters. In that space group the positions of the Sb14 atoms would need to be placed at a symmetry center and the positions of the atom pairs Sb2&Sb3, Pr4&Pr7, Pr5&Pr6, Sb6&Sb20, etc. (Figs. 2 and 3) are combined to one

[1] They may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) by quoting the registry numbers CSD-412686 ($Pr_{9-x}Sb_{21-y}$), CSD-412687 ($Nd_{9-x}Sb_{21-y}$), and CSD-412685 (Ho_2Sb_5).

Table 3
Atomic parameters of $Pr_{8.303(5)}Sb_{20.03(1)}$ and $Nd_{8.30(2)}Sb_{19.98(9)}$[a]

Atom	x	y	z	U (pm^2)
Pr1/Nd1	0.0000(1)/0.0000(5)	0	0.0000(3)/0.0000(9)	116(11)/163(44)
Pr2/Nd2	0.21627/0.21526	0	0.17921/0.17734	94(3)/88(7)
Pr3/Nd3	0.32505(6)/0.3243(2)	0	0.4468(1)/0.4453(4)	74(3)/75(7)
Pr4/Nd4	0.42792(6)/0.4270(2)	0	0.6897(1)/0.6878(4)	86(3)/88(8)
Pr5/Nd5	0.46564(7)/0.4649(2)	0	0.3971(1)/0.3960(4)	92(3)/93(7)
Pr6/Nd6	0.59555(6)/0.5949(2)	0	0.8219(1)/0.8200 (3)	84(3)/80(7)
Pr7/Nd7	0.64070(6)/0.6397(2)	0	0.5402(1)/0.5388(3)	81(3)/97(8)
Pr8/Nd8	0.74246(7)/0.7420(2)	0	0.7909(1)/0.7895(4)	75(2)/75(7)
Pr9/Nd9	0.84633(5)/0.8456(1)	0	0.0503(1)/0.0495(3)	80(3)/89(7)
Sb1	0.0097(1)/0.0095(5)	0.2457(10)/0.244(3)	0.9648(2)/0.9616(13)	193(11)/118(49)
Sb2	0.01061(8)/0.0096(2)	0	0.7632(1)/0.7619(4)	99(3)/106(9)
Sb3	0.05569(8)/0.0551(2)	0	0.4491(1)/0.4466(4)	109(3)/133(10)
Sb4	0.09216(7)/0.0914(2)	0	0.2068(1)/0.2046(4)	141(3)/136(8)
Sb5	0.11760(7)/0.1167(2)	0	0.0077(1)/0.0053(4)	111(3)/116(10)
Sb6	0.16022(7)/0.1597(2)	0	0.7200(1)/0.7187(4)	81(3)/90(10)
Sb7	0.20882(7)/0.2078(2)	0	0.4267(1)/0.4249(4)	89(3)/87(9)
Sb8	0.26879(7)/0.2685(2)	0	0.9691(1)/0.9678(4)	94(3)/88(9)
Sb9	0.31057(7)/0.3098(2)	0	0.6843(1)/0.6832(4)	77(3)/64(9)
Sb10	0.36793(8)/0.3676(2)	0	0.2340(1)/0.2327(4)	107(3)/90(9)
Sb11	0.41275(7)/0.4125(2)	0	0.9435(2)/0.9425(4)	117(3)/84(9)
Sb12	0.5101(2)/0.5094(4)	0	0.9744(4)/0.9728(11)	278(26)/1867(7 9 3)
Sb13	0.51578(7)/0.5153(2)	0	0.1911(1)/0.1902(4)	146(3)/170(9)
Sb14	0.53400(7)/0.5328(2)	0	0.6012(1)/0.5999(4)	139(3)/164(8)
Sb15	0.65402(7)/0.6536(2)	0	0.3020(1)/0.3011(4)	113(3)/136(10)
Sb16	0.69153(8)/0.6911(2)	0	0.9959(2)/0.9945(4)	113(3)/129(10)
Sb17	0.75792(7)/0.7573(2)	0	0.5545(2)/0.5532(4)	93(3)/103(10)
Sb18	0.79502(7)/0.7938(2)	0	0.2687(2)/0.2674(4)	95(3)/113(10)
Sb19	0.86337(7)/0.8628(2)	0	0.8102(1)/0.8096(4)	109(3)/114(10)
Sb20	0.90636(7)/0.9055(2)	0	0.5122(1)/0.5107(4)	83(3)/73(9)
Sb21	0.94269(7)/0.9419(2)	0	0.2037(1)/0.2022(4)	103(3)/93(9)

[a] Positional parameters were standardized with the program STRUCTURE TIDY [15]. All atoms were refined with anisotropic displacement parameters. The last column contains the equivalent isotropic U values. All atoms occupy the position 2*a* of space group *Cm* (No. 8) with the exception of the Sb1 atoms at the Wyckoff position 4*b*. This position has occupancy values (site occupation factors, s.o.f.) of 0.350(6)/0.24(4) for the Pr/Nd compounds, respectively. In addition to these positions deviations from the ideal occupancies were also found for the Pr1/Nd1 and Sb12 positions with s.o.f. values of 0.151(3)/0.148(10) and 0.164(4)/0.24(5). These occupancy values correspond to occupancies of 30.3(5)/30(2) %, 35.0(6)/24(4) %, and 32.8(9)/48(9) % for the positions of the Pr1(Nd1), Sb1, and Sb12 atoms, respectively. The x and z parameters of the Pr2/Nd2 positions were not refined in the final least-squares cycles to define the origin of this polar space group (*Cm*).

Table 4
Atomic parameters of Ho_2Sb_5[a]

Atom	x	z	U (pm^2)
Ho1	0.04658(4)	0.36227(4)	85(1)
Ho2	0.33189(4)	0.57798(3)	68(1)
Ho3	0.33906(4)	0.85514(3)	67(1)
Ho4	0.60885(4)	0.77115(3)	66(1)
Sb1	0.02889(6)	0.09174(6)	133(1)
Sb2	0.13971(5)	0.67885(5)	94(1)
Sb3	0.27696(6)	0.06069(5)	96(1)
Sb4	0.28396(5)	0.34734(5)	75(1)
Sb5	0.57395(5)	0.26554(5)	66(1)
Sb6	0.57482(5)	0.55157(5)	70(1)
Sb7	0.58099(5)	0.97553(5)	75(1)
Sb8	0.84747(6)	0.17056(5)	97(1)
Sb9	0.85605(5)	0.48139(5)	80(1)
Sb10	0.86047(6)	0.77911(5)	98(1)

[a] All atoms occupy the 2*e* position x, $\frac{1}{4}$, z of space group $P2_1/m$ (No. 11). The positional parameters were standardized with the program STRUCTURE TIDY [15]. The last column contains the equivalent isotropic U values of the anisotropic displacement parameters.

position each. The centrosymmetric space group $C2/m$ is violated mainly near the positions of the partially occupied sites of the atoms Pr1(Nd1), Sb1, and Sb12. The refinements in the centrosymmetric group resulted in considerably more disorder in the vicinity of these partially occupied sites. This is best demonstrated by comparing the positions of the pairs Pr1&Sb4 and Sb5&Sb13 in Figs. 2 and 3. In space group $C2/m$ the position of the Pr1 atom transforms by a two-fold rotation axis to the position of the Sb4 atom, and the position of the Sb5 atom transforms to the position of the Sb13 atom. The refinements of the structure in the centrosymmetric space group $C2/m$ led for all of these four sites to partial occupancies and/or very large displacement parameters. In contrast, the refinements in the lower symmetric space group *Cm* led to full occupancy and reasonable displacement parameters for the three sites of the antimony atoms Sb4, Sb5, and Sb13; and only the position of the Pr1(Nd1) atom is partially occupied. The choice for placing a rare earth

