

Further Studies of the Isotherms of $\text{LaNi}_{5-x}\text{Sn}_x - \text{H}$

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Abstract

Complete hydrogen isotherms have been measured using highly stoichiometric, activated LaNi_5 , over a wide temperature range, 373 K to 228 K. Van't Hoff plots for hydride formation and decomposition have been constructed using the isotherms in the low temperature range from 228 K to 298 K. The following thermodynamic results have been obtained from these plots: $|\Delta H_{\text{plat}}| = 15.4 \text{ kJ/ mol } \frac{1}{2}\text{H}_2$ and $|\Delta S_{\text{plat}}| = 54.4 \text{ J/K mol } \frac{1}{2}\text{H}_2$. These should be regarded as reliable in view of the nearly stoichiometric LaNi_5 employed and the wide and low temperature range because the latter avoids degradation of the alloy which can be a factor at higher temperatures due to the inherent instability of the H-containing alloy.

It has been observed previously in the $\text{LaNi}_5 - \text{H}$ system that the absorption plateau measured with virgin alloys, i.e., before activation, is significantly higher than the subsequent values. This phenomenon was investigated in this research using the $\text{LaNi}_{5-x}\text{Sn}_x$ alloys with $x=0, 0.05, 0.10, 0.20, 0.25$ and 0.32 . Isotherms for the virgin and

activated alloys were measured at 373 K. The initial plateau pressures for hydride formation relative to values for activated material decrease with increase of x . An important result is that the initially high plateau pressure for hydride formation must reflect a hysteresis effect because the difference between the plateau pressures before and after activation almost vanishes at a Sn content of $x=0.32$ where hysteresis itself nearly vanishes. The plateau pressure ratio, $(P_{\text{initial}}/P_{\text{subsequent}})_f$, where the f subscript reflects hydride formation, decreases markedly with increase of x .

Introduction

Many pressure-composition isotherms have been reported in the literature using samples of LaNi_5 which were not very close to 1-to-5 stoichiometric ratio of La-to-Ni and also where there was significant plateau sloping. In order to obtain the most reliable plateau thermodynamic parameters from isotherm data for $\text{LaNi}_5\text{-H}$, closely stoichiometric material must be employed and isotherms must be measured over a wide, low temperature range where degradation will not be a factor. In this research both absorption and desorption isotherms were measured from 228 K to 373 K. Earlier isotherms measured at low temperature for $\text{LaNi}_5\text{-H}$ were generally not very horizontal [1].

It has been previously shown [2, 3] that the plateau pressure for hydride formation, p_p , for the initial isotherm of $\text{LaNi}_5\text{-H}$ is much greater than the subsequent plateau pressures for hydride formation whereas the decomposition plateau pressures for the activated alloy, p_d , are basically unchanged.

$\text{LaNi}_{5-x}\text{Sn}_x$ alloys have been shown to be of interest technologically [4, 5] and fundamentally [6, 7]. Hysteresis for the activated forms of these alloys decreases significantly with increase of x . In this research the initial and subsequent formation plateau pressures have been measured for a series of $\text{LaNi}_{5-x}\text{Sn}_x\text{-H}$ systems. The dependence of the difference in the formation plateau pressures on alloy composition x were determined and related to the hysteresis of the activated alloys for this system.

Experimental

LaNi₅ was prepared at the Ames Laboratory of Iowa State University by arc-melting the elements. The purity of the Ni was 99.99% and the La was 99.95% (including oxygen). The button was melted seven times inverting it after each melting. The arc-cast button was wrapped in Ta foil, sealed in an evacuated quartz tube and annealed at 1223 K for 100 h. It was shown to be single phase from metallography and the powder X-ray diffraction (XRD) patterns showed that the angles of the reflections were equal for randomly selected regions within the ingot. The ratio of Ni-to-La in the LaNi₅ was 5.00 ± 0.01 based on electron microprobe analysis.

The LaNi_{5-x}Sn_x samples with $x=0.1$ and 0.2 were also prepared at Iowa State University using a similar procedure and then they were annealed *in vacuo* at 1223 K for 120 h. The alloys were also subjected to elemental analysis and the results have been reported elsewhere [7]. The $x=0.05$ alloy was prepared at the University of Vermont by arc-melting equal amounts of the $x=0.0$ and 0.10 the alloys from the Ames Laboratory and then annealing the resultant alloy in a sealed quartz vessel for 96 h at 1133 K. The remaining alloys were prepared by Hydrogen Components, Inc. of Littleton, CO; they were prepared by arc-melting and remelted 6 x and annealed at 1223 K for 91 h.

Isotherms were measured in an all metal apparatus with electronic diaphragm gauges (M. K.S. Instruments). The temperatures were controlled with liquid baths to within ± 0.2 K.

Results and Discussion

XRD and Optical Microscopy.

The results of XRD are shown in Table 1, The unit cell volumes are plotted in Figure 1 along with the data of Cantrell *et al* [5], Wasz and co-workers [8], and Luo *et al* [9]. The agreement of the present data with the other data is good for values of x up to 0.2 but for $x > 0.2$ the unit cell volumes of the data of Wasz *et al* are smaller than those of the present data and those reported by Wasz *et al level-off* at a constant unit cell volume at $x \approx 0.45$. Wasz *et al* stated that the solubility limit of Sn in LaNi_{5-x}Sn_x is $x \leq 0.45$. Wasz *et al* had prepared their samples by mechanically alloying LaNi₅ with the appropriate amounts of Sn; the ball-milled products were then annealed at

Table 1: Lattice Parameters and Unit Cell Volume by XRD as a Function of x for the $\text{LaNi}_{5-x}\text{Sn}_x$ -- H System.

x	a_o/nm	c_o/nm	$V/\text{nm}^3/10^{-3}$
0	0.5006	0.3993	86.75
0.05	0.5017	0.3990	86.98
0.10	0.5039	0.4000	87.97
0.20	0.5057	0.4018	89.00
0.25	0.5063	0.4030	89.46
0.32	0.5074	0.4038	90.05
0.40	0.5089	0.4057	90.99
0.50	0.5108	0.4074	92.06 (91.91, re-annealed)

1073 K. With this procedure it is assumed that Sn substitution occurred in a stoichiometric phase $\text{LaNi}_{5-x}\text{Sn}_x$ with $x \leq 0.45$ accompanied by secondary phases, e.g., $\text{Ni}(\text{Sn})$ and LaNi_5Sn . However, hyper-stoichiometric LaNi_{5+y} with $y \leq 0.4$ is known [10, 11] at suitable temperatures where the excess Ni is retained as Ni-atom pairs substituting for some of the La atoms [12]. It is likely that the procedure used by Wasz *et al* [8] could easily have formed a ternary alloy phase with $(\text{Ni} + \text{Sn}) > 5.0$ which would restrict the Sn solubility to $x < 0.45$. It can be seen in Figure 1 that the present data continue to be described by a linear relationship to $x=0.5$. In the light of the work of Wasz *et al* the alloy having the apparent composition of $\text{LaNi}_{4.5}\text{Sn}_{0.5}$ was re-annealed at 1133 K for 3 d and then re-examined by XRD; no significant changes in the lattice parameters were found indicating that it is a viable phase. It will be shown below that a relationship between the plateau pressures and the composition is also linear to $x=0.5$ supporting the XRD results by independent evidence that the $\text{LaNi}_{4.5}\text{Sn}_{0.5}$ alloy is a homogeneous phase.

