Journal of Alloys and Compounds, 194 (1993) 41–45
JALCOM 516

Interaction of intermetallic compounds with hydrogen at pressures up to 250 MPa: the $LaCo_{5-x}Mn_x$–H_2 and $CeNi_5$–H_2 systems

S. N. Klyamkin and V. N. Verbetsky
Department of Chemistry, Lomonosov Moscow State University, Lenin Hills, 119899 Moscow (Russian Federation)

(Received May 15, 1992; in final form September 10, 1992)

Abstract

A new method has been proposed for the synthesis and thermodynamic study of intermetallic hydrides at pressures of gaseous hydrogen up to 250 MPa. From preliminary experiments on hydrogen compressibility and consideration of available *p–V–T* data for hydrogen at high pressures we have chosen a modified van der Waals equation giving a calculation error of 0.1%–0.5% or less. Absorption and desorption isotherms for the $LaCo_{5-x}Mn_x$–H_2 ($x=0.05$) and $CeNi_5$–H_2 systems were measured at temperatures from 195 K up to room temperature. The highest hydrogen content obtained in a hydride composition of $LaCo_{5-x}Mn_x$ does not exceed 8 at. H per formula unit, and for the high pressure plateau $\Delta H_{abs}=\Delta H_{des}=14.4$ kJ (mol H_2)$^{-1}$ and $\Delta S_{abs}=\Delta S_{des}=110.2$ J K^{-1} (mol H_2)$^{-1}$. In the $CeNi_5$–H_2 system the existence of a single plateau and considerable hysteresis were observed.

1. Introduction

The use of high gaseous pressures is one of the most effective methods employed in studies of the chemistry of metal hydrides. Owing to the rise in hydrogen chemical potential with increasing hydrogen pressure, hydrides which are thermodynamically or kinetically unobtainable at low pressures can be formed and investigated under equilibrium conditions in the higher pressure region. The efficiency of such an approach has been shown by Filipek and Baranowski [1] and Ponyatovsky *et al.* [2], who have succeeded in synthesizing at gaseous hydrogen pressures up to 30–90 kbar a wide range of hydrides of transition metals and their alloys which had previously been considered not to form hydrides. At the same time, for intermetallic compounds inclined to hydride formation, interesting results may be obtained by the use of substantially lower pressures (1–2 kbar), primarily for the synthesis of new hydrogen-rich phases. In this pressure range Lakner *et al.* [3] obtained intermetallic hydrides and deuterides corresponding to maximum theoretically predicted hydrogen compositions [4] and measured the pressure–composition (P–C) isotherms at room temperature. In spite of the absence of X-ray data and thermodynamic parameters for the hydrogenation–dehydrogenation reactions studied, great possibilities of the method using hydrogen pressures up to 2 kbar were shown in ref. 3.

In this work we present the results of a study of hydrogen interaction with the intermetallic compounds $LaCo_{5-x}Mn_x$ and $CeNi_5$ at pressures up to 250 MPa in an experimental apparatus developed in the High Pressure Chemistry Laboratory of the Chemical Department of Moscow State University.

2. Experimental details

2.1. Sample preparation and characterization

The intermetallic compounds were prepared by arc melting the pure metals in a water-cooled copper crucible with tungsten electrodes under an inert atmosphere. The ingots were turned over and re-melted several times to ensure homogeneity. The alloys were annealed under vacuum at 900 °C for 24 h. The compositions of the prepared alloys were confirmed by chemical analysis. X-Ray studies of the initial alloys and their stable or poisoned hydrides were carried out using a DRON-2 powder X-ray diffractometer (Cu Kα radiation, Ni filter, Si standard) (Table 1). The hydrogen

TABLE 1. Crystal structure data for $CeNi_5$, $LaCo_{4.95}Mn_{0.05}$ and its hydride

Composition	*a* (nm)	*b* (nm)	*c* (nm)	*V* (10^{-3} nm^3)
$LaCo_{4.95}Mn_{0.05}$	0.5112(2)		0.3972(2)	89.88
$LaCo_{4.95}Mn_{0.05}H_{3.5}$	0.9000(11)	0.5394(5)	0.4087(2)	99.04
$CeNi_5$	0.4876(3)		0.3998(3)	82.30

0925-8388/93/$6.00

contents in the samples after the experiments were determined by high temperature vacuum extraction.