Table 5
Interatomic distances in the structures of $Pr_{8.303(5)}Sb_{20.03(1)}$ and $Nd_{8.30(2)}Sb_{19.98(9)}$[a]

		Pr/Nd			Pr/Nd			Pr/Nd			Pr/Nd			Pr/Nd
*Ln*1:	[2Sb1	119.5/119.9]	*Ln*6:	2Sb6	322.0/319.9	Sb2:	2Sb1	293.0/288.0	Sb9:	2Sb19	304.0/303.2	Sb15:	2Sb4	298.3/298.2
	[2Sb12	218.3/217.6]		2Sb2	327.2/326.5		2Sb14	317.8/315.8		2Sb17	306.6/305.1		2Sb7	305.7/302.9
	1Sb2	325.5/324.2		2Sb5	331.4/328.9		1*Ln*1	325.5/324.2		1*Ln*3	328.7/326.7		1*Ln*7	328.9/326.0
	2Sb1	326.6/326.9		1Sb14	332.3/330.4		2*Ln*4	326.7/325.2		2*Ln*8	331.2/328.8		2*Ln*2	332.5/330.4
	2Sb11	331.5/330.9		1Sb12	334.8/333.2		2*Ln*6	327.2/326.5		1*Ln*4	334.9/332.9	Sb16:	2Sb5	301.7/301.2
	1Sb21	334.5/331.5		1Sb16	344.2/343.3		2Sb12	357.1/354.6	Sb10:	2Sb18	305.0/305.3		2Sb8	311.6/310.4
	2Sb13	335.2/332.3		2Sb1	344.6/340.6	Sb3:	2Sb14	307.1/306.8		2Sb21	307.4/305.1		1*Ln*8	325.9/323.4
	1Sb5	335.4/331.4	*Ln*7:	1Sb14	323.7/322.5		2*Ln*5	336.4/335.0		1*Ln*3	324.3/322.2		2*Ln*2	330.0/327.4
	1Sb4	365.9/360.4		2Sb6	324.6/323.0		2*Ln*7	337.6/335.9		2*Ln*9	329.1/326.9		1*Ln*6	344.2/343.3
*Ln*2:	2Sb18	325.0/323.4		1Sb15	328.9/326.0		1Sb4	354.1/350.8		1*Ln*5	339.3/337.0	Sb17:	2Sb7	300.8/300.4
	2Sb16	330.0/327.4		1Sb17	333.8/333.4	Sb4:	1Sb5	286.3/284.3	Sb11:	1Sb12	277.6/275.0		2Sb9	306.6/305.1
	2Sb15	332.5/330.4		2Sb7	335.9/334.3		2Sb15	298.3/298.2		2Sb1	296.4/295.6		1*Ln*8	327.9/325.1
	1Sb8	334.6/332.4		2Sb3	337.6/335.9		2Sb13	304.4/302.5		2Sb19	305.1/303.7		2*Ln*3	330.1/328.1
	1Sb7	338.2/335.8	*Ln*8:	2Sb6	325.0/323.7		1Sb3	354.1/350.8		2*Ln*9	328.3/327.4		1*Ln*7	333.8/333.4
	1Sb5	347.9/346.4		2Sb8	325.6/324.0		1*Ln*2	360.4/357.8		2*Ln*1	331.5/330.9	Sb18:	2Sb10	305.0/305.3
	1Sb4	360.4/357.8		1Sb16	325.9/323.4		1*Ln*1	365.9/360.4		1*Ln*4	351.0/349.2		2*Ln*2	325.0/323.4
*Ln*3:	2Sb20	321.5/320.1		1Sb17	327.9/325.1	Sb5:	1Sb4	286.3/284.3	Sb12:	[2Sb1	109.2/109.9]		2*Ln*3	327.3/325.6
	1Sb10	324.3/322.2		2Sb9	331.2/328.8		2Sb16	301.7/301.2		[2*Ln*1	218.3/217.6]		1*Ln*9	342.9/340.5
	2Sb18	327.3/325.6		1Sb19	344.2/342.4		2Sb1	325.8/322.2		1Sb11	277.6/275.0	Sb19:	2Sb9	304.0/303.1
	1Sb9	328.7/326.7	*Ln*9:	2Sb8	319.4/317.4		2*Ln*6	331.4/328.9		1Sb13	292.7/291.4		2Sb11	305.1/303.7
	2Sb17	330.1/328.1		2Sb11	328.3/327.5		1*Ln*1	335.4/331.4		2Sb1	318.2/316.2		1*Ln*9	333.9/331.1
	1Sb7	330.8/329.9		1Sb21	328.8/326.6		1*Ln*2	347.9/346.4		1*Ln*6	334.9/333.2		2*Ln*4	334.7/333.1
*Ln*4:	2Sb20	323.0/320.7		2Sb10	329.1/327.0		2Sb12	373.1/371.0		2Sb2	357.1/354.6		1*Ln*8	344.2/342.4
	2Sb2	326.7/325.2		1Sb19	333.9/331.1	Sb6:	2*Ln*6	322.0/319.9		2Sb5	373.1/371.0	Sb20:	2*Ln*3	321.5/320.1
	2Sb19	334.7/333.1		1Sb18	342.9/340.5		2*Ln*7	324.6/323.0	Sb13:	1Sb12	292.7/291.4		2*Ln*5	321.9/320.0
	1Sb9	334.9/332.9	Sb1:	[1Sb12	109.2/109.9]		2*Ln*8	325.0/323.7		2Sb21	300.1/299.4		2*Ln*4	323.0/320.8
	1Sb14	336.7/333.6		[1*Ln*1	119.5/119.9]	Sb7:	2Sb17	300.8/300.4		2Sb4	304.5/302.5	Sb21:	2Sb13	300.1/299.4
	1Sb11	351.0/349.2		[1Sb1	209.5/207.0]		2Sb15	305.7/302.9		2Sb1	324.3/325.4		2Sb10	307.4/305.1
*Ln*5:	2Sb20	321.9/320.0		[1Sb1	216.8/217.8]		1*Ln*3	330.8/329.9		1*Ln*5	326.1/323.8		1*Ln*9	328.8/326.6
	1Sb14	323.1/320.3		1Sb2	293.0/288.0		2*Ln*7	335.9/334.3		2*Ln*1	335.2/332.3		1*Ln*1	334.5/331.5
	1Sb13	326.1/323.8		1Sb11	296.3/295.6		1*Ln*2	338.3/335.8	Sb14:	2Sb3	307.1/306.8		2*Ln*5	339.4/338.0
	2Sb3	336.5/335.0		1Sb12	318.2/316.2	Sb8:	2Sb16	311.6/310.4		2Sb2	317.8/315.8			
	1Sb10	339.3/337.0		1Sb13	324.3/325.4		2*Ln*9	319.4/317.4		1*Ln*5	323.1/320.3			
	2Sb21	339.4/338.0		1Sb5	325.8/322.2		2*Ln*8	325.6/323.9		1*Ln*7	323.7/322.5			
				1*Ln*1	326.6/326.9		1*Ln*2	334.6/332.4		1*Ln*6	332.3/330.4			
				1*Ln*6	344.6/340.7					1*Ln*4	336.7/333.6			

[a] Distances were calculated with the lattice constants as obtained from the single-crystal data (Table 2). All distances shorter than 398 pm are listed. Short distances listed in brackets correspond to partially occupied atomic sites and therefore do not need to occur. The standard deviations are all less than or equal to 0.4 and 0.8 pm for the praseodymium and neodymium compounds, respectively. Exceptions are distances between partially occupied atomic sites (*Ln*1, Sb1, Sb12), where they may be twice as large.

atom at this site—and not (also with partial occupancy) an antimony atom—was made on the basis of its local environment which consists only of antimony atoms, as is the case for all other rare earth sites. Also the interatomic distances favor this decision. Similarly, the sites assigned to the Sb1 and Sb12 atoms cannot be occupied by rare earth atoms because these sites have relatively short distances to fully occupied antimony sites (Table 5) which are too short for *Ln*–Sb distances. The equivalent isotropic U values of the Sb12 atoms in the praseodymium and neodymium compounds are very large, especially the U value of the latter compound (Table 3). A look at the corresponding anisotropic displacement parameters revealed that only the U_{22} values of these atoms are unusually high. This indicates that the Sb12 atoms may occupy various positions along the y-axis, depending on the occupancies of the *Ln*1 and Sb1 sites.