Alloys with $x < 0.20$ showed broadening of the x-ray reflections after cycling but those with $x \geq 0.20$ did not. There was no change in the angle of the reflections before and after the cycling. The alloys were examined by optical microscopy before and after cycling. Those with $x < 0.20$ disintegrated into fine particles after cycling whereas the sizes of the alloy pieces remained unchanged for those with compositions $x \geq 0.20$.

Isotherms for $\text{LaNi}_5 - \text{H}$

A series of isotherms at temperatures from 228 to 323 K are shown in Figure 2 for a closely-stoichiometric sample which has been hydrided and dehydrided (cycled) 2.5x at ≤ 323 K prior to the measurements. Usually more than one isotherm was measured at each temperature but only one is shown for each temperature (Fig. 2) in order to avoid the proliferation of data points and accompanying confusion in the Figure. The plateau pressures are seen to be remarkably horizontal for both hydride formation and decomposition especially at the lowest temperatures; this behavior contrasts with some low temperature isotherms reported in the literature which are very sloping [1]. The formation plateau at 323 K is the only one which exhibits any significant sloping. The locations of the phase boundaries are nearly constant with increase of temperature and only at the highest temperature shown, 323 K, is there an indication of a decrease in the upper phase boundary, (dilute + hydride) /hydride, and an increase in the lower phase boundary, dilute/(dilute + hydride), isotherms at temperatures >323 K were also reassured after measurement of these low temperature isotherms, but, because there may be a small amount of disproportionation and plateau splitting [9], they have not been included in Figure 2.

The loss of work due to hysteresis can be computed from the expression

$$\frac{1}{2}RT \ln (p_f/p_d) \quad (1)$$

where p_f and p_d are the plateau pressures for hydride formation and decomposition, respectively. Hysteresis is relatively small for activated samples of LaNi_5 .

Some error may be introduced into the plateau pressure values by the so-called "aliquot effect" which is the term to describe the effect of the rate of the hydrogen uptake/evolution on the plateau pressures [13, 14]. Formation plateau pressures for some temperatures were determined using both fast and slow rates of hydrogen uptake, i.e., large and small aliquots of hydrogen, and, for the temperatures where this was done, the average p_f values were used. The difference in the degree of hysteresis found between fast and slow rates of uptake was approximately 100 J/ mol $\frac{1}{2}\text{H}_2$. These results appear to indicate that there is a small decrease of the work lost because of hysteresis with increase of temperature (Table 2).

There has been some discussion by Flanagan et al [15] about which measure of hysteresis is the more temperature independent quantity and therefore

Table 2: Plateau Pressures and Hysteresis for the $\text{LaNi}_5 - \text{H}$ System. Hysteresis is in units of $\text{J/ mol } \frac{1}{2}\text{H}_2$.

T/K	p_f/MPa	p_d/MPa	$\frac{1}{2}RT \ln(p_f/p_d)$]
228	0.0051	0.0034	384
238	0.0095	0.0066	361
248	0.0181	0.0133	329
262	0.0416	0.030	360
273	0.071	0.055	317
298	0.218	0.174	308
323	0.588	0.449	361

the most fundamental quantity which reflects hysteresis, $\frac{1}{2}RT \ln(p_f/p_d)$ or $\frac{1}{2}R \ln(p_f/p_d)$. The former is the uncompensated heat, or lost work, and the latter is the entropy produced [16]. Unfortunately even a small amount of experimental scatter such as found in the present results due to the “aliquot effect” precludes any such choice. In any case, Table 2 shows the lost work (or uncompensated heat) evaluated from the experimental data at different temperatures and no systematic variation of this quantity with temperature can be discerned (Table 2).

van't Hoff Plot for $\text{LaNi}_5 - \text{H}$

The van't Hoff plots from the isotherms in Figure 2 and other isotherms which were measured are shown in Figure 3. The ΔH_{plat} and ΔS_{plat} values were determined from these plots and are tabulated in Table 3. These van 't Hoff plots differ from those shown earlier for highly stoichiometric LaNi_5 [9] because the earlier plots were determined specifically to to examine the effect of plateau splitting on the plots and were determined over a higher temperature range. Data for $T \geq 323$ K have been omitted in Figure 3 on the grounds that splitting or degradation may occur. The thermodynamic values determined from Figure 3 should be accurately reflect activated LaNi_5 which has not undergone any degradation. The average of the thermodynamic parameters determined from the formation and decomposition van't Hoff plots should correspond to a value determined by calorimetry and neither

should not be influenced by hysteresis [16]. Values from the literature are shown for comparison in Table 3.

The average results determined from the present data for $|\Delta H_{\text{plat}}|$ and $|\Delta S_{\text{plat}}|$, i.e., $15.4 \pm 0.2 \text{ kJ/mol } \frac{1}{2} \text{H}_2$ and $54.0 \pm 0.5 \text{ J/K mol } \frac{1}{2} \text{H}_2$, are believed to accurately reflect the reaction of stoichiometric LaNi_5 with H_2 . The present results are somewhat larger than calorimetric data of Luo *et al* [18] and the results from the p-c-T data of Sandrock *et al* [21] but in view of the somewhat different temperature ranges the agreement can be considered to be good. The agreement with the data of Biris *et al* [22] is good and their results were determined using apparently a closely stoichiometric alloy according to analysis but it may not have been homogeneous due to lack of annealing. The isotherms were measured from 263 to 338 K so that the temperature range is narrower than the present research and does not extend as low. From the view point of the behavior of the stoichiometric alloy, the precise calorimetric data of Murray *et al* [17] and the calorimetric data of Bowerman *et al* [20] contain systematic errors which most likely arise from the non-stoichiometry of the alloys.

Comparison of Plateau Pressures for Hydride Formation of the Virgin and Activated $\text{LaNi}_{5-x}\text{Sn}_x$.

