Journal of Solid State Chemistry **146,** 211–216 (1999)
Article ID jssc.1999.8335, available online at http://www.idealibrary.com on IDEAL®

Sulfur Nonstoichiometry of PrS_2: A Series of New Sulfur-Deficient Phases

I. G. Vasilyeva[1] and S. V. Belaya

Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3, Acad. Lavrentyev Pr., Novosibirsk, 630090, Russia

Received October 28, 1998; in revised form February 12, 1999; accepted April 21, 1999

A series of new sulfur-deficient polysulfides, $PrS_{1.900(2)}$, $PrS_{1.846(6)}$, $PrS_{1.766(8)}$, and $PrS_{1.702(7)}$, in addition to stoichiometric PrS_2, has been found by the detailed study of the PrS_2–$PrS_{1.5}$ system in the temperature range 350–1000°C. The phase individuality of the polysulfides has been proved on the basis of data of a sensitive static tensimetric method with a quartz Bourdon gauge, X-ray single-crystal structure analysis, and Raman spectroscopy. The vapor pressure and evaporation thermodynamic parameters of the polysulfides have been determined. Information on a structural distortion of the (S_2^{2-})-polyanionic fragment in the sulfur-deficient phases has been extracted from the Raman spectra components assigned to vibrations of this fragment. © 1999 Academic Press

Key Words: **praseodymium disulfide; sulfur-deficient phases; static tensimetry; X-ray single-crystal analysis; Raman spectroscopy.**

INTRODUCTION

A series of sulfur-deficient phases where the highest polysulfides themselves are sulfur-deficient phases was discovered in the $SmS_{1.90}$–$SmS_{1.50}$ (1) and $DyS_{1.84}$–$DyS_{1.50}$ systems (2). The highest polysulfide in the Pr system was found to be a strictly stoichiometric disulfide (3), and it is to be expected that PrS_2 might behave differently when it loses sulfur. Unfortunately, information on the PrS_2 nonstoichiometry is insufficient and conflicting, even when it was obtained by identical techniques. In (4, 5) the authors believe that the Pr disulfide is a nonstoichiometric phase over the PrS_2–$PrS_{1.70}$ compositional range with unit cell lattice parameters $a \sim 0.4$ and $c \sim 0.8$ nm and space group $P4/nmm$ determined from the powder X-ray diffraction data. An individual phase of the Pr_4S_7 ($PrS_{1.75}$) composition with parameters $a \sim 0.798$ and $c \sim 0.807$ nm and space group $P4b2$ was identified by the same technique (6, 7). However, the nature of rare earth disulfide nonstoichiometry is too involved to be solved by the powder X-ray diffraction experiment alone. Therefore, this study reports pressure measurements over PrS_2 and intermediate PrS_{2-x} solids of different weights in a silica Bourdon gauge as a function of temperature, combining the results with those obtained by X-ray single-crystal structural analysis and Raman spectroscopy. The problem of PrS_2 nonstoichiometry associated with these results is discussed.

EXPERIMENTAL

Samples for Tensimetric Study

The general requirements for the tensimetric study are that samples must be in equilibrium, be contamination-free, and have a surface inert to absorbtion of any volatile impurities. Therefore, crystals of high quality were needed. Pr polysulfide crystals were grown from a KI flux in sealed ampules using Pr_2S_3–S mixtures in molar ratios ranging from 1 to 4. The mixtures were taken so that disulfide or trisulfide may be obtained, if the latter exists. The mixture and flux were heated at 973 K for 30 days, and crystals grew as thin well-crystallized plates with mirror-smooth surfaces. The crystals were extracted from the reaction mixture using treatment by water and after that by toluene to remove the solvent and excess sulfur. The crystals were viewed through a microscope to reject crystals contaminated by the flux. The typical size and average weight were about $3 \times 2 \times 0.05\ mm^3$ and ~ 4 mg, respectively. The gross crystal composition was determined by spectrophotometric analysis of sulfur to be $PrS_{2.000(5)}$. This composition was reproduced for crystals of different syntheses, no matter what the sulfur pressure was in the ampule during the procedure. The disulfide held its composition after annealing under sulfur pressures equal to 1×10^3 and $\sim 2.5 \times 10^3$ kPa. The high-pressure experiment was performed in thick-walled high-purity silica glass ampules inserted in a special steel block. This quality of silica was known to be suited for high-pressure measurements (8, 9). The temperatures for the disulfide and sulfur were 973 and 923 K in the first case, and in the second one, 1023 and 1015 K, respectively. The lower

---

[1] To whom correspondence should be addressed. Fax: (7-3832) 34-44-89. E-mail: kamarz@che.nsk.su.