4. Discussion

The two antimonides $Pr_{9-x}Sb_{21-y}$ and $Nd_{9-x}Sb_{21-y}$ crystallize with a new structure type which we have originally determined for the neodymium compound some years ago [11], but the details are published here for the first time. Since our present structure refinement of the new isotypic praseodymium compound is more accurate we mostly refer to the data of the latter compound in the following discussion.

We have just described that the structure of $Pr_{9-x}Sb_{21-y}$ is almost centrosymmetric, corresponding

Table 6
Interatomic distances in the structure of Ho_2Sb_5[a]

Ho1:	2Sb9	313.8	Ho4:	1Sb7	306.3	Sb3:	2Sb7	290.0	Sb7:	2Sb3	290.0
	1Sb4	314.3		2Sb5	311.7		1Ho3	325.0		1Ho4	306.3
	2Sb2	315.2		1Sb6	312.3		2Ho4	330.8		2Sb7	314.4
	1Sb9	330.8		2Sb4	319.6		1Sb1	335.3		2Ho3	321.7
	2Sb10	332.0		1Sb10	325.3	Sb4:	2Sb6	295.0		1Ho3	326.4
	1Sb8	338.0		2Sb3	330.8		2Sb10	312.3	Sb8:	1Sb1	283.2
Ho2:	2Sb5	312.9	Sb1:	1Sb8	283.2		1Ho1	314.3		2Sb2	299.2
	1Sb2	315.3		2Sb10	295.9		2Ho4	319.6		2Ho3	315.6
	2Sb9	318.5		2Sb1	333.4		1Ho2	327.3		1Ho1	338.0
	2Sb6	320.5		1Sb3	335.3	Sb5:	2Ho3	308.0	Sb9:	2Sb2	312.5
	1Sb6	326.5	Sb2:	2Sb8	299.2		2Ho4	311.7		2Ho1	313.8
	1Sb4	327.3		2Sb9	312.5		2Ho2	312.9		2Ho2	318.5
Ho3:	2Sb5	308.0		2Ho1	315.2	Sb6:	2Sb4	295.0		1Ho1	330.8
	2Sb8	315.6		1Ho2	315.3		2Sb6	301.9	Sb10:	2Sb1	295.9
	2Sb7	321.7		1Ho3	323.8		1Ho4	312.3		2Sb4	312.3
	1Sb2	323.8					2Ho2	320.5		1Ho4	325.3
	1Sb3	325.0					1Ho2	326.5		2Ho1	332.0
	1Sb7	326.4									

[a] Distances were calculated with the lattice constants as obtained from the single-crystal data. All distances shorter than 380 pm are listed. Standard deviations are all less than 0.2 pm.

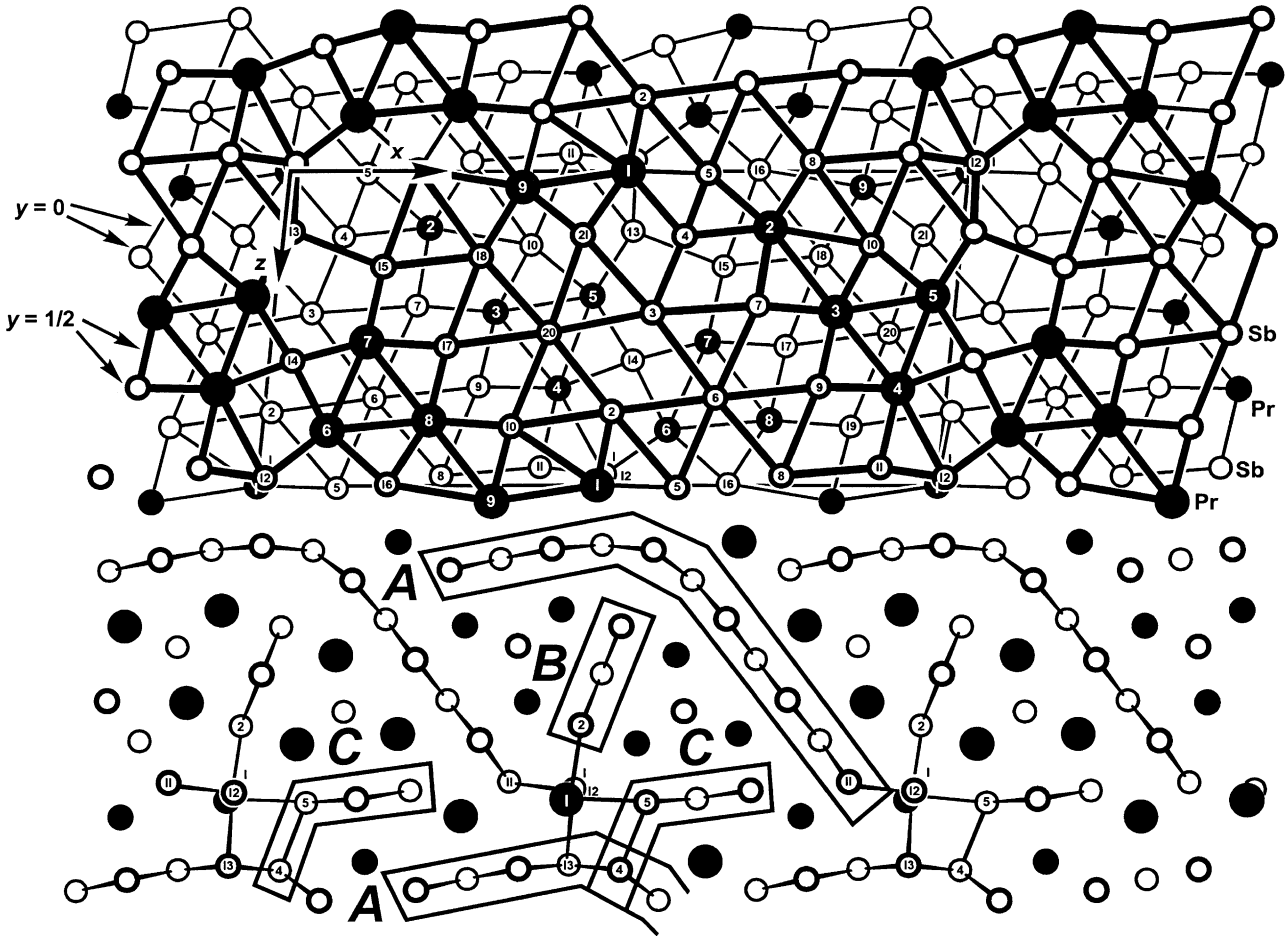

Fig. 2. The crystal structure of $Pr_{9-x}Sb_{21-y}$. Most atoms are situated on mirror planes at $y = 0$ and 1/2. They are connected by thin and thick lines, respectively, which do not necessarily represent chemical bonds. The structure contains three different kinds *A*, *B*, and *C* of infinite bands of antimony polyanions which are projected perpendicular to the short translation period *y* in Fig. 7. In addition to the Sb–Sb bonds within these bands, the bands of antimony polyanions are connected to each other via the antimony atoms of the partially occupied sites Sb1 and Sb12, thus forming a two-dimensionally infinite antimony polyanion extending parallel to the $(20\bar{1})$ plane of the monoclinic cell.