2.2. High pressure apparatus

A schematic diagram of the experimental apparatus used for the study of hydrogen interaction with metals at high pressures is shown in Fig. 1. The apparatus includes a vacuum system, a system for hydrogen purification and preliminary compression using a metal hydride accumulator, a system for high pressure creation, a "pressure transmission medium–hydrogen" separator with a shift gauge and an autoclave containing the sample. The vacuum system (a mechanical pump with a liquid nitrogen trap, a measuring vessel and a vacuum transducer) provides sample degassing down to 0.01 Torr pressure and equilibrium pressure measurements below 0.1 MPa during experiments. The hydrogen accumulator, based on a Ti–Fe–V alloy, accomplishes purification of hydrogen from 99.99% to 99.9999% and its introduction into the low pressure hydrogen vessel at pressures up to 16 MPa. The silicone oil which provides the transmission of pressure to hydrogen was compressed to 250 MPa by a UNGR hydraulic pump. The "oil–hydrogen" separator is the essential hydrogen pressurizing and measuring element of the experimental apparatus. It comprises a stainless steel cylinder and a mobile piston with an electric shift gauge. The separator is connected to the reaction autoclave and the hydrogen buffer and is placed in the high pressure vessel filled with oil. An increase in oil pressure leads to movement of the separator piston and thus to compression of hydrogen. The shift gauge allows us to continuously record the piston position and thus determine the volume of high pressure hydrogen.

The hydrogen pressure was measured in different ranges by "Sapphire" D16 (to 16 MPa), D100 (to 100 MPa) and D250 (to 250 MPa) transducers.

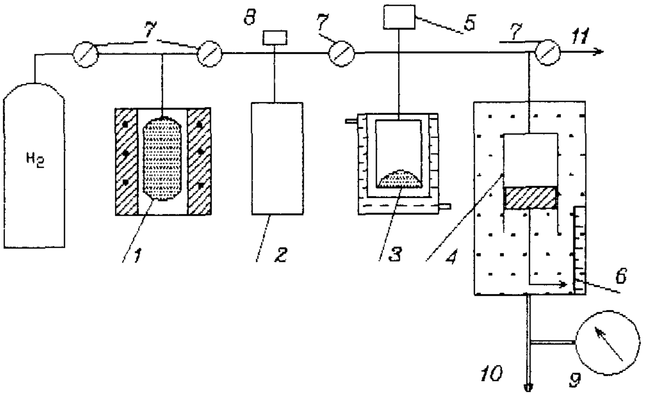

Fig. 1. Schematic diagram of experimental apparatus: 1, metal hydride accumulator; 2, low pressure hydrogen vessel; 3, autoclave with sample; 4, separator; 5, high pressure transducer; 6, shift gauge; 7, needle valves; 8, low pressure transducer; 9, high pressure oil manometer; 10, to high pressure hydraulic pump; 11, to vacuum system.

The high pressure experimental apparatus used in our work has the following parameters: working pressure, up to 250 MPa; working temperature, 77–673 K; separator gas volume, 90.34 cm^3; volume of reaction autoclave, 5.10 cm^3; maximum hydrogen compression degree, 30; sample mass, 5–12 g; measurement accuracies of – pressure, 0.1%–0.4%; temperature, 0.2–1 K; volume, 0.02 cm^3; hydrogen content in hydrides, 5×10^{-3} mass%.

2.3. Calculations

The composition determination of the hydride phases formed was carried out volumetrically with the help of a computer code using a high pressure hydrogen state equation. The state equation was chosen on the basis of the literature and our own experimental data on hydrogen compressibility along with a number of theoretical p–V–T expressions [5–8]. The accomplished analysis permitted us to determine that in the temperature range 100–1000 K and pressure range 0–300 MPa the maximum calculation accuracy (0.1%–0.5%) is provided by using the modified van der Waals equation proposed in ref. 9:

$$\left(p+\frac{a(p)}{V^{\alpha}}\right)[V-b(p)]=RT \tag{1}$$

where

$$a(p)=\exp\{a_1+a_2\ln(p)-\exp[a_3+a_4\ln(p)]\} \tag{2}$$

$$b(p)=\begin{cases}\sum b_i\ln(p) & \text{at } p\geqslant 100 \text{ bar}\\ b(100) & \text{at } p<100 \text{ bar}\end{cases} \tag{3}$$

$$\alpha(T)=\begin{cases}\alpha_0+\alpha_1T+\alpha_2T^2 & \text{at } T\leqslant 300\text{ K}\\ \alpha(300) & \text{at } T>300\text{ K}\end{cases} \tag{4}$$

Values of a_i, b_i and α_i are cited in ref. 9.