The change in the values of p_i between the initial and subsequent isotherms can best be expressed thermodynamically by

$$\frac{1}{2}RT \ln \left(p_f^i / p_f^s \right) \quad (2)$$

where i and s refer to initial and subsequent isotherms, respectively; the plateau pressures for the subsequent isotherms are nearly independent of the number of cycles. For the purpose of comparison of isotherms for the virgin alloys with those of the activated alloys a temperature of 373 K was chosen. This represents a compromise allowing both formation and decomposition plateaux to be measured over the range of x values available and the concomitant large variation of their plateau pressures with x . These values are shown in Table 4 for the various $\text{LaNi}_{5-x}\text{Sn}_x - \text{H}$ systems where it can be seen that the difference between the initial and subsequent p_i values decreases with x . Each alloy is discussed below.

Table 3: Thermodynamic Properties for the $\text{LaNi}_5\text{-H}$ and $\text{LaNi}_{4.95}\text{Sn}_{0.05}\text{-H}$ Systems. ΔH_{plat} and ΔS_{plat} are in units of $\text{kJ}/\text{mol } \frac{1}{2}\text{H}_2$ and $\text{J}/\text{K mol } \frac{1}{2}\text{H}_2$, respectively.

plateau or technique	$ \Delta H_{\text{plat}} $	$ \Delta S_{\text{plat}} $
LaNi_5		
formation (this work)	15.7	54.8
decomposition (this work)	15.1	53.9
av. (this work)	15.4	54.4
calorimetry[17]	16.0	57.3 (average)
calorimetry[18]	15.0	53.6
calorimetry[19]	15.8	56.2
calorimetry[20]	14.8	52.5
p-c-T data (stoichiom.)[21]	15.2	53.8
p-c-T data [22]	15.4	54.8
$\text{LaNi}_{4.95}\text{Sn}_{0.05}$		
formation	15.2	53.1
decomposition	16.0	54.2
average	15.6	53.7

* Calculated from the referenced data using the measured enthalpy and the average of the formation and decomposition plateau pressures. ** The enthalpy was taken from their decomposition plateau plot and in order that this be close to the average for the formation and decomposition, $0.2 \text{ kJ}/\text{mol } \frac{1}{2}\text{H}_2$ was subtracted from it. *** Average of absorption and desorption values.

Table 4: Initial and Subsequent Hydride Formation Plateau Pressures at 373K for the $\text{LaNi}_{5-x}\text{Sn}_x\text{-H}$ Systems where p_f is in MPa and $\frac{1}{2}RT \ln(p_f^i/p_f^s)$ in $\text{kJ/mol } \frac{1}{2}\text{H}_2$.

x value	p_f^i	p_f^s	$\frac{1}{2}RT \ln(p_f^i/p_f^s)$
0	5.7	2.47	1.13
0.05	3.4	1.8	0.99
0.10	1.88	1.40	0.46
0.20	0.84	0.71	0.27
0.25	0.64	0.57	0.16
0.32	0.33	0.31	0.13
0.40	0.18	0.17	0.13

LaNi₅ - H

Because data for the $\text{LaNi}_5\text{-H}$ system were not available in the literature for the parent alloy-H system at 373 K, isotherms were measured for both the virgin and activated forms of the alloy at 373 K where the pressures are quite high especially for the inactivated form, i.e., 1.0 MPa, (Fig. 4), and where some plateau splitting can be seen in the decomposition plateau. An enormous difference in its plateau pressures, p_f , can be seen and there is a very dramatic difference found between the dilute phase solubilities in the initial, virgin isotherm and the subsequent ones. The extent of the plateau region is significantly greater for the virgin than for the activated sample. It seems that activation removes some of the available interstitial sites which contribute to the plateau region in the virgin alloy.

LaNi_{5-x}Sn_x - H

x=0.05. Figure 5 shows the isotherms for the virgin and activated $\text{LaNi}_{4.95}\text{Sn}_{0.05}\text{-H}$ system where, like the parent compound, there is also a very large difference in the virgin and activated isotherms. A difference in behavior between this alloy and the parent LaNi_5 alloy is that this alloy does not show any splitting; this has been described elsewhere [9]. The dilute phase volatility differences between the initial and subsequent

isotherms are significant but smaller than for the parent system.

Thermodynamic data have not been reported for this alloy composition in the previous study of $\text{LaNi}_{5-x}\text{Sn}_x\text{-H}$ alloys [6]. Results for this alloy are therefore included in Table 3 where the thermodynamic parameters have been determined from p-c-T data. The average value of the $|\Delta H_{\text{plat}}|$ is greater than for the parent compound. This value for $x=0.05$ supports the value for $\text{LaNi}_5\text{-H}$ determined in this research (Table 3) and the calorimetrically determined value [18] because a plot of $|\Delta H_{\text{plat}}|$ against x for the $\text{LaNi}_{5-x}\text{Sn}_x\text{-H}$ system, including this value for $x=0.05$, extrapolates at $x=0.0$, i.e. $\text{LaNi}_5\text{-H}$, to an enthalpy value lying between 15.0 and 15.5 $\text{kJ/mol}\frac{1}{2}\text{H}_2$. This result indicates that values outside of this range which have been reported in the literature (Table 3) are unlikely. A similar extrapolation without the value determined here for $x=0.05$ is shown in Figure 4 of reference [6] and leads to similar conclusions.

$x=0.10$. Figure 6 shows virgin and second isotherms for the $\text{LaNi}_{4.90}\text{Sn}_{0.10}\text{-H}$ system. The difference in the p_i values has decreased compared to alloys of smaller x values. The difference in the dilute phase solubilities for the initial and subsequent isotherms has become small.

$x=0.20$. The alloy with this stoichiometry has been the alloy of choice of the $\text{LaNi}_{5-x}\text{Sn}_x$ series for several hydrogen storage purposes as described in, e.g., [4]. Figure 7 shows that the difference in the p_i values between the virgin and activated forms is not very large. For the first time in these studies of the effect of increasing x values on the formation plateaux, it is found that $\frac{1}{2}RT \ln(p_i^i/p_i^s) < \frac{1}{2}RT \ln(p_i/p_d)$ where the hysteresis is evaluated for the activated form. The difference in the dilute phase solubilities for the initial and subsequent isotherms has also become small. For this alloy and for those with $x > 0.2$, the coincidence of the volatility data in the hydride phase region for the initial and subsequent isotherms is noteworthy. This may also be the case for the alloys with $x < 0.20$ but because of the high pressures for the virgin alloys in this region it could not be established in this work.

$x=0.25$. For this system the trend continues where $\frac{1}{2}RT \ln(p_i^i/p_i^s)$, decreases as compared with alloys with $x < 0.25$ (Fig. 8). The dilute phase volatility for this alloy appears to be quite different in the activated and virgin conditions but this is probably experimental error due to slow kinetics in the virgin alloy.