0022-4596/99 $30.00

temperature held the desired sulfur pressure constant. Being invariant to the sulfur pressure, $PrS_{2.00}$ was found to be the highest polysulfide in the system.

To obtain polysulfides intermediate between $PrS_{2.0}$ and $PrS_{1.50}$, distillation of the sulfur from disulfide to the colder end of a sealed ampule was used. Different amounts of sulfur were distilled off for 3–6 h at appropriate temperature gradients, for instance, 800–400, 750–300, and 700–280°C, and the composition formed was then determined colorimetrically, dissolving the distilled sulfur in toluene (the accuracy ~ 1 at.% S). A small amount of some iodine-bearing products was also detected in the distilled phase. Most likely, they appeared as by-products of the KI melt and silica ampule interaction. Flux contamination is a common problem of crystal growth, and the growth of the PrS_2 crystals in layers seems to favor this. That is why a minor amount of KI unleachable by the cleaning procedure was sometimes observed in the PrS_2 crystals. However, the crystals of intermediate polysulfides were always free from KI, which was removed from the crystals during their preparation. This quality of the crystals was found to fit well for the tensimetric study. Usually, 3–5 crystals of PrS_2 were taken to measure the density with an accuracy of 0.5% by a microburette in alcohol. For the tensimetric experiment 10–30 crystals were crushed just before being placed in the membrane chamber.

Tensimetric Equipment and Procedure

The total vapor pressure, $P = f(T)$, above solids of different compositions was measured in the temperature range 350–1000°C by means of a quartz Bourdon gauge with a membrane as a null-point instrument calibrated previously with metallic cadmium as described in (1, 10). Pressure was measured only with increasing temperatures using a step-by-step procedure (steps of 10–15 K, sometimes 6 K). Equilibrium was established for about 5 days along lines 1–3 and 10–15 days along lines 4–5. We account that equilibrium was achieved when it was keeping constant within 133 Pa for a day. Six runs marked as a, b, c, d, e, and f in Fig. 1 were carried out with the $PrS_{2.00}$ composition, taking the different ratios of its weight (m, mg) to the chamber volume (V, cm^3). The runs g, h, and i were performed with $PrS_{1.94}$, $PrS_{1.87}$, and $PrS_{1.75}$ compositions, respectively. Using the ratio m/V given in Fig. 1, we tried to transform these polysulfides to the sesquisulfide by limiting the sulfur pressure to 200 kPa, a capability of the tensimetric equipment. The tensimetric procedure consisted of registration of transitions from the three-phase equilibrium, *solid–solid–vapor*, to the two-phase equilibrium, *solid–vapor*. These transitions, as the breaking points of the monovariant lines, reflected changes in the number and composition of condensed phases when one of them, evaporating sulfur in a closed membrane chamber, turned into another. To calculate the composition of the solids formed at the breaking points of the three-phase lines, the sulfur amount evaporated has to be determined and subtracted from its initial amount.

Structure Study

The PrS_2 single crystals grown from flux were suited for the X-ray single-crystal study. The crystal that was $0.165 \times 0.195 \times 0.038$ mm with large edges parallel to the (001) was taken, and its structure was determined and refined to final values of factors $R = 0.0188$ and $R_w = 0.0202$ for the 2134 symmetrical nonequivalent reflections observed. Unfortunately, all intermediate polysulfides obtained from single-crystalline initial PrS_2 were polycrystalline and the X-ray single-crystal study was impossible for them. The X-ray powder diffraction patterns are found to add little to the phase identification of the polysulfides, and Raman spectroscopy was choosen to support structurally the tensimetric results showing individual polysulfide phases. Two findings established by us were taken into account: the $(S_2)^{-2}$ layer, as a structural fragment of disulfide, $(PrS)_2^+ \cdot (S_2)^{-2}$, was found to have its own spectroscopic "fingerprint" (3); any sulfur loss from stoichiometric disulfide changes the structure of the $(S_2)^{-2}$ layers and that of the polysulfide itself (11). Therefore, a variation in the shape of the $(S_2)^{-2}$ layer vibration band was taken as a tentative phase characteristic of the intermediate polysulfides, even without referring these Raman spectra to any structural type. The profile of the band 380–420 cm^{-1} was recorded only for single-phase samples rather than for their mixtures. The Raman device consisted of a double monochromator equipped with a standard photon-counting unit. The excitation source was a He–Ne laser (line = 632.8 nm).