The accuracy of the calculations depends considerably on taking into account the sample expansion during its hydrogen saturation. Preliminary calculations showed that at 200 MPa the error caused by an indefinite sample volume could reach 10%. In order to minimize this error, we used the assumption (for the compounds studied in this work) of a linear dependence of the sample volume on its hydrogen content. In addition, we checked the calculated values against our own X-ray experimental data.

3. Results and discussion

3.1. $LaCo_{5-x}Mn_x$–H_2 system

$LaCo_5$ is the first $CaCu_5$-type compound for which the formation of a hydride phase with the maximum predicted hydrogen content, $LaCo_5H_9$, was established [3]. This hydride corresponded to a plateau on the P–C isotherm with the equilibrium absorption pressure 1250 atm at 21 °C. An almost twofold pressure increase (to 2500 atm) produced no further composition changes.

For the object of our study we chose the compound $LaCo_{4.95}Mn_{0.05}$, for which the partial substitution of Co by Mn led to a significant decrease in equilibrium pressure without any change in the general character of the P–C isotherms [3].

The X-ray parameters of the prepared sample do not differ from previous literature data [3, 10], but traces of another phase, probably La_2Co_7, could not be completely avoided.

The first hydriding of $LaCo_{4.95}Mn_{0.05}$ at a pressure of about 2 MPa and room temperature proceeds with a small (a few seconds) induction period and is completed in 5–10 min with the formation of a hydride containing 4.2 H atoms per formula unit 4.2 (at.H.f.u.$^{-1}$). This composition corresponds to that of a γ-hydride obtained under similar conditions for the $LaCo_5$–H_2 system [10]. An increase in pressure to 90 MPa causes almost no further changes in hydride composition: the additional hydrogen absorption is about 0.5 at.H.f.u.$^{-1}$ (Fig. 2). These results differ significantly from those of ref. 3, where a similar rise in pressure caused a hydrogen content increase to 5.5 at.H.f.u.$^{-1}$.

The highest plateau in terms of its length and sloping factor is similar to that obtained in ref. 3, but corresponding to the above-mentioned difference, the maximum hydride composition at room temperature is $LaCo_{4.95}Mn_{0.05}H_{7.5}$. Only a temperature drop to 195 K increases the hydrogen content up to 8 at.H.f.u.$^{-1}$, mainly owing to additional solubility over the rising branch of the isotherm. We should note that at 294 and 273 K the pressure rise from the value corresponding to the highest plateau to 250 MPa causes no significant increase in hydrogen solubility in the hydride phase.

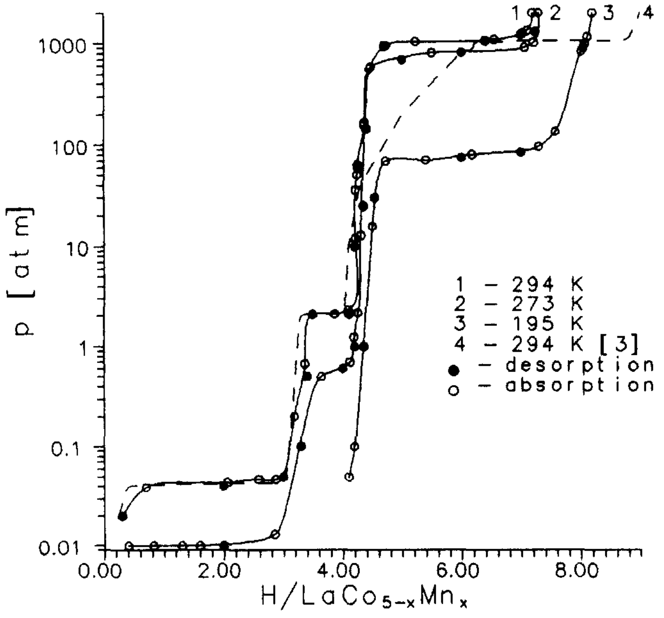

Fig. 2. P–C isotherms for $LaCo_{4.95}Mn_{0.05}$–H_2 system.