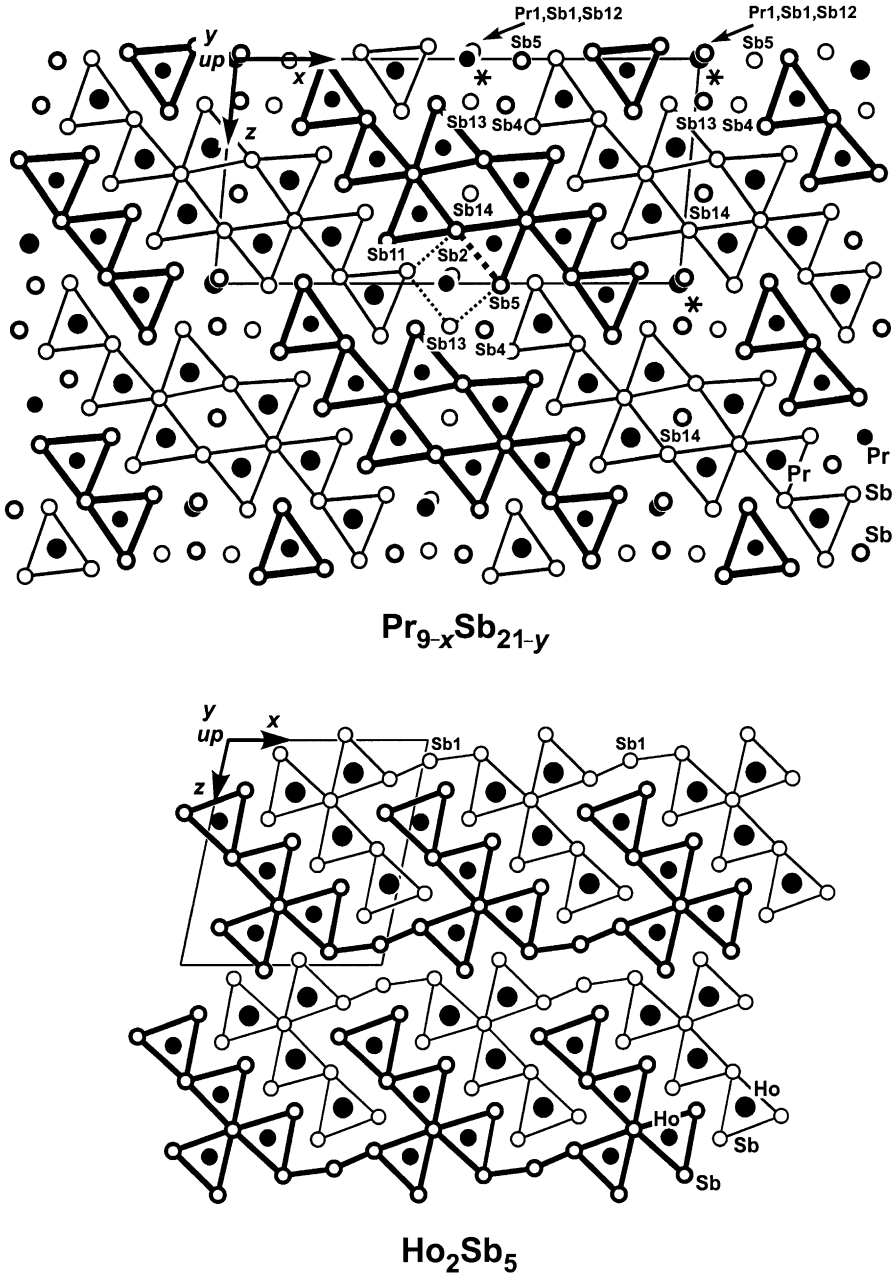

Fig. 3. Linking of the trigonal prisms of antimony atoms in the structures of $Pr_{9-x}Sb_{21-y}$ and Ho_2Sb_5. Atoms connected by thick and thin lines are separated from each other by half a translation period of the projection direction. Generally, all rare earth atoms of the two structures have nine antimony neighbors (exceptions are the Pr1 and Pr2 atoms with 10 antimony neighbors). Six of these antimony neighbors of each rare earth atom form trigonal prisms. Most of the prisms have their prism axes oriented parallel to the *y* direction of the two structures; they are emphasized in these drawings. These prisms share their triangular faces with equivalent prisms above and below; they share only edges with adjacent prisms located at the same projection heights. Exceptions are the trigonal prisms formed by the Sb2, Sb5, Sb11, and Sb13 atoms in the coordination spheres of the Pr1 atoms; one of these prisms is outlined with dashed lines. It has its prism axis perpendicular to the *y*-axis of the monoclinic cell. Almost all antimony atoms participate in the formation of the prisms; exceptions are the Sb1, Sb4, and Sb12 atoms of the praseodymium compound and the Sb1 atom of Ho_2Sb_5. The structure of $Pr_{9-x}Sb_{21-y}$ is almost centrosymmetric, space group $C2/m$. In that space group the position of the Sb14 atom would correspond to a center of symmetry. Some positions of two-fold rotation axes of the space group $C2/m$, located between these symmetry centers, are marked by asterisks in the upper right-hand corner. It can be seen that almost all atomic positions obey the center of symmetry (at the position of the Sb14 atom) and the two-fold rotation axis (at the position of the asterisks) with the exception of the positions of the atoms around the pseudo-two-fold axis.

to the space group $C2/m$. It can be seen in the upper right-hand corner of Fig. 3 that the atomic positions in the vicinity of the site of the Sb14 atom are practically centrosymmetric with the center of symmetry at the Sb14 position. Only further away from the Sb14 site the atomic positions of the Sb4, Sb5, and Sb13 atoms and the partially occupied sites Pr1, Sb1, and Sb12 (these latter three sites are all superimposed in the projection

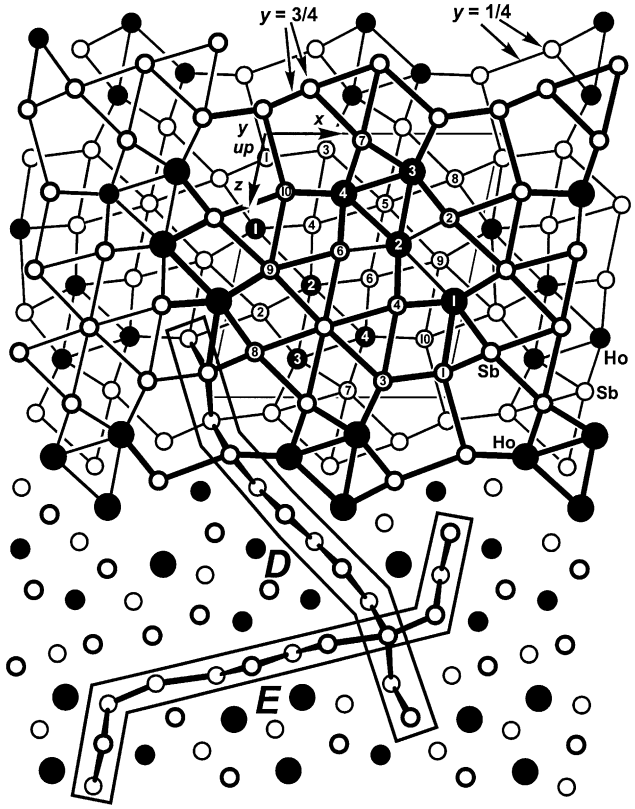

Fig. 4. Projection of the crystal strucutre of Ho_2Sb_5. All atoms are situated on mirror planes, which are separated from each other by half a translation period of the projection direction. These atoms are connected by heavy ($y = 3/4$) and light ($y = 1/4$) lines, which do not necessarily correspond to chemical bonds. The antimony atoms form a three-dimensionally infinite network. Two fragments *D* and *E* of this network are outlined. These fragments are shown from a different viewpoint in Fig. 7.