RESULTS AND DISCUSSION

Phase Relationship in the $PrS_{1.50}$–$PrS_{2.00}$ System

Figure 1 gives the P–T dependence measured over polysulfides of different compositions and m/V ratios. The dependence reflects the sulfur evaporation process and successive transformations of the highest polysulfide to reduced polysulfides. It can be seen that all points of the $P = f(T)$ dependence measured above the polysulfides independent of m/V ratios fall well on appropriate straight lines marked as 1–5. Every straight line corresponds to the three-phase equilibrium of two adjacent polysulfides and the sulfur vapor phase. Between each pair of monovariant lines, divariant ranges appear where experimental points fall on almost horizontal lines. The intermediate polysulfide exists here in equilibrium with sulfur vapor. The view of the P–T diagram shows that in the PrS_2–$PrS_{1.5}$ system, together with PrS_2, four other polysulfides exist and they all have no marked homogeneity regions. This finding seems to

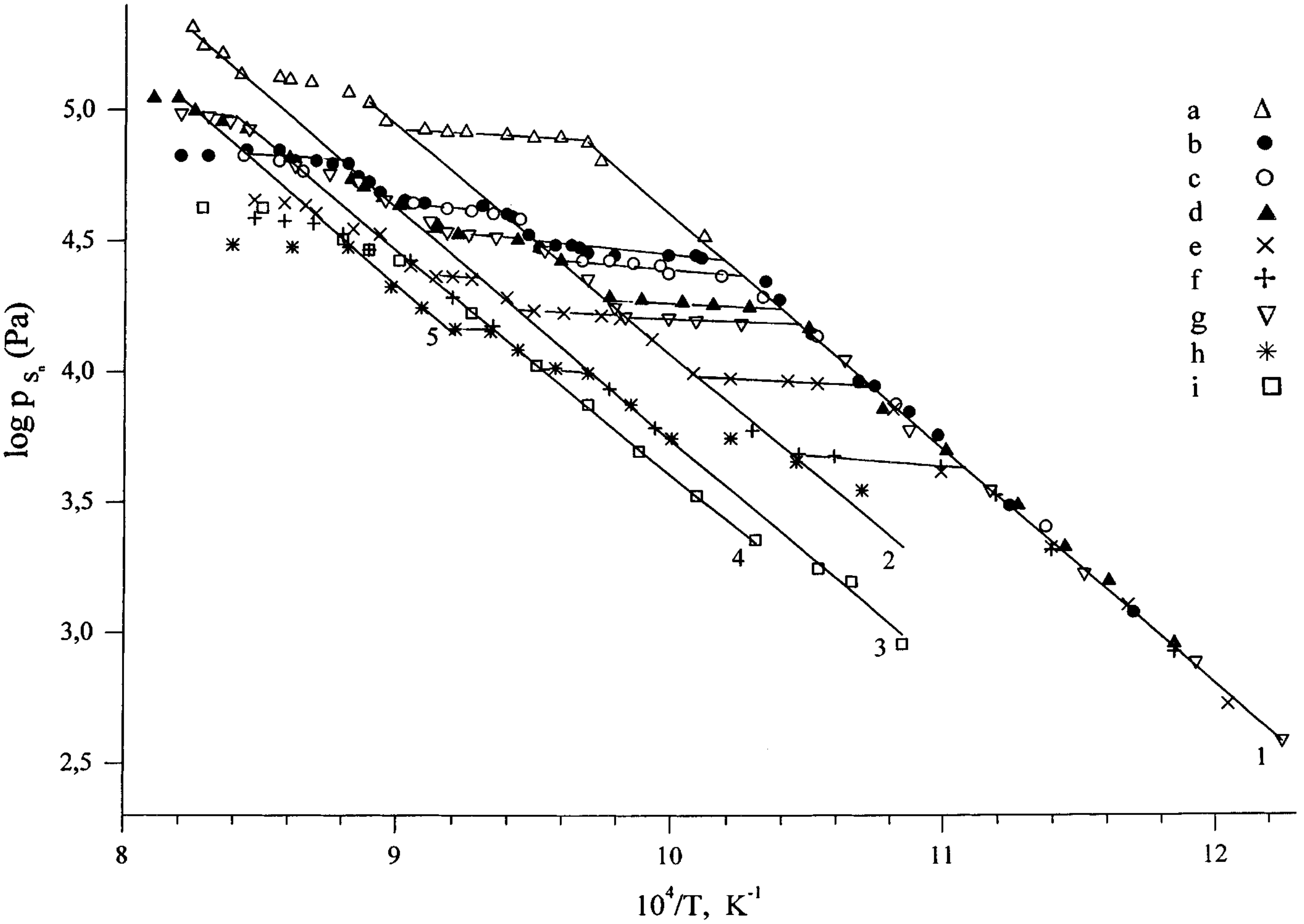

FIG. 1. P_{S_n}–$1/T$ dependence measured over $PrS_{2.00}$, $PrS_{1.94}$, $PrS_{1.85}$, and $PrS_{1.75}$ solids of different m/V ratios, g/cm^3: $PrS_{2.00}$: a, 27.0; b, 12.0; c, 7.0; d, 4.0; f, 3.7; e, 3.3. $PrS_{1.94}$: g, 8.9. $PrS_{1.85}$: h, 2.9. $PrS_{1.75}$: i, 4.5.

be less reliable for $PrS_{1.70}$ since few points might be obtained in the appropriate narrow divariant range. The breaking points of the three-phase lines were taken to determine the upper boundary composition of the intermediate polysulfides. The compositions were calculated as the difference between the number of moles of sulfur and Pr of the initial disulfide (N_S, N_{Pr}) and those in the vapor phase, (N_S^v, N_{Pr}^v which is zero) by the equation

$$x, \text{at.\%}\ S = 100 \cdot \{N_S - V/RTm_S \cdot \textstyle\sum m_n \cdot (P_{Sn}/P)\}/ \\ (N_{Pr} \pm \{N_S - V/RTm_S \cdot \textstyle\sum m_n \cdot (P_{Sn}/P)\}, \quad [1]$$