The desorption and absorption isotherms almost coincide. At pressures above 100 MPa the extent of plateau hysteresis is only 2–3 MPa, while for other pressures it does not exceed the pressure measurement error. The reaction enthalpy changes in the low pressure range calculated on the basis of experimental pressure values (p_1 and p_2 in Table 2) for two temperatures are in good agreement with data [10] for the $\gamma \rightarrow \beta^1$ and $\beta^1 \rightarrow \alpha$ phase transitions in the $LaCo_5$–H_2 system. The values of ΔH and ΔS for the third (the highest) plateau do not contradict the obtained stability of the hydride phase with maximum hydrogen content. However, the absence of available data for the enthalpy of intermetallic hydride formation at high pressures does not permit detailed discussion of the values obtained.

Quenching of the sample with maximum hydrogen content ($LaCo_{4.95}Mn_{0.05}H_8$) to 77 K followed by its poisoning by air allowed us to confirm this hydride composition by high temperature vacuum hydrogen extraction analysis. However, we did not succeed in an X-ray analysis because the hydride decomposes to the β^1 phase (about 3.5 at.H.f.u.$^{-1}$) during sample preparation. The use of more effective poisons (CO, SO_2) would probably lead to better results.

3.2. $CeNi_5$–H_2 system

The first thermodynamic data for the $CeNi_5$–H_2 system appeared in 1977 [11]. However, in spite of a comparatively low equilibrium pressure (48 atm), these results could not be repeated in later studies and many researchers confirmed that $CeNi_5$ does not interact with hydrogen at pressures up to 150 atm. The data obtained in the present study provide an explanation of these considerations.

The characteristic features of the $CeNi_5$–H_2 system are very low rates of hydride formation and decomposition, especially in the first cycle, and a large hysteresis value. At room temperature the reaction of the alloy (its X-ray parameters are given in Table 1) with hydrogen only begins at 40 MPa; the equilibrium absorption pressure is only achieved after long (about 24 h) exposure and is about 25 MPa at this temperature. After three activating absorption–desorption cycles (Table 3) the reaction rate is increased but the time to achieve equilibrium is still 2–3 h (which is several times greater than for $LaCo_{4.95}Mn_{0.05}$) and does not vary with pressure. It is interesting to note that at the same time the sample with maximum hydrogen content ($CeNi_5H_{7.1}$) quenched by liquid nitrogen and air poisoned evolves

TABLE 2. Thermodynamic data for $LaCo_{4.95}Mn_{0.05}$–H_2 system

	Temperature (K) 294	273	195	$-\Delta H_{des}$ (kJ (mol H_2)$^{-1}$)	ΔS_{des} (J K^{-1} (mol H_2)$^{-1}$)
p_1 (MPa)	0.04	0.01	-	46.4	132
p_2 (MPa)	0.21	0.06	-	34.1	125
p_3/f_3 (MPa)	106.0/146.0	84.0/112.3	7.9	14.4±0.7	110.2±3.2

TABLE 3. Absorption and desorption plateau pressures and hysteresis factors for $CeNi_5$–H_2 system

	Temperature (K) 296	273	195
p_{abs} (MPa)	24.8	19.5	0.84
p_{des} (MPa)	7.25	3.57	0.07
$\ln(p_{abs}/p_{des})$	1.23	1.73	2.48

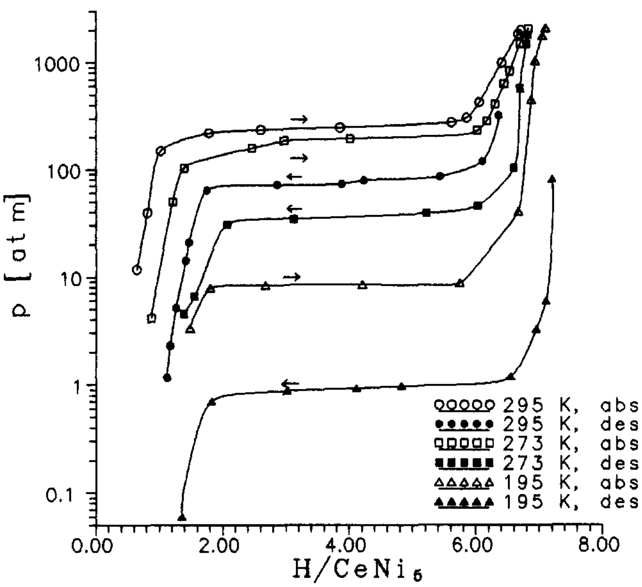

Fig. 3. P–C isotherms for $CeNi_5$–H_2 system.

all its hydrogen within several seconds on heating to room temperature. This fact prevented us from obtaining reliable X-ray data for the hydride phase.

The measured P–C isotherms are shown in Fig. 3 and the thermodynamic functions calculated on their basis for the $\alpha+\beta$ two-phase region are shown in Table 4. An analysis of the data represented allowed us to note the following regularities.