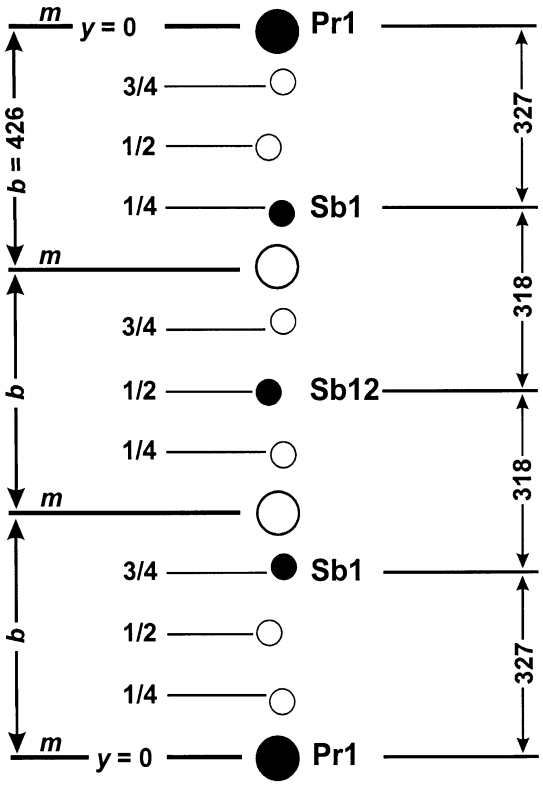

Fig. 5. A model for the atomic order of the partially occupied sites of the Pr1, Sb1, and Sb12 atoms in $Pr_{9-x}Sb_{21-y}$. All atomic positions for three translation periods *b* are shown. They have been found with occupancy parameters close to 1/3. Occupied positions for the model with ordered occupancy are represented by filled circles. Interatomic distances are given in pm units.

along the *y*-axis) violate this center of symmetry. We should point out that the structure has two problems in the vicinity of the just enumerated atoms which are not related from a symmetry point of view. If the sites of the Pr1, Sb1, and Sb12 atoms were fully occupied the structure would still have the noncentrosymmetric space group *Cm*.

For the partially occupied sites of the Pr1(Nd1), Sb1, and Sb12 atoms, we have found occupancies (in %) of 30.3(5)/30(2), 35.0(6)/24(4), and 32.8(9)/48(9), respectively, for the Pr/Nd compounds. These values are all close to 33%. In Fig. 5 we show a model for the sequence of occupied and nonoccupied sites, assuming exactly one-third occupancy for each site. Since the Sb1 atoms are situated at a four-fold (4*b*) and the Pr1 and Sb12 atoms at a two-fold position (2*a*); a total of four atoms (Pr1, 2Sb1, and 1Sb12) occur within three translation periods *b*. With these idealized occupancies the content of the tripled unit cell of the praseodymium compound would correspond to $Pr_{25}Sb_{60} = 5Pr_5Sb_{12} = 3Pr_{8.33}Sb_{20}$ as compared to the result of the refinement of the occupancy values of $Pr_{8.303(5)}Sb_{20.03(1)}$. We have not found any evidence for the tripled *b*-axis in the Weissenberg diffractograms of the neodymium compound. And we should add, that according to our experience, in many cases of other structure determinations, where we had developed models for an ordered arrangement of partially occupied sites along only one direction, we had failed to find the corresponding superstructure reflections. In $Pr_{9-x}Sb_{21-y}$ atomic order might well occur *within* one string of Pr1, Sb1, and Sb12 atoms along the *b*-axis. However, long-range order *between* many such strings is required to produce sharp superstructure reflections.

The three new lanthanoid antimonides $Pr_{8.303(5)}Sb_{20.03(1)}$, $Nd_{8.30(2)}Sb_{19.98(9)}$, and Ho_2Sb_5 have similar compositions with 70.69(2), 70.65(14), and 71.43 at% antimony, respectively. We have only prepared few samples in the corresponding binary lanthanoid–antimony systems, and it might well be that there are systems, where both of the two structure types ($Nd_{9-x}Sb_{21-y}$ and Dy_2Sb_5) are thermodynamically stable at different temperatures or pressures.

Since the compositions of $Pr_{8.303}Sb_{20.03}$ and Ho_2Sb_5 differ by less than 1 at%, it is no surprise that their crystal structures are closely related. In both structures