where P and T are coordinates of the phase transition points, V is the chamber volume, m_n is the molecular weight of the sulfur species, P_{Sn} is the partial pressure of the sulfur species, and $N_S^v = V/RTm_S \cdot \sum m_n (P_{Sn}/P)$. The partial pressures of the sulfur species at the breaking points were determined using the set of equations $P = \sum P_{Sn}$ and $K_n = (P_{S2})^{n/2}/P_{Sn}$ for $n = 1$–8. The equilibrium constants of polymerization for a wide temperature range are given in (8). Results of the calculation are given in Table 1 where runs are marked as in those Fig. 1.

Error of the Composition Calculation

In the tensimetric experiment the error for the composition of the intermediate polysulfides must be about 0.06 at.% S, if the other errors of the measurements are ± 2 K for temperature, ± 0.00005 g for sample weights, $\pm 1 \times 10^{-4}$ cm^3 for the chamber volume, and ± 133 Pa for the pressure. There was such an accuracy for the compositions of line 1, where all the points were below or near 975 K (melting point of KI). For the points at or above 1100 K the composition error was more than that required since the scatter in the pressure values of lines 2–5 was more

TABLE 1
Compositions of Intermediate Polysulfides Calculated in Breaking Points

	1		2		3		4		5	
Run	at.% S	*T* (K)	at.% S	*T* (K)	at.% S	*T* (K)	at.% S	*T* (K)	at.% S	*T* (K)
a	65.54	1030	64.75	1139	63.90	1215	—	—	—	—
b	65.56	980	64.79	1075	63.90	1134	62.96	1157	60.02	1183
c	65.58	975	65.01	1066	64.02	1130	62.99	1166	—	—
d	65.54	957	64.75	1052	63.90	1136	62.93	1183	60.00	1210
e	65.54	927	64.94	1017	63.66	1075	63.09	1123	60.04	1160
f	65.51	901	64.79	970	63.90	1028	—	—	—	—
g	65.58	961	64.87	1048	63.79	1139	63.06	1183	59.98	1212
h	—	—	65.12	961	63.89	1069	62.96	1099	60.01	1126
i	—	—	—	—	63.83	935	63.00	1111	60.03	1149
	$PrS_{1.900(2)}$		$PrS_{1.846(6)}$		$PrS_{1.766(8)}$		$PrS_{1.702(7)}$		$PrS_{1.500(4)}$	