$x=0.32$. This is the alloy with the largest content Sn where the isotherms before and after activation showed a distinct difference in p_f^i and p_f^s (Fig. 9) and for this alloy the value of $\frac{1}{2}RT$ in (p_f^i/p_f^s) is quite small.

$x=0.40, 0.50$. These alloys basically show no difference between the initial and subsequent cycles and their isotherms will not be shown.

Dilute Phase Solubilities

There is known to be a large difference between the dilute phase behavior of the parent compound before and after activation [23, 24]. The differences were somewhat, difficult to measure for the $\text{LaNi}_{5-x}\text{Sn}_x\text{-H}$ alloys because, in some cases, equilibrium was sluggish for the virgin form. In any case, the difference is greatest for parent compound and then decreases closely paralleling the differences p_f^i and p_f^s making it clear that the two phenomena are related. For some of the higher values of x a trend is no longer clear, e.g., the $x=0.25$ alloy seems to have a greater difference than the $x=0.20$ alloy but as noted above this is probably a failure to establish equilibrium for the virgin form.

Conclusions

The greater plateau pressures for hydride formation for the initial isotherm as compared with subsequent ones for alloys of the $\text{LaNi}_{5-x}\text{Sn}_x\text{-H}$ system are plotted as a function of x in Figure 10 along with the plateau pressures for the activated alloys. The difference between p_f^i and p_f^s decreases with x but it does not exactly parallel the differences between p_f^s and P_d because there is a much greater initial decrease from $x=0$ to 0.1 for the former p_f values. The activated alloys exhibit a rather constant degree of hysteresis up to $x=0.25$. The difference between the dilute phase solubilities of the activated alloy compared with the virgin sample exhibits a large change with increase of x .

The difference between the initial and subsequent formation plateau pressures is probably related to the upheaval caused by the initial hydride formation. (A similar effect may be present for hydride decomposition for a virgin sample, i.e., one which had been hydrided by passing around the critical point thus avoiding the changes which normally accompany hydride formation.) In earlier work it was found that the calorimetric enthalpy for

the hydriding reaction is not noticeably different for the initial and subsequent hydride formation [2.5]. This result was puzzling since the difference in free energies, $\frac{1}{2}RT \ln p_i$, for the initial and subsequent hydride formation reactions is $1.2 \text{ kJ/mol } \frac{1}{2}H_2$ which if this were due to the enthalpy should be readily detectable by reaction calorimetry.

It has been pointed out on the basis of the existing calorimetric data for metal-hydrogen systems that there does not appear to be a net heat evolution during the irreversible branches of an isothermal hysteresis cycle, and therefore the work of hysteresis is evolved as heat during the reversible branches of the hysteresis cycle [16]. In the reversible branch at which takes place at a small H content where the p_{H_2} is increased from the decomposition plateau, p_d , to the formation plateau, p_f , work is done by the surroundings on the gas, H_2 , where the majority of the H resides, and for the other reversible branch where p_{H_2} is reduced at a high H content from p_f to p_d , a smaller amount of work is done on the surroundings by the system and for these two reversible steps there is a net work done on the system which must be evolved as heat, i.e., $\frac{1}{2}RT \ln(p_f/p_d)$ per mol $\frac{1}{2}H_2$ [15]. On the other hand, during the irreversible branches of hydride formation and decomposition there is no net heat change and the irreversibility is reflected by the entropy production, $\frac{1}{2}RT \ln(p_f/p_d)$, [15]. The entropy production is probably associated with the interface movement and the volume change which takes place at the interface. In the present context the fact that there is no difference in enthalpies for the initial hydride formation and subsequent formation reactions [25] may have the same origin, i.e., the increase in p_f , free energy $= \frac{1}{2}RT \ln p_f$, for the initial, as compared to subsequent hydride formation may be mainly due to entropy and therefore is not detected in the calorimetric experiments. The entropy production may arise both from interface movement and the disintegration into fine particles for the initial hydride formation. At small x values the latter may be more important for the initial hydride formation and the former more important for the activated alloy.

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- [17] J. Murray, M. Post, J. Taylor, *J. Less-Common Mets.*, **80** (1981) 201.
- [18] W. Luo, S. Luo, J. Clewley, T. Flanagan, R. Bowman, J. Cantrell, *J. Alloys Compounds*, 202 (1993) 147.
- [19] W. Hubbard, P. Rawlins, P. Connick, R. Stedwell, P. O'Hare, *J. Chem. Thermo.*, 15 (1983) 785.
- [20] B. Bowerman, C. Wulff, T. Flanagan, *Zeit. Physik. Chem. N. F.*, 116 (1979) 197.
- [21] G. Sandrock, P. Goode], E. Huston, P. Golben, *Zeit. Physik. Chem.*, 164 (1989) 1285.
- [22] A. Biris, R. Bucur, P. Ghete, E. Indrea, D. Lupu, *J. Less-Common Mets.*, 49 (1973) 477.
- [23] J. Lynch, J. Reilly, *J. Less-Common Mets.*, 87 (1982) 225.
- [24] T. Flanagan, N. Mason, G. Biehl, *J. Less-Common Mets.*, 91 (1983) 107.
- [25] W. Luo, J. Clewley, T. Flanagan, *J. Alloys Compounds*, 179 (1993) 77.

Fig. 1 A plot of the unit cell volumes of hydrogen-free $\text{LaNi}_{5-x}\text{Sn}_x$ as a function of x . The straight-line is a least squares line drawn through the present data. \bullet , present data; O, [5]; Δ , [8]; \square , [9].

Fig. 2 Hydrogen isotherms for well-activated LaNi_5 . Open symbols represent absorption and filled ones desorption.

Fig. 3 Van't Hoff plots for well-activated LaNi_5 . The plot with open symbols is for hydride formation and that with filled symbols is for decomposition.

Fig. 4 Initial and subsequent isotherms for $\text{LaNi}_5\text{-H}$ at 373 K. The formation plateau pressure is quite high, 6.0 MPa, and consequently absorption has not been extended into hydride-phase.

Fig. 5 Initial and subsequent isotherms for $\text{LaNi}_{4.95}\text{Sn}_{0.05}\text{-H}$ at 373 K.