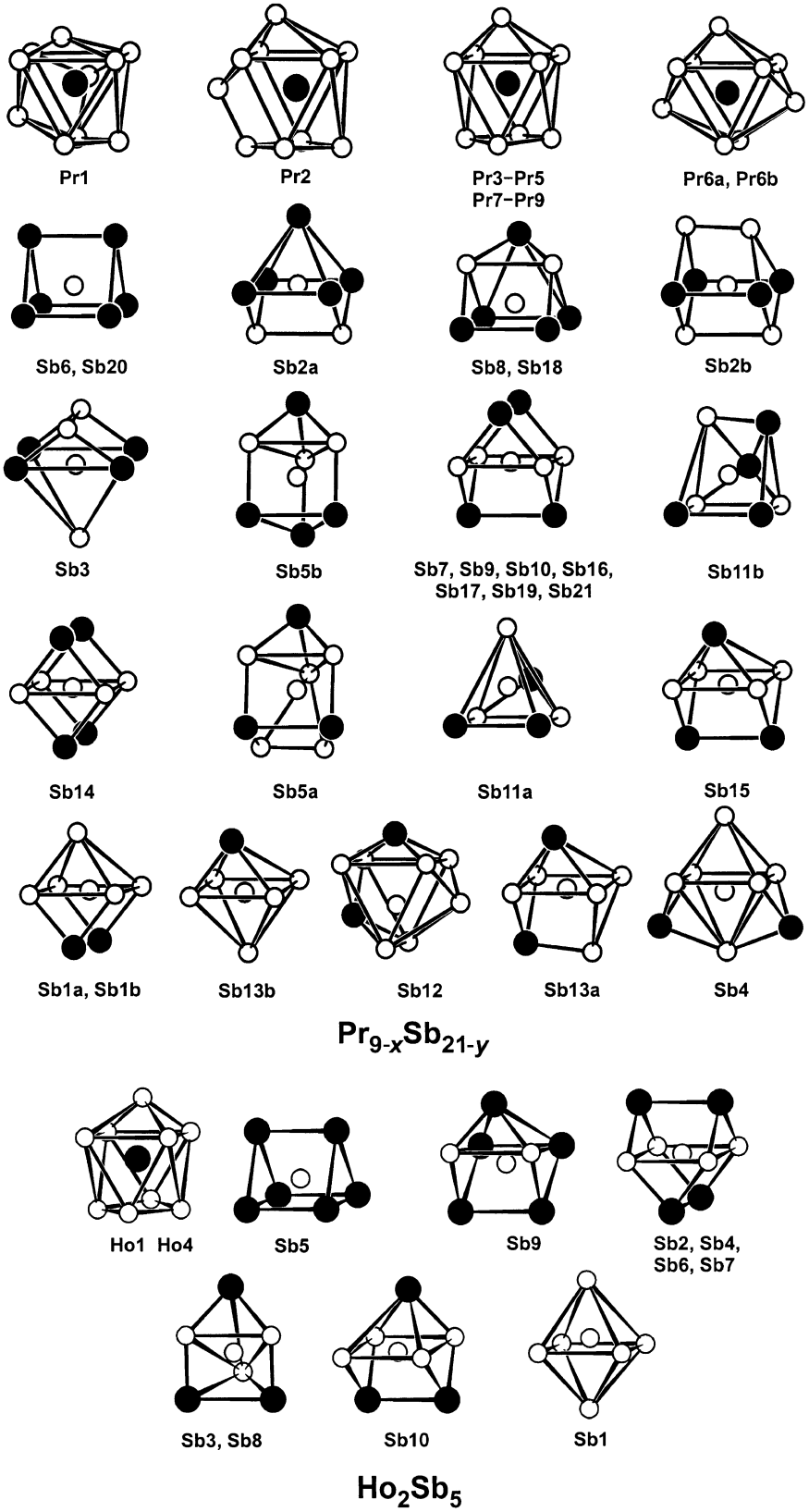

Fig. 6. Coordination polyhedra in the structures of $Pr_{9-x}Sb_{21-y}$ and Ho_2Sb_5. Several atoms have very similar coordinations. For instance, the Pr3–Pr5 and Pr7–Pr9 atoms are coordinated by tricapped trigonal prisms which may also be viewed as distorted monocapped tetragonal antiprisms of antimony atoms; only one of these is shown. On the other hand, the Sb2 atoms of this compound have two different coordinations (coordinations of the Sb2a and Sb2b atoms), depending on which one of the neighboring sites with partial occupancy (Pr1 or Sb1 and Sb12) are occupied. The coordination polyhedra of the antimony atoms are arranged according to the numbers of their rare earth neighbors: the Sb6 and Sb20 atoms of $Pr_{9-x}Sb_{21-y}$ have (only) six Pr neighbors, while the Sb13b atom has only one Pr neighbor (in addition to five antimony neighbors), thus demonstrating the great variety of antimony coordinations.

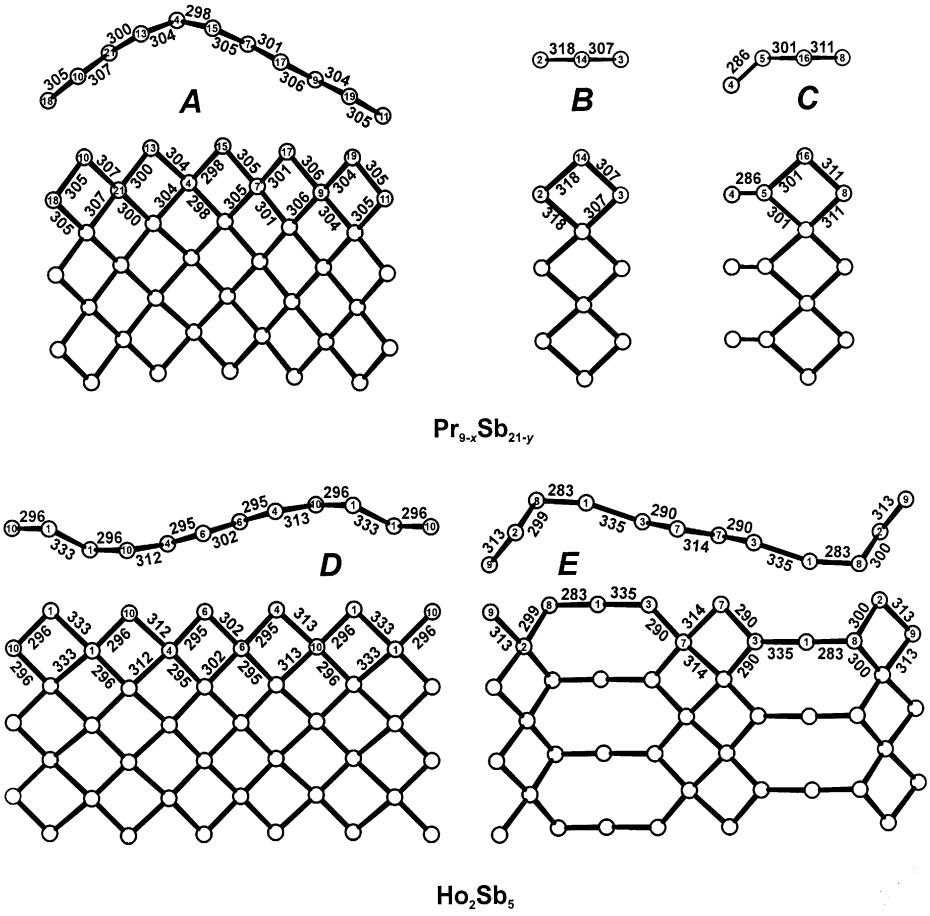

Fig. 7. The antimony polyanions in the structures of $Pr_{9-x}Sb_{21-y}$ and Ho_2Sb_5. The structure of $Pr_{9-x}Sb_{21-y}$ contains a two-dimensionally infinite antimony polyanion. Three fragments *A*, *B*, and *C* of this polyanion in the form of bands are outlined in Fig. 2. These bands are shown here in views along the short translation period *y* and perpendicular to this direction. Interatomic distances (pm) are indicated. Similarly, the structure of Ho_2Sb_5 contains a three-dimensionally infinite network of antimony atoms. Two fragments of this network as outlined in Fig. 4 are shown here.

almost all atoms (the only exceptions are the Sb1 atoms of the Pr compound) are situated on two mirror planes extending perpendicular to the *y*-axes of their monoclinic cells (Figs. 2–4). The rare earth atoms have mostly nine antimony neighbors. Of these, six are forming trigonal prisms which have three additional antimony neighbors outside the rectangular faces of the prisms. Only the Pr1 and Pr2 atoms have a 10th antimony neighbor, somewhat further away, capping a triangular or a rectangular face, respectively. The Pr–Sb distances vary between 319.4 (Pr9–Sb8) and 365.9 pm (Pr1–Sb4) with average Pr–Sb distances between 326.8 pm (Pr3) and 332.4 pm (Pr4) for the seven praseodymium sites with nine antimony neighbors. For the Pr1 and Pr2 sites with 10 antimony neighbors the average Pr–Sb distances are—as expected—longer with 334.8 and 335.6 pm, respectively. In calculating these distances, we assumed that the atoms with partially occupied sites (Pr1, Sb1, Sb12) have occupancies of 1/3 each, as discussed above.

All of the four different holmium atoms of Ho_2Sb_5 have nine antimony neighbors with Ho–Sb distances varying between 306.3 pm (Ho4–Sb7) and 338.0 pm (Ho1–Sb8) and with average distances of 322.8, 319.2, 318.4, and 318.7 pm for the Ho1, Ho2, Ho3, and Ho4 atoms, respectively. This structure has been discussed in more detail for the prototype Dy_2Sb_5 [10] and much of that discussion also applies to the closely related $Nd_{9-x}Sb_{21-y}$ type structure.

The near-neighbor coordinations of the antimony atoms in both structures show a greatly surprising diversity, which never is found in more ionic compounds. Thus, the near-neighbor environments of these rare earth antimonides violate Pauling's rules, which remain valid for ionic compounds. One extreme case is represented by the Sb6 and Sb20 atoms of $Pr_{9-x}Sb_{21-y}$ and the Sb5 atom of Ho_2Sb_5 (Fig. 6). These atoms are coordinated only by six rare earth atoms forming trigonal prisms. The other extreme case is most clearly represented by the Sb1 atom of Ho_2Sb_5, which has only six antimony neighbors forming a distorted octahedron with Sb–Sb bond lengths varying between 283.2 and 335.3 pm and no holmium neighbor up to 388 pm. The Sb4 atom of $Pr_{9-x}Sb_{21-y}$ has a similar distorted octahedral antimony coordination with Sb–Sb distances

extending between 286.3 and 354.1 pm. However, in addition it has two Pr neighbors at the rather long distances of 360.4 and 365.9 pm (the 10th antimony neighbors of the Pr2 and Pr1 atoms, respectively, discussed above). The near-neighbor coordinations of the other antimony atoms of both structure types vary between these extreme cases. The shortest Sb–Sb distances occur for the near-neighbor interactions Sb11–Sb12 with 277.6 pm in $Pr_{9-x}Sb_{21-y}$ (Table 5) and Sb1–Sb8 with 283.2 pm in Ho_2Sb_5 (Table 6). These distances are considerably shorter than the three short bonding Sb–Sb distances of 290.8 pm in elemental α-antimony [16, 17].