apparent. The appearance of uncontrolled volatile species was a reason for the scatter. These volatile species remained in the gas phase after the membrane chamber was cooled to 300 K. The residual pressure of ~100 Pa is common for a tensimetric experiment, especially one carried out over 2–3 months (10, 12, 13). However, in runs a–c the residual pressure was as great as 2 kPa. The largest weights of PrS_2 were taken in the runs where the quantity of KI impurity may also be large. The melt of KI attacking the quartz chamber begins to produce volatile by-products. We found that the rates of by-product formation were ≤ 133 Pa/h at temperatures near 1100 K and ≤ 260 Pa/h at or above 1200 K. Of course, in the treatment of the tensimetric experiment results, preference was given to the runs with small residual pressure, i.e., to d, e, f, g, h, and i. Results of the a–c runs were needed to correct the total pressure by means of extraction of pressure produced by the by-products. For temperatures above 1200 K the by-product pressure was directly extrapolated from the room temperature to the appropriate temperature; for temperatures below 1200 K it was calculated on the basis of the rate of formation of the by-products and the duration of this run. The maximum value of the corrections was about 8 kPa, i.e., 4–8% of the total pressure. The corrected values of runs a–c are plotted on the graph, Fig. 1, where one can see the good repeatability of all runs. This fact allows one to consider that a minor inclusion of KI flux does not affect the formation of the intermediate polysulfides. And no KI dissolved in PrS_2 was found by a structural study of the crystals. Nevertheless, a new effective cleaning procedure is desirable to get the polysulfide crystals free from flux impurity. It is now in progress.

The character of the divariant lines was found to resemble that of lines from thermal expansion of ideal gas combined with dissociation of gaseous sulfur polymers. No sulfur evaporated from the condensed phase was observed at the points of the lines. Further evidence is that if there is a homogeneity range for the intermediate polysulfides, it must be very narrow, within the error limit, i.e., ≤ 0.5 at.% S. These fractional compositions, being stoichiometric phases, must be converted to the rational formulas, for instance, $Pr_{10}S_{19}$, Pr_7S_{13}, Pr_4S_7, and Pr_3S_5. They are shown in the P_s–T–x diagram in Fig. 2. The equilibrium diagram shows that in the $PrS_{2.00}$–$PrS_{1.50}$ system the stoichiometric PrS_2 coexists together with the sulfur-deficient phases, $PrS_{1.900}$, $PrS_{1.846}$, $PrS_{1.766}$, and $PrS_{1.702}$, in that range where previously one grossly nonstoichiometric phase, PrS_{2-x} was shown. As one can see, the stability fields of the polysulfides are rather narrow, and thus, there is a severe problem in preparing single-phase polysulfides if the sulfur pressure is uncontrolled. As a result, previously multiphase samples prepared by direct synthesis were very often taken as single-phase ones, which led to a mistake in the composition determination. We succeeded here in compositional identification of the closely spaced phases by using the proper tensimetric procedure, where the formation of single-phase polysulfides was controlled by a given equilibrium sulfur pressure.

Thermodynamics of the Evaporation Reactions

Each polysulfide evaporates incongruently, and polysaccharides take part in the appropriate monovariant reactions [2–7] written below per 1 mol of S_2 as the main gaseous species. Thermodynamic parameters of the reactions were determined from the $\ln P_{S2}$–$1/T$ lines 1–5 constructed from 40, 21, 20, 22, and 15 points, respectively. The partial pressures of S_2 were calculated from the total pressure using the

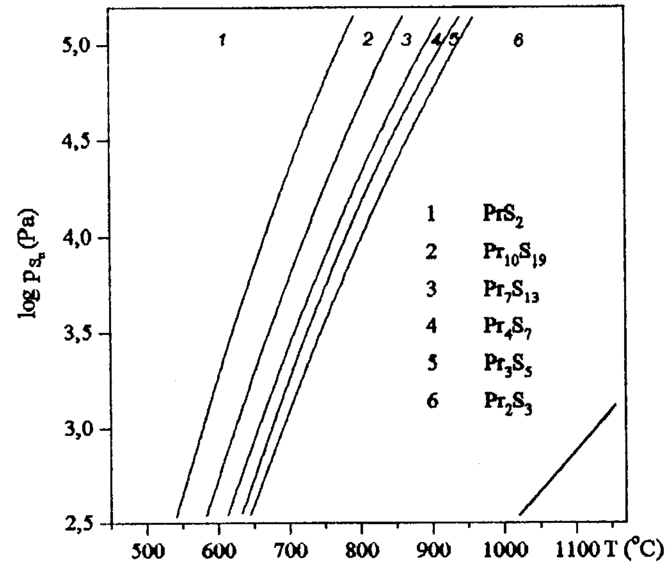

FIG. 2. The solidus portion of the pressure-dependent diagram of phases detected in the present study, $P_{\text{total}} \geq 350$ Pa. Phase stability fields are marked as 1–6.