References

- [1] B. Anreev, Y. Zel'vaenskii, A. Shafiev, V. Shitikov, *Russ. J. Phys. Chem.*, **52** (1978) 789.
- [2] T. Flanagan, G. Biehl, *J. Less-Common Mets.*, **82** (1981) 383.
- [3] K. Nomura, H. Uruno, S. One, H. Shinozuka, S. Suda, *J. Less-Common Mets.*, **107** (1985) 221.
- [4] S. Lambert, D. Chandra, W. Cathey, F. Lynch, R. Bowman, *J. Alloys Compounds*, **187** (1992) 113.
- [5] J. Cantrell, T. Beiter, R. Bowman, *J. Alloys Compounds*, **207-208** (1994) 372.
- [6] S. Luo, W. Luo, J. Clewley, T. Flanagan, L. Wade, *J. Alloys Compounds*, **231** (1995) 467.
- [7] S. Luo, W. Luo, J. Clewley, T. Flanagan, R. Bowman, *J. Alloys Compounds*, **231** (1995) 473.
- [8] M. Wasz, P. Desch, R. Schwarz, *Phil. Mag. A*, **74** (1996) 15.
- [9] S. Luo, J. Clewley, T. Flanagan, R. Bowman, J. Cantrell, *J. Alloys Comp.*, **253-254** (1997) 226.
- [10] K. H. J. Buschow, H. van Ma], *J. Less-Common Mets.*, **29** (1972) 203.
- [11] W. Coene, P. Notten, F. Hakkens, R. Einerhand, J. Daams, *Phil. Mag. A*, **65** (1992) 1485.
- [12] P. Notten, R. Einerhand, J. Daams, *J. Alloys Comp.*, **210** (1994) 221.
- [13] C.-N. Park, T. Flanagan, *Ber. Bunsenges. Physik. Chem.*, **89** (1985) 1300.
- [14] E. Gray, C. Buckley, E. Kisi, *J. Alloys Compounds*, **215** (1994) 201.
- [15] T. Flanagan, C.-N. Park, W. Oates, *Prog. in Solid State Chem.*, **23** (1995) 291.
- [16] T. Flanagan, J. Clewley, T. Kuji, C.-N. Park, D. Everett, *J. C. S., Faraday. Trans.*, **1** **82** (1986) 2589.

Fig 1

LaNi_{5-x}Sn_x - H

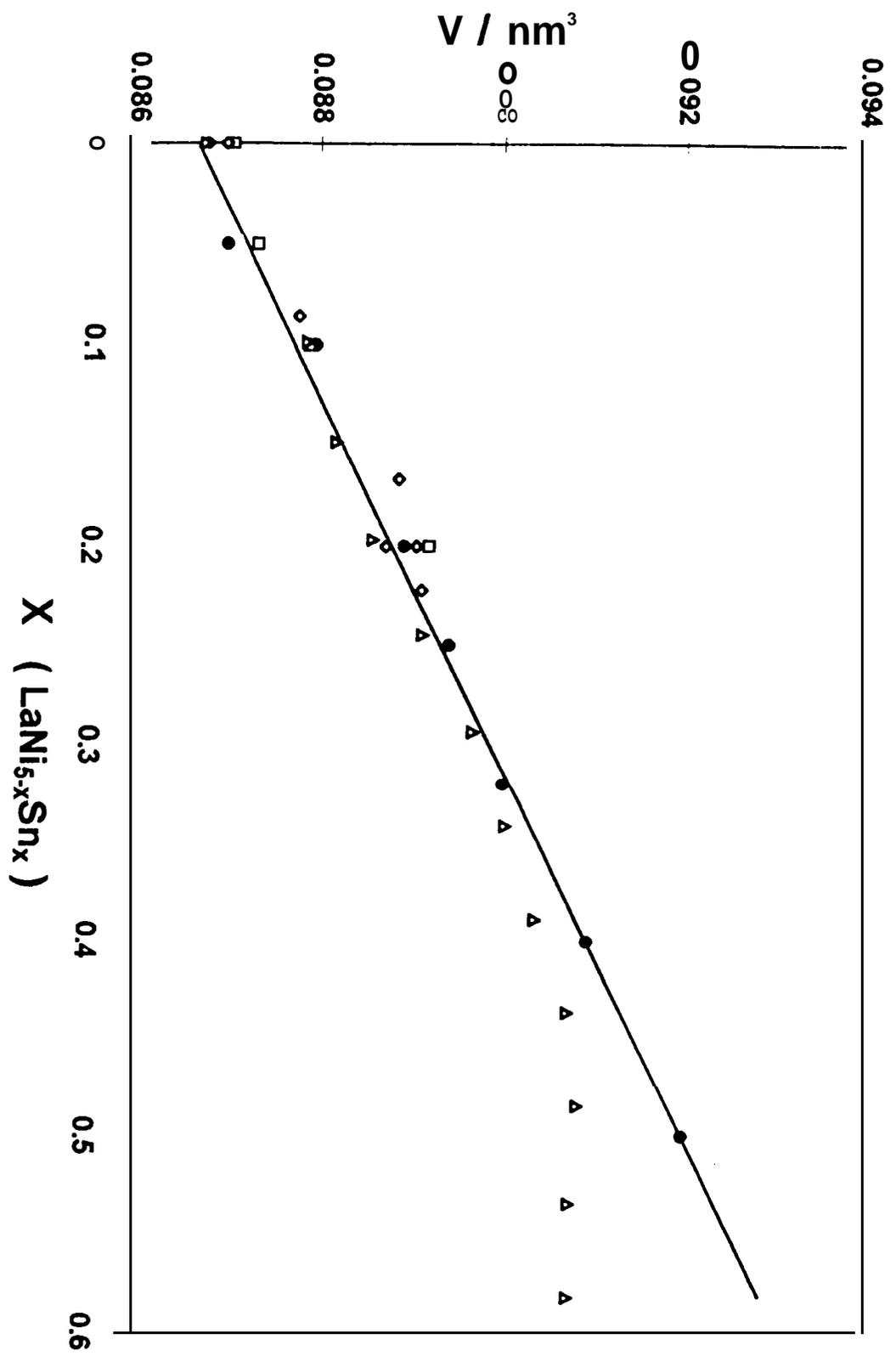


Fig. 6 Initial and subsequent isotherms for $\text{LaNi}_{4.90}\text{Sn}_{0.10} - \text{H}$ at 373 K.

Fig. 7 initial and subsequent isotherms for $\text{LaNi}_{4.80}\text{Sn}_{0.20} - \text{H}$ at 373 K.

Fig. 8 Initial and the subsequent isotherms for $\text{LaNi}_{4.75}\text{Sn}_{0.25} - \text{H}$ at 373 K.
This shows a significant difference in the dilute phase volatility but this may alloy appears to behave somewhat anomalously, e.g., see Figure 10, although its unit cell dimensions appear to be reasonable (Fig. 1).