The hydrogen content in the β-hydride which is in equilibrium with α-$CeNi_5$ changes weakly with temperature: from 6.0 at.H.f.u.$^{-1}$ 295 at K to 6.5 at.H.f.u.$^{-1}$ at 195 K. The additional hydrogen solubility in the β phase caused by a pressure rise to 250 MPa does not exceed 0.7 at.H.f.u.$^{-1}$ and a second plateau (as for $LaCo_{4.95}Mn_{0.05}$) was not found at any experimental temperature. Comparison with Lakner *et al.*'s data [3] shows that among the AB_5 compounds (A≡La, Ce; B≡Ni,Co) $CeNi_5$ is analogous to $LaNi_5$, which is also characterized by a single, long plateau.

As may be seen from Tables 3 and 4, the $CeNi_5$–H_2 system is characterized by an extremely large hysteresis: for example, at room temperature the equilibrium absorption and desorption pressures differ by a factor of 3.6, which is, however, smaller than that in ref. 11. The lower desorption pressure reported in ref. 11 compared with our results (4.8 and 7.3 Mpa respectively) may be explained by the fact that the time of full equilibrium attainment in the $CeNi_5$–H_2 system is very long and the authors of ref. 11 were probably concerned with non-equilibrium values.

It is necessary to note that the extent of hysteresis depends greatly on the temperature: the $\ln(p_{abs}/p_{des})$ parameter is increased by 40% when the temperature decreases from 295 to 273 K and by a factor of 2 on further decrease to 195 K. A hysteresis temperature dependence of this type is very characteristic of "intermetallic compound–hydrogen" systems and coincides with the dependence determined in ref. 12 for Mn-substituted $CeNi_5$. At the same time, in the $CeNi_{5-x}Al_x$–H_2 system [12] the hysteresis increases weakly with increasing temperature, but the authors have given no explanation of this anomalous behaviour. Data for $CeNi_5$ itself are not available in the literature.

Calculations of thermodynamic functions for the $\alpha\rightarrow\beta$ and $\beta\rightarrow\alpha$ transitions were carried out on the basis of experimental equilibrium pressures for the $CeNi_5H_4$ composition at various temperatures. The values of enthalpy (ΔH) and entropy (ΔS) changes calculated by the van't Hoff equation (Fig. 4, Table 4) differ significantly for absorption and desorption reactions. These differences, 25% for ΔH and 11% for ΔS, are consequences of the large hysteresis and are close to the corresponding values for the $CeNi_{5-x}Mn_x$–H_2 system (24% and 11%) [12].

In Fig. 5 and Table 4 the thermodynamic functions are compared with literature data for $CeNi_5$ [11] and $CeNi_{5-x}Mn_x$ [12]. As a criterion to characterize the correlation degree, we chose the unit cell volume of the initial intermetallic compound, which in turn determines the dimensions of interstitial sites occupied by hydrogen during hydride formation. For isostructural compounds it is this parameter which is connected

TABLE 4. Thermodynamic data for $CeNi_5$–H_2 and $CeNi_{5-x}Mn_x$–H_2 systems

	$CeNi_5$	$CeNi_{5-x}Mn_x$ [12]		$CeNi_5$ [11]
		$x=0.5$	$x=0.75$	
ΔH_{des} (kJ (mol H_2)$^{-1}$)	22.2±0.2	24.1	25.2	14.1
$-\Delta H_{abs}$ (kJ (mol H_2)$^{-1}$)	16.7±0.4	18.8	22.0	–
ΔS_{des} (J K^{-1} (mol H_2)$^{-1}$)	111.4±0.9	97.1	86.6	80.0
$-\Delta S_{abs}$ (J K^{-1} (mol H_2)$^{-1}$)	99.3±1.7	90.0	84.8	–