TABLE 2
Thermodynamic Parameters of the Evaporation Reactions [2–7]

Reaction	$\ln P_{S2}$ (atm)[a] $\pm 2\sigma$	σ^2	$\Delta_r H^\circ_T$ (kJ/mol)	$\Delta_r S^\circ_T$ (J/mol·K)
[2]	$19.31 - 20328/T$	$44869/T^2 - 94.4/T + 0.05$	169.0 ± 1.2	161.0 ± 1.2
[3]	$17.15 - 19311/T$	$70811/T^2 - 134.8/T + 0.06$	160.5 ± 2.2	142.5 ± 2.1
[4]	$17.60 - 20582/T$	$27293/T^2 - 51.0/T + 0.02$	171.1 ± 1.4	146.4 ± 1.3
[5]	$16.37 - 19669/T$	$37103/T^2 - 65.6/T + 0.03$	168.8 ± 1.6	141.0 ± 1.4
[6]	$16.80 - 20401/T$	$442935/T^2 - 772/T + 0.34$	169.6 ± 5.5	139.7 ± 4.8
[7]			42.3 ± 1.3	

[a] 1 atm = 101.3 kPa.

sulfur constants of molecular gas reactions (8). The least squares treatment (95% confidence limit) gave the temperature dependence of the equilibrium pressure, standard dispersion, the enthalpy, and the entropy calculated from the second law, Table 2.

$$20\,PrS_{2.000}(s) = 20\,PrS_{1.900}(s) + S_2(g) + \Delta_r H^\circ_T \quad (800\text{–}1052\,K) \qquad [2]$$

$$37\,PrS_{1.900}(s) = 37\,PrS_{1.846}(s) + S_2(g) + \Delta_r H^\circ_T \quad (952\text{–}1110\,K) \qquad [3]$$

$$25\,PrS_{1.846}(s) = 25\,PrS_{1.766}(s) + S_2(g) + \Delta_r H^\circ_T \quad (909\text{–}1220\,K) \qquad [4]$$

$$30\,PrS_{1.766}(s) = 30\,PrS_{1.702}(s) + S_2(g) + \Delta_r H^\circ_T \quad (980\text{–}1220\,K) \qquad [5]$$

$$10\,PrS_{1.702}(s) = 10\,PrS_{1.500}(s) + S_2(g) + \Delta_r H^\circ_T \quad (909\text{–}1220\,K) \qquad [6]$$

$$\Sigma\, 20\,PrS_{2.000}(s) = 20\,PrS_{1.500}(s) + 5\,S_2(g) + \Sigma\Delta_{r[2-6]} H^\circ_T$$

$$\text{or } PrS_{2.000}(s) = PrS_{1.500}(s) + 0.25\,S_2(g) + \Delta_r H^\circ_T \quad (800\text{–}1220\,K) \qquad [7]$$

These data were then used in the appropriate thermochemical cycles to determine the standard heats of the PrS_2 formation. The required thermodynamic parameters of Pr, S, Pr_2S_3, and the values of the heat capacity of PrS_2 at 298 and 800 K taken from (14, 15) are given in Table 3.

The heat of formation of the PrS_2 phase from Pr(s) and S(s) was calculated to be $\Delta_f H^\circ_{800} = -598.3$ kJ/mol at 800 K and $\Delta_f H^\circ_{298} = -586.6$ kJ/mol at 298 K (accuracy of about 7%). The last value is close to that, 589.9 kJ/mol, estimated from those in the series LaS_2–NdS_2, based on some calorimetrical measurements. Good agreement of both values means that there were no substantial errors in our experiments (the procedure of measurements and purity of crystals), and therefore, the heat of formation of the $PrS_{2.00}$ obtained here tensimetrically may be recommended as a reliable value.