In the lower parts of Figs. 2 and 4, we have outlined the antimony networks occurring in the structures of $Pr_{9-x}Sb_{21-y}$ and Ho_2Sb_5. All of the Sb–Sb bonds of the two structures as listed in Tables 5 and 6 are shown with the exception of the Sb–Sb bonds involving the antimony atoms of the partially occupied sites Sb1 and Sb12 and the rather long Sb3–Sb4 bond of 354.1 pm. Three fragments A, B, C of these polyanions in the structure of $Pr_{9-x}Sb_{21-y}$ and two fragments D and E in the structure of Ho_2Sb_5, are outlined in these figures. They are shown in Fig. 7 from different viewpoints.

Chemical bonding in Dy_2Sb_5 has been discussed in detail earlier using oxidation numbers (formal charges) for the Dy–Sb interactions. The Sb–Sb interactions were rationalized on the basis of an extended Zintl–Klemm concept using bond-length–bond-strength relationships [10]. In analogy with this analysis, we can rationalize chemical bonding in $Pr_{8.303}Sb_{20.03}$ and Ho_2Sb_5. For the Sb6 and Sb20 atoms of $Pr_{8.303}Sb_{20.03}$ and the Sb5 atom of Ho_2Sb_5 we can safely assume the oxidation number –3, since these antimony atoms have only dysprosium or holmium atoms as neighbors and since they are the more electronegative components in these compounds. Thus, their 5*s* and 5*p* orbitals will fully participate in chemical bonding with the rare earth atoms. We count 8 electrons for these orbitals (octet rule) and obtain the oxidation number –3. On the other hand, the Sb1 atom of Ho_2Sb_5 has only antimony neighbors. Thus, like the antimony atoms in elemental antimony, they obtain the

Table 7
Antimony–antimony bond distances d_{ij} (pm), their bond orders (bond strengths, bond valences) v_{ij}, and formal charges of the antimony atoms in the structure of Ho_2Sb_5[a]

Atom	Neighbor	d_{ij}	v_{ij}	$\sum v_{ij}$	Total bond order/atom	Formal charge
Sb1:	1Sb8	283.2	1×0.917	0.917		
	2Sb10	295.9	2×0.651	1.302		
	2Sb1	333.4	2×0.236	0.472		
	1Sb3	335.3	1×0.224	0.224	2.92	−0.08
Sb2:	2Sb8	299.2	2×0.595	1.190		
	2Sb9	312.5	2×0.415	0.830	2.02	−0.98
Sb3:	2Sb7	290.0	2×0.763	1.526		
	1Sb1	335.3	1×0.224	0.224	1.75	−1.25
Sb4:	2Sb6	295.0	2×0.667	1.334		
	2Sb10	312.3	2×0.418	0.836	2.17	−0.83
Sb5:	—	—	—	0	0	−3.00
Sb6:	2Sb4	295.0	2×0.667	1.334		
	2Sb6	301.9	2×0.553	1.106	2.44	−0.56
Sb7:	2Sb3	290.0	2×0.763	1.526		
	2Sb7	314.4	2×0.395	0.790	2.32	−0.68
Sb8:	1Sb1	283.2	1×0.917	0.917		
	2Sb2	299.2	2×0.595	1.190	2.11	−0.89
Sb9:	2Sb2	312.5	2×0.415	0.830	0.83	−2.17
Sb10:	2Sb1	295.9	2×0.651	1.302		
	2Sb4	312.3	2×0.418	0.836	2.14	−0.86
Total formal charge						−11.30

[a] Bond orders v_{ij} were calculated for the interatomic distances d_{ij} using the formula $v_{ij} = \exp[(280-d_{ij})/37]$. The total formal charge (oxidation number) of +12 for the four holmium atoms of the formula Ho_4Sb_{10} is nearly compensated by the total formal charge of −11.30 of the 10 antimony atoms.

Table 8
Antimony–antimony bond distances d_{ij} (pm), their bond orders v_{ij}, and formal charges of the antimony atoms in $Pr_{8.303(5)}Sb_{20.03(1)}$ using the formula $v_{ij} = \exp[(280-d_{ij})/37]$[a]

Atom	Neighbor	d_{ij}	v_{ij}	$\sum v_{ij}$	Total bond order/atom	Formal charge/atom/f.u.
Sb1:	1Sb2	293.0	1×0.704	0.704		
	1Sb11	296.3	1×0.644	0.644		
	1Sb12	318.2	0.328×0.356	0.117		
	1Sb13	324.3	1×0.302	0.302		
	1Sb5	325.8	1×0.290	0.290	2.06	−0.66
Sb2:	2Sb1	293.0	0.700×0.704	0.493		
	2Sb14	317.8	2×0.360	0.720	1.21	−1.79
Sb3:	2Sb14	307.1	2×0.481	0.962	0.96	−2.04
Sb4:	1Sb5	286.3	1×0.843	0.843		
	2Sb15	298.3	2×0.610	1.220		
	2Sb13	304.4	2×0.517	1.034	3.10	(+0.10)
Sb5:	1Sb4	286.3	1×0.843	0.843		
	2Sb16	301.7	2×0.556	1.112		
	2Sb1	325.8	0.700×0.290	0.203	2.16	−0.84
Sb6:	—	—	—	0	0	−3.00
Sb7:	2Sb17	300.8	2×0.570	1.140		
	2Sb15	305.7	2×0.499	0.998	2.14	−0.86
Sb8:	2Sb16	311.6	2×0.426	0.852	0.85	−2.15
Sb9:	2Sb19	304.0	2×0.523	1.046		
	2Sb17	306.6	2×0.487	0.974	2.02	−0.98
Sb10:	2Sb18	305.0	2×0.509	1.018		
	2Sb21	307.4	2×0.477	0.954	1.97	−1.03
Sb11:	1Sb12	277.6	0.328×1.067	0.350		
	2Sb1	296.4	0.700×0.642	0.449		
	2Sb19	305.1	2×0.507	1.014	1.81	−1.19
Sb12:	1Sb11	277.6	1×1.067	1.067		
	1Sb13	292.7	1×0.709	0.709		
	2Sb1	318.2	0.700×0.356	0.249	2.03	–0.32
Sb13:	1Sb12	292.7	0.328×0.709	0.233		
	2Sb21	300.1	2×0.581	1.162		
	2Sb4	304.5	2×0.516	1.032		
	2Sb1	324.3	0.700×0.302	0.213	2.64	−0.36
Sb14:	2Sb3	307.1	2×0.481	0.962		
	2Sb2	317.8	2×0.360	0.720	1.68	−1.32
Sb15:	2Sb4	298.3	2×0.610	1.220		
	2Sb7	305.7	2×0.499	0.998	2.22	−0.78
Sb16:	2Sb5	301.7	2×0.556	1.112		
	2Sb8	311.6	2×0.426	0.852	1.96	−1.04
Sb17:	2Sb7	300.8	2×0.570	1.140		
	2Sb9	306.6	2×0.487	0.974	2.11	−0.89
Sb18:	2Sb10	305.0	2×0.509	1.018	1.02	−1.98
Sb19:	2Sb9	304.0	2×0.523	1.046		
	2Sb11	305.1	2×0.507	1.014	2.06	−0.94