Fig. 9 Initial and the subsequent isotherms for $\text{LaNi}_{4.68}\text{Sn}_{0.32} - \text{H}$ at 373 K.

Fig. 10 Plots of $\log p_{\text{plat}}/P_{\text{a}}$ (373 K) against x ($\text{LaNi}_{5-x}\text{Sn}_x - \text{H}$). \circ , p_{f} , virgin, inactivated sample; \square , p_{f} , activated sample; \triangle , p_{d} , activated sample.

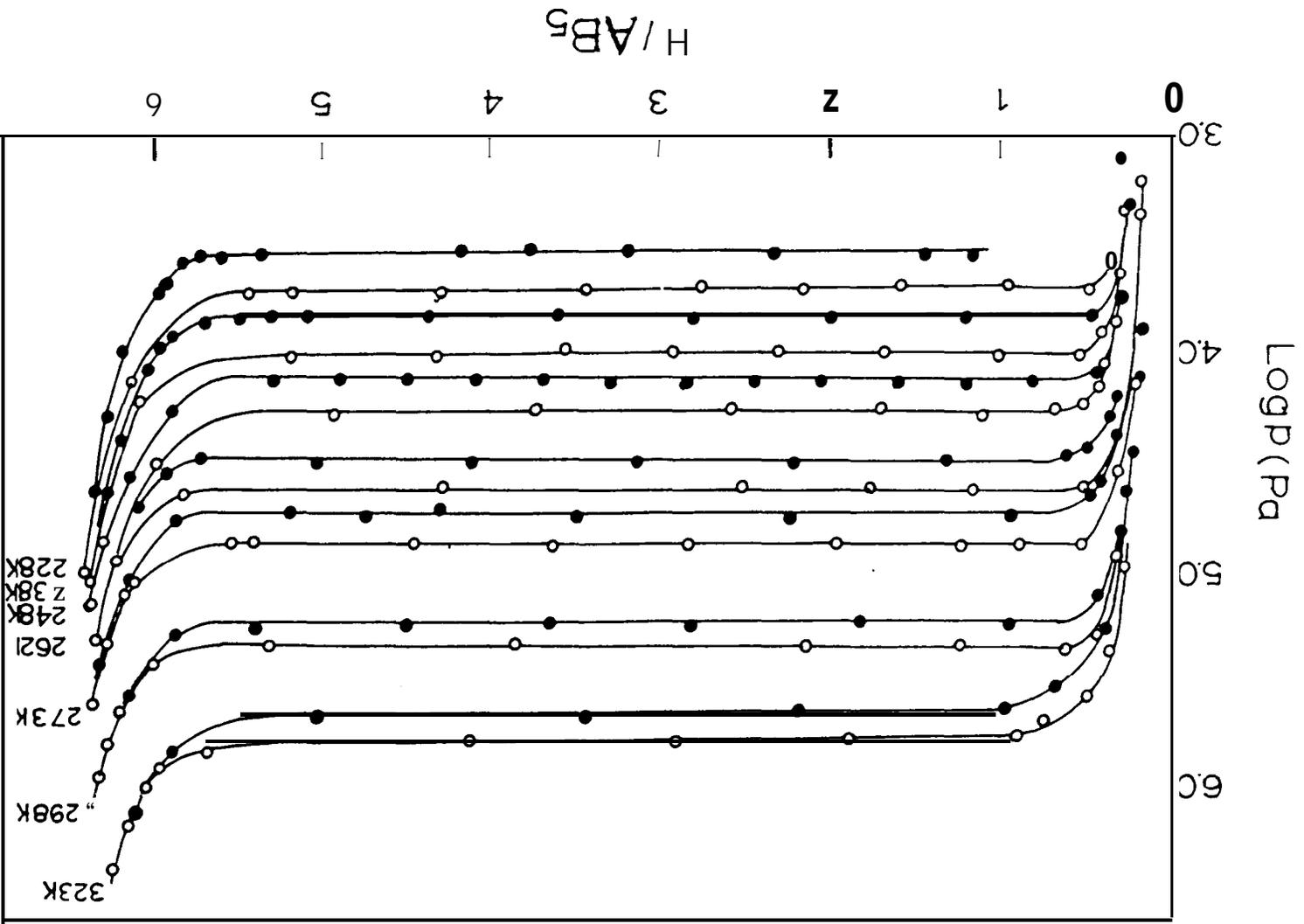
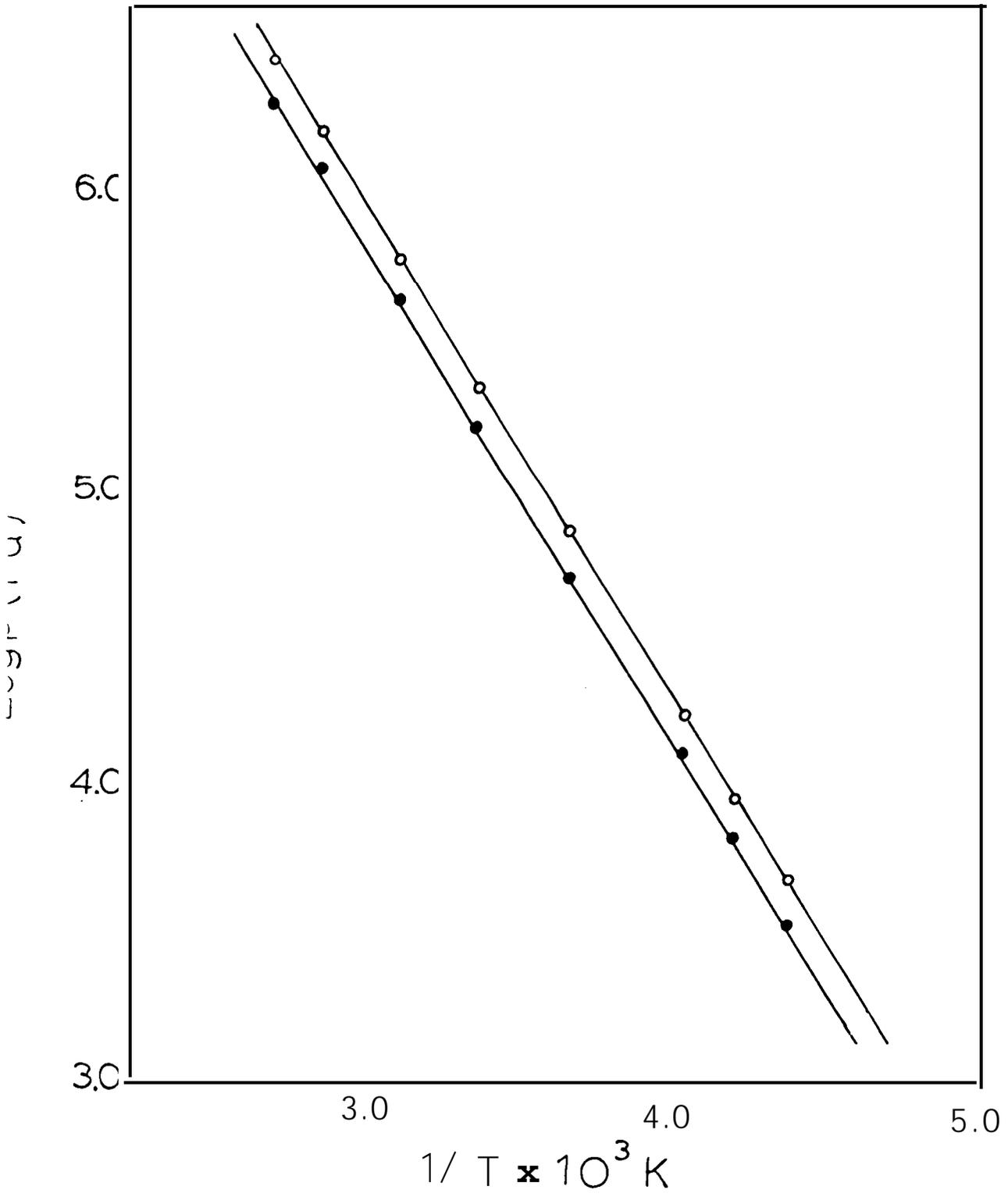
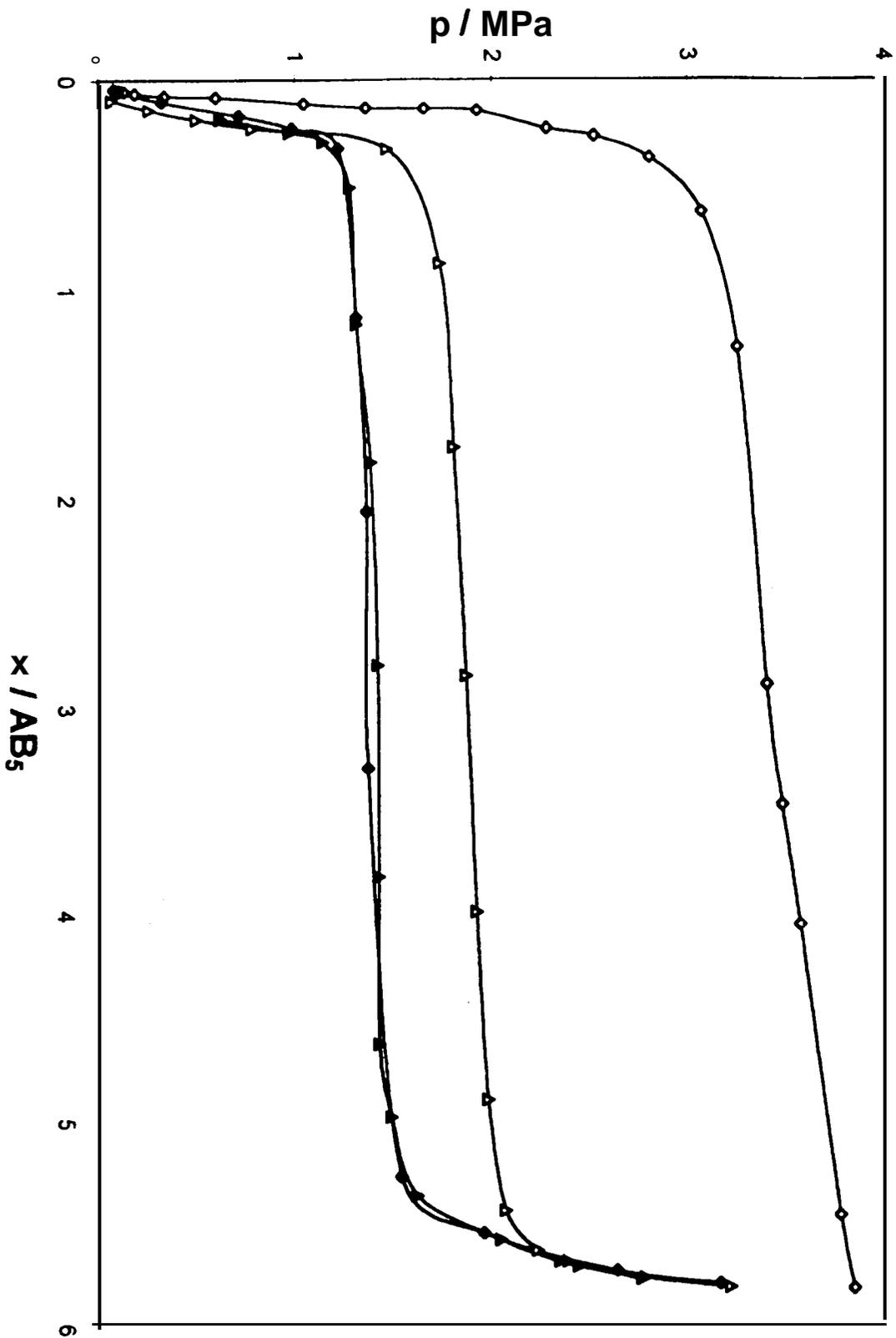