Structural Characterization

The intermediate polysulfides can be described by a homologous series of the generic formula, Ln_nS_{2n-x}, with $n = 3, 4, 7, 10$, and structures of these chemical homologues should be close to each other. However, the structural problems in the Pr polysulfides, except PrS_2, arise since single crystals suited for single-crystal X-ray studies have not been obtained up to now. The structure of PrS_2 was determined to be monoclinic with unique axes along the [100] direction and $a = 0.4054(1)$, $b = 0.8058(1)$, $c = 0.8079(1)$, $\alpha \approx 90.0^\circ$, $V = 0.264\ \text{nm}^3$, space group $P2_1/b11$, $Z = 4$, $d_{\text{calc.}} = 5160$, and $d_{\text{exp}} = 5160 \pm 20\ \text{kg/m}^3$. Special attention was given to assigning the structure as having monoclinic rather than pseudo-orthorombic symmetry, and these detailed structural data will be published elsewhere. The room-temperature Raman spectrum of the structure of the type, given in Fig. 3, spectrum 1, shows two resolved bands near 400 cm^{-1}, typical for the (S_2^{2-}) layer as expected according to the symmetry analysis (3, 16). The single band of the $PrS_{1.90}$ polysulfide (Fig. 3, spectrum 2) was found to be identical to that of the $SmS_{1.90}$ polysulfide (3), the structure of which was recently solved by us (1). Therefore, one

TABLE 3
Thermodynamic Properties of Substances Taking Part in the Reactions [2–7] (kJ/mole)

Substance	$C_{p,298}$	$C_{p,800}$	$\Delta_f H^\circ_{298}$
Pr(s)	0.0276	0.0356	—
S(s)	0.0226	0.0309	—
S_2(g)	0.0324	0.0364	127.5
Pr_2S_3(s)	0.1226	0.1431	− 1142.2
PrS_2(s)	0.0744	0.0766	—

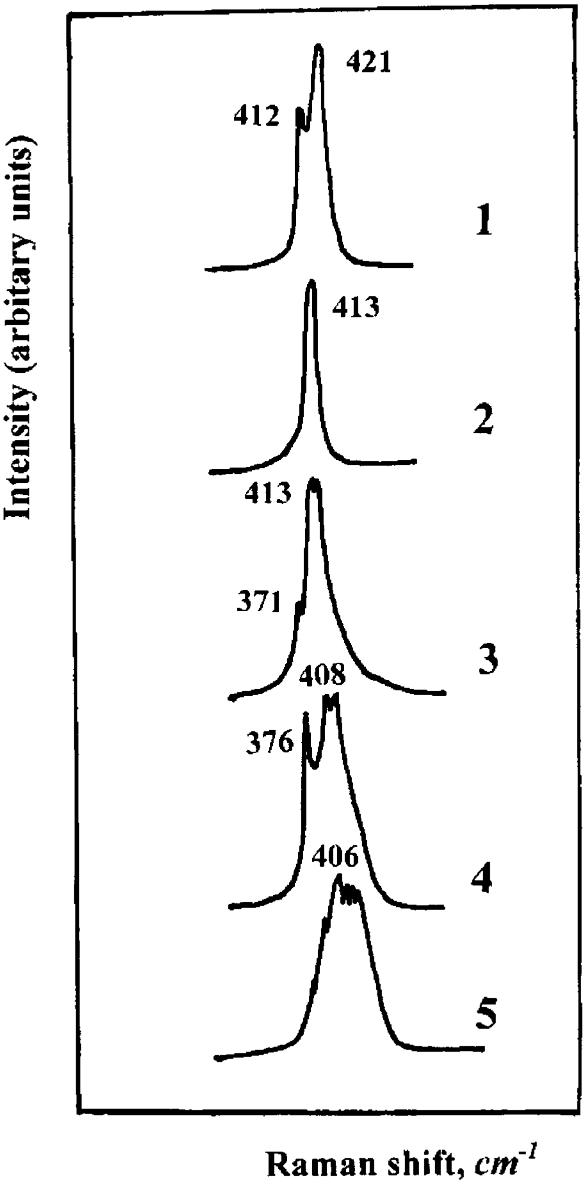

FIG. 3. The profile of the S_2^{-2} layer band at around 400 cm^{-1} in the room-temperature Raman spectra of the Pr polysulfides of different compositions: 1, $PrS_{2.00}$; 2, $PrS_{1.90}$; 3, $PrS_{1.85}$; 4, $PrS_{1.76}$; 5, $PrS_{1.70}$.