Table 8 (*continued*)

Atom	Neighbor	d_{ij}	v_{ij}	$\sum v_{ij}$	Total bond order/atom	Formal charge/atom/f.u.
Sb20:	—	—	—	0	0	−3.00
Sb21:	2Sb13	300.1	2×0.581	1.162		
	2Sb10	307.4	2×0.477	0.954	2.12	−0.88
Total formal charge per formula unit (f.u.)						−25.85

[a] In calculating the bond orders v_{ij}, one has to account for the partial occupancies of the Sb1 and Sb12 sites of 35.0 and 32.8%, respectively. The formal charge per antimony atom is obtained by subtracting −3 from the value of the total bond order of this atom. Exceptions occur for the Sb1 and Sb12 sites, where the thus obtained formal charges have to be multiplied by the occupancy values of these atoms; in addition for the Sb1 atoms the differing multiplicity has to be considered. The total formal charge (oxidation number) of $3 \times 8.303 = 24.91$ of the praseodymium atoms is practically compensated by the total formal charge of −25.85 of the antimony atoms.

oxidation number zero. According to the Zintl–Klemm concept [18–20] the Sb1 atom of Ho_2Sb_5 should form three two-electron Sb–Sb bonds. However, as we can see from Table 6 the Sb1 atom forms six Sb–Sb bonds with bond lengths varying between 283.2 and 335.3 pm. Similarly, the other antimony atoms in the structures of Ho_2Sb_5 and $Pr_{9-x}Sb_{21-y}$ form many Sb–Sb bonds with greatly varying bond lengths. In analyzing the structure of Dy_2Sb_5 (10) fractional bonds were assigned to such Sb–Sb interactions. It was recommended to use the equation $v_{ij} = \exp[(R - d_{ij})/b]$ to obtain bond strengths (bond orders, bond valences) v_{ij} from observed bond distances d_{ij}. For the variables R and b good fits were obtained with $R = 280$ pm and $b = 37$ for various rare earth polyantimonides, including $Nd_{9-x}Sb_{21-y}$ whose structure is reported here. In Tables 7 and 8 we show the evaluations of the Sb–Sb bonding within the antimony polyanions of Ho_2Sb_5 and $Pr_{9-x}Sb_{21-y}$. For each Sb–Sb bond with a bond distance d_{ij} the corresponding bond order v_{ij} is listed, the sum of the bond orders Σv_{ij} for equivalent bonds, properly accounting for the antimony sites of the praseodymium compound with fractional occupancy, and the total bond order for that atom. Finally, the formal charge (oxidation number) is given. It is obtained by subtracting the number 3 from the total bond orders. (As examples for the extreme cases: an oxidation number of –3 should be obtained for an antimony atom with no Sb–Sb bonds; and an antimony atom which has only antimony neighbors should have the oxidation number zero and a total bond order of +3.) Ideally, the formal charge of the rare earth atoms should be matched exactly by the formal charge of the antimony atoms. It can be seen from the evaluations shown in Tables 7 and 8 that this is nearly the case for both compounds. The total of +12 for the formal charge of the four holmium atoms of the formula Ho_4Sb_{10} is almost matched by the total charge of –11.30 of the 10 antimony atoms in that formula. In $Pr_{8.303}Sb_{20.03}$ the praseodymium atoms have a formal charge of $3 \times 8.303 = 24.91$ which is practically compensated by the charge of –25.85 obtained for the antimony atoms at the 21 atomic sites of that compound.

More evaluations of the just presented kind are needed to better understand chemical bonding for compounds forming polyanions with fractional bonds between the heavier main group elements with their tendency for higher coordination numbers. In that context, we wish to draw the attention of the reader to a paper by O'Keeffe and Brese who have proposed R and b values for most homopolar bonds between main group elements [21]. We have recently analyzed chemical bonding within the antimony polyanions of $(U_{2/3}Gd_{1/3})Sb_2$ and $(U_{1/2}Ho_{1/2})_3Sb_7$ in order to assign oxidation numbers to the uranium atoms in these compounds [22].

Acknowledgments

We thank Dipl.-Ing. U. Ch. Rodewald for the competent data collections on the four-circle diffractometer. H.-J. Göcke and K. Wagner investigated our samples with the scanning electron microscope. We are also indebted to Dr. G. Höfer (Heraeus Quarzschmelze) for a generous gift of silica tubes. This work was also supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the International Centre for Diffraction Data.

References

[1] A. Borsese, R. Ferro, R. Capelli, S. Delfino, J. Less-Common Met. 55 (1977) 77.
[2] M.N. Abdusalyamova, O.R. Burnashev, K.E. Mironov, J. Less-Common Met. 77 (1981) 81.
[3] M.N. Abdusalyamova, O.R. Burnashev, K.E. Mironov, J. Less-Common Met. 102 (1984) L19.
[4] M.N. Abdusalyamova, O.R. Burnashev, K.E. Mironov, J. Less-Common Met. 125 (1986) 1.

[5] M.N. Abdusalyamova, O.R. Burnashev, K.E. Mironov, O.I. Rahmatov, N.D. Faslyeva, Izv. Akad. Nauk SSSR, Neorg. Mater. 24 (1988) 495.
[6] M.N. Abdusalyamova, O.I. Rahmatov, N.D. Faslyeva, A.G. Tchuiko, J. Less-Common Met. 141 (1988) L23.
[7] G. Cacciamani, G. Borzone, N. Parodi, R. Ferro, Z. Metallkd. 87 (1996) 562.
[8] W.G. Moffatt, The Handbook of Binary Phase Diagrams, General Electric, Schenectady, NY, 1978.
[9] Th.B. Massalski (Ed.), Binary Phase Diagrams, American Society of Metals, Metals Park, OH 44073, 1986.
[10] W. Jeitschko, R.O. Altmeyer, U.Ch. Rodewald, Z. Anorg. Allg. Chem. 627 (2001) 1932.
[11] R.O. Altmeyer, W. Jeitschko, Z. Kristallogr. 186 (1989) 5.
[12] K. Yvon, W. Jeitschko, E. Parthé, J. Appl. Crystallogr. 10 (1977) 73.
[13] E. Parthé, L. Gelato, B. Chabot, M. Penco, K. Cenzual, R.E. Gladyshevskii, in: TYPIX, Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types, Vols. 1–4 of Gmelin Handbook of Inorganic and Organometallic Chemistry, 8th Edition. Springer, Berlin, 1993, 1994.
[14] G.M. Sheldrick, SHELX-97, A Program Package for the Solution and Refinement of Crystal Structures, Universität Göttingen, Germany, 1997.
[15] L.M. Gelato, E. Parthé, J. Appl. Crystallogr. 20 (1987) 139.
[16] C.S. Barrett, P. Cucka, K. Haefner, Acta Crystallogr. 16 (1963) 451.
[17] J. Donohue, The Structures of the Elements, Wiley, New York, 1974.
[18] H. Schäfer, B. Eisenmann, W. Müller, Angew. Chem. 85 (1973) 742;
H. Schäfer, B. Eisenmann, W. Müller, Int. Ed. Engl. 12 (1973) 694.
[19] R. Marchand, W. Jeitschko, J. Solid State Chem. 24 (1978) 351.
[20] R. Nesper, Prog. Solid State Chem. 20 (1990) 1.
[21] M. O'Keeffe, N.E. Brese, Acta Crystallogr. B 48 (1992) 152.
[22] T. Schmidt, W. Jeitschko, Inorg. Chem. 40 (2001) 6356.