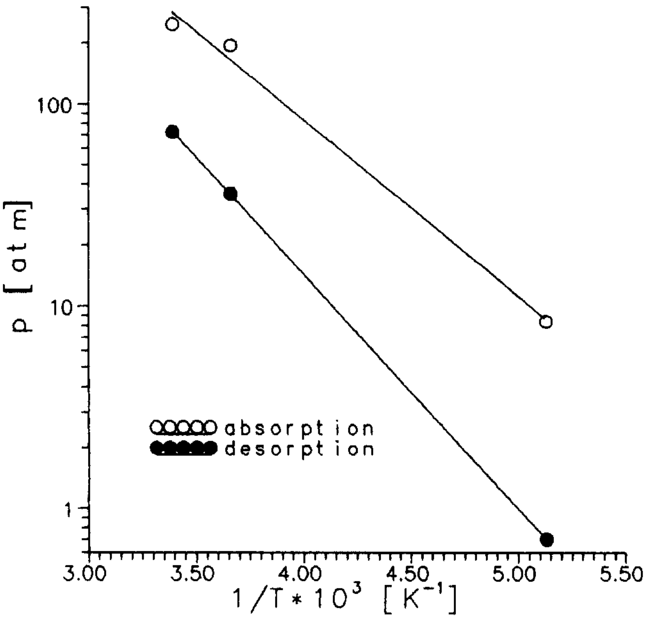

Fig. 4. Van't Hoff plots for $CeNi_5$–H_2 system.

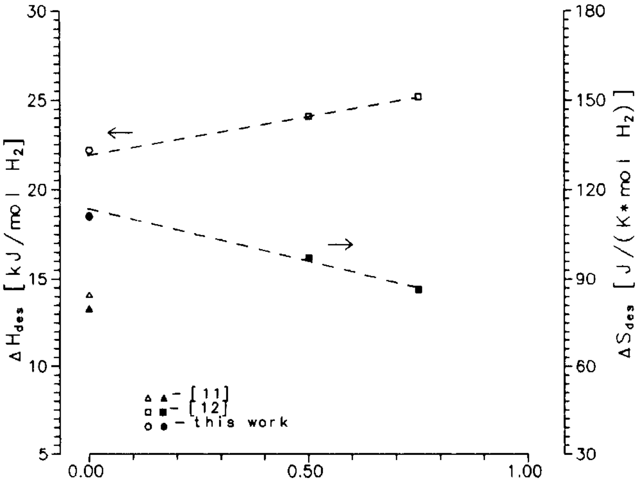

Fig. 5. Dependence of thermodynamic functions on composition for $CeNi_5$–H_2 and $CeNi_{5-x}Mn_x$–H_2 systems.

linearly with the values of thermodynamic functions, *i.e.* the hydride thermal stability. It may be seen from Fig. 5 that our results differ from those known for $CeNi_5$ [11] but are in good agreement with the $CeNi_{5-x}Mn_x$–H_2 system parameters [12]. The absence of significant deviations from linearity gives reason to consider $CeNi_5$ from the point of view of hydride formation as a compound belonging to the set of formerly studied $CaCu_5$-type intermetallic compounds and thus displaying no anomalous electronic effects as supposed by Pourarian and Wallace [12].

References

1 S. Filipek and B. Baranowski, *Proc. 6th Int. Symp. on High-purity Materials Science and Technology, Dresden, May 1985,* Oberlung-Witz, 1985, p. 90.

2 E. G. Ponyatovsky, V. E. Antonov and I. T. Belash, in A. M. Prokhorov and A. S. Prokhorov (eds.), *Problems in Solid State Physics, Advances in Science and Technology in the USSR, Physics Series,* Mir Publishers, Moscow, 1985, p. 109.

3 J. F. Lakner, F. S. Uribe and S. A. Steward, *J. Less-Common Met., 73* (1980) 87.

4 T. Takeshita, W. E. Wallace and R. S. Craig, *Inorg. Chem., 13* (1974) 2283.

5 A. Michels, W. de Graff, T. Wassenaar, J. M. H. Levelt and P. Louwerse, *Physica, 25* (1959) 25.

6 R. L. Mills, D. H. Liebenberg, J. C. Bronson and L. C. Schmidt, *J. Chem. Phys., 66* (1977) 3076.

7 D. S. Tsiklis, V. Ya. Maslennikova, S. D. Gavrilov, A. N. Egorov and G. V. Timofeeva, *Dokl. Akad. Nauk, 220* (1975) 1384.

8 H. R. Shaw and D. R. Wones, *Am. J. Sci., 262* (1964) 918.

9 H. Hemmes, A. Driessen and R. Griessen, *J. Phys. C: Solid State Phys., 19* (1986) 9571.

10 F. A. Kuijpers, *Philips Res. Rep. Suppl. 2* (19730 1.

11 C. E. Lundin, F. E. Lynch and C. B. Magee, *J. Less-Common Met., 56* (1977) 19.

12 F. Pourarian and W. E. Wallace, *Int. J. Hydrogen Energy, 10* (1985) 49.