Fig. 2

Fig. 3



$\text{LaNi}_{4.95}\text{Sn}_{0.05} - \text{H}$ 373 K



LaNi₅-H 373 K (oil bath)

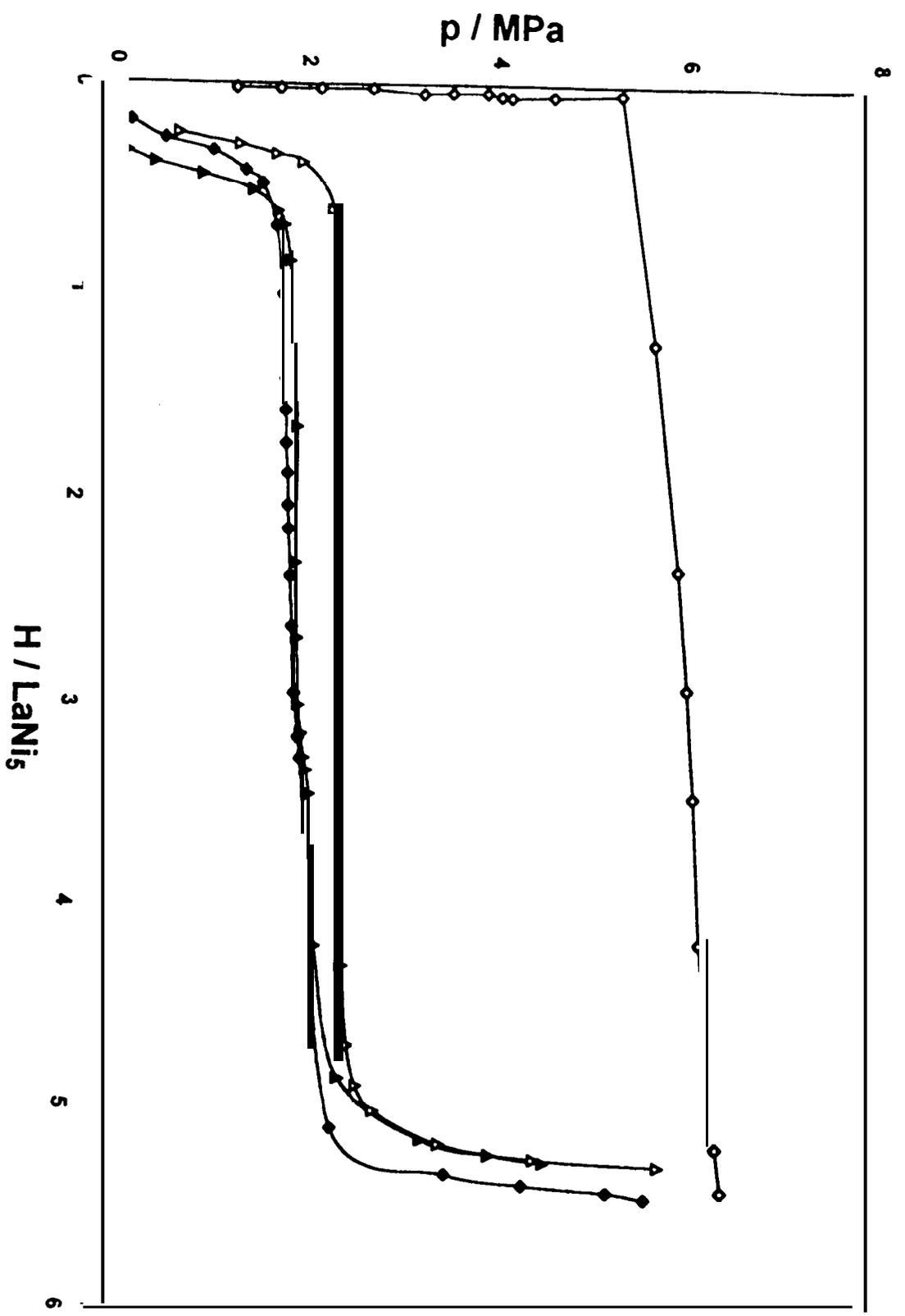
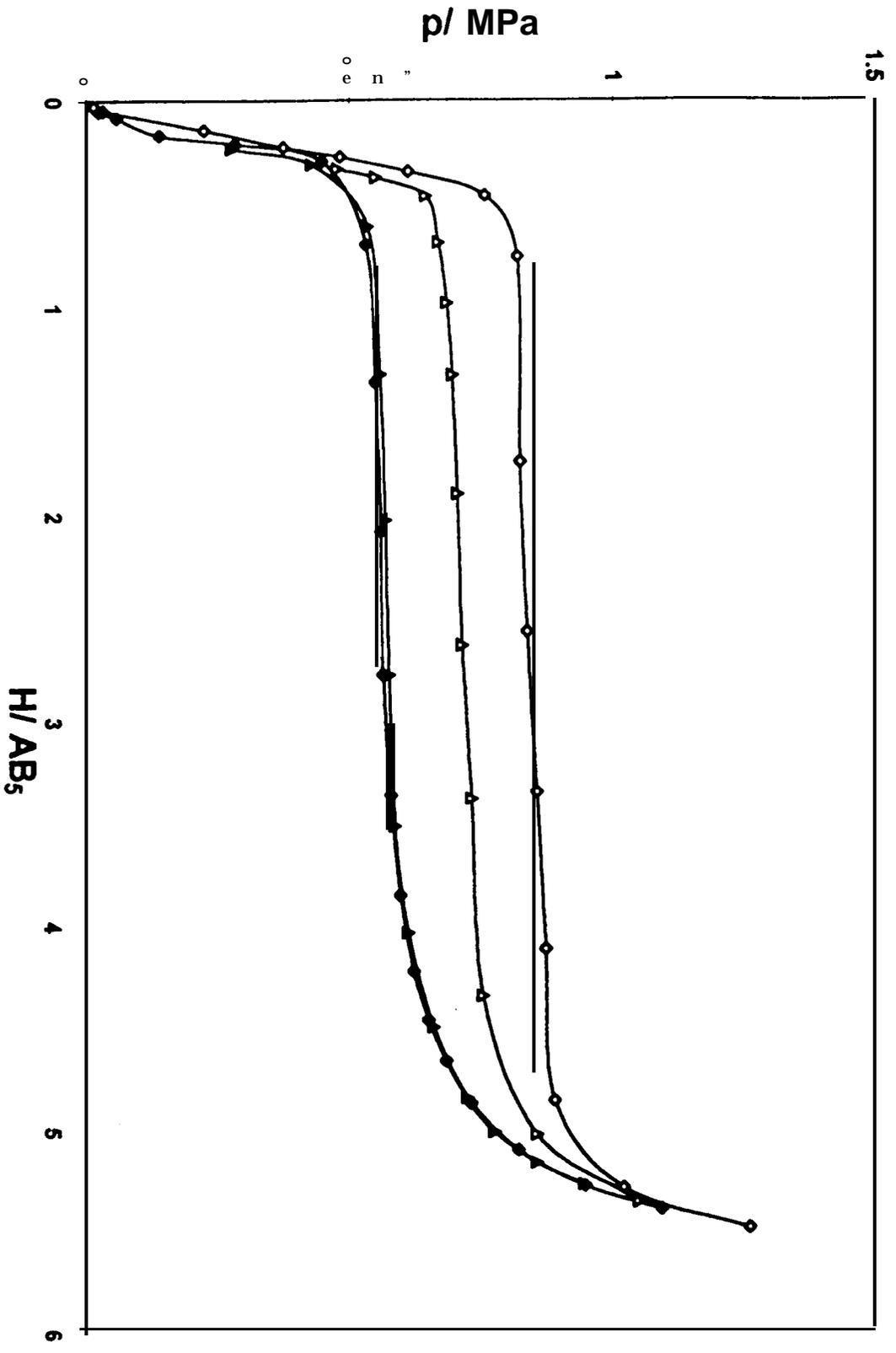