can accurately describe the $PrS_{1.90}$ polysulfide structure by the tetragonal space group $P4_2/n$. The Raman spectra of the other reduced polysulfides differ from the PrS_2 spectrum as well from that of $PrS_{1.90}$. They demonstrate a shoulder (Fig. 3, spectrum 3) or a band (Fig. 3, spectrum 4) at about 376 cm^{-1}, reproducing well from sample to sample and broadening the main band at about 400 cm^{-1} with a decrease in the S/Pr ratio. The Raman spectra of the reduced Pr–polysulfides are not available in the literature and their interpretation is not easy, as the main peak is broad. The broadening may result from disorder in the anionic fragment of the (S_2^{2-}) layer or from an order leading to superlattice cells. The latter assumption is best suited here when it is considered that the reduced Dy-polysulfides, $DyS_{1.85}$ and $DyS_{1.76}$, really show close superlattice cells of the PbFCl type ($P4/nmm$) according to our recent structural study (17). If this is the case, only the single-crystal X-ray study may give reliable structural information for the new Pr–polysulfides identified compositionally in the paper. Fortunately, now we have the P_s–T–x diagram of the PrS_2–$PrS_{1.5}$ system, which provides information on how to grow single-phase crystals of the reduced Pr–polysulfides. The process of crystal growth of the Pr–polysulfides is now in progress.

In summary, we clearly confirmed the existence of new sulfur-deficient polysulfide phases $Pr_{10}S_{19}$, Pr_7S_{13}, Pr_4S_7, and Pr_3S_5 in the $PrS_{2.00}$–$PrS_{1.50}$ system. They appear to be intermediate between $PrS_{2.00}$ and $PrS_{1.50}$ in structural respects, in particular regarding the anion (S_2^{2-}) layer arrangement. The stoichiometry of the title phases, the absence of a homogeneity range, and their evaporation parameters were determined by the static tensimetric study. We have found that this technique is an excellent tool for compositional characterization of the intermediate polysulfides.

ACKNOWLEDGMENTS

The authors are very grateful to B. Kolesov and E. Belyaeva for valuable assistance. This work was supported by Grant 96-03-33010 from the Russian Foundation of Fundamental Researches.

REFERENCES

1. I. G.Vasilyeva and E. I. Belyaeva, *J. Solid State Chem.* **142,** 261 (1999).
2. I. G. Vasileva and T. Y. Shilkina, *Zh. Neorg. Khim.* **44,** 193 (1999).
3. B. A. Kolesov and I. G. Vasilyeva, *Mater. Res. Bull.* **27,** 775 (1992).
4. E. I. Jarembash and A. A. Eliseev, "Rare Earth Elements Chalcogenides," Izd. Nauka, Moscow, 1975. [In Russian]
5. A. A. Yeliseev and A. A. Grizik, *in* "Rare Earth Semiconductors," (V. Zhuse and I. Smirnov, Eds.), pp. 146–177, Izd. Nauka, Leningrad, 1997. [In Russian]
6. S. Ring and M. Tecotzky, *Inorg. Chem.* **3,** 182 (1964).
7. G. F. Balashevski and V. K. Val'tzev, *Zh. Neorg. Khim.* **28,** 1677 (1983).
8. H. Rau, T. Kutty, and de G. Carvalho, *J. Chem. Thermodyn.* **5,** 291 (1973).
9. L. R. Holland, *J. Cryst. Growth* **66,** 501 (1984).
10. V. Lazarev, Ja. Greenberg, and B. Popovkin, "Current topics in material science," Vol. 1, p. 657. North-Holland, Amsterdam, 1978.
11. N. V. Podberezskaya, S. A. Magarill, N. V. Pervuhina, I. G. Vasilyeva, and S. V. Borisov, *Russ. J. Struct. Chem.* **37,** 963 (1996).
12. S. Datz and W. Smith, *J. Phys. Chem.* **63,** 938 (1959).
13. G. J. Russell and J. Woods, *J. Cryst. Growth* **46,** 323 (1979).
14. S. P. Gordienko, B. V. Fenochka, and G. Sh. Viksman, "Thermodynamics of Lanthanide Compounds," Chap. 10. Naukova Dumka, Kiev, 1979. [In Russian]
15. A. I. Kriklya, A. S. Bolgar, and L. N. Kartuzova, *Zh. Thermophys. Visokhich Temp.* **25,** 919 (1987).
16. B. Le Rolland, P. Molinie, P. Colombet, and P. F. McMillan, *J. Solid State Chem.* **113,** 312 (1994).
17. N. V. Podberezskaya, D. Ju. Naumov, I. G. Vasilyeva, N. V. Pervuhina, S. A. Magarill, and S. V. Borisov, *Russ. J. Struct. Chem.* **39,** 804 (1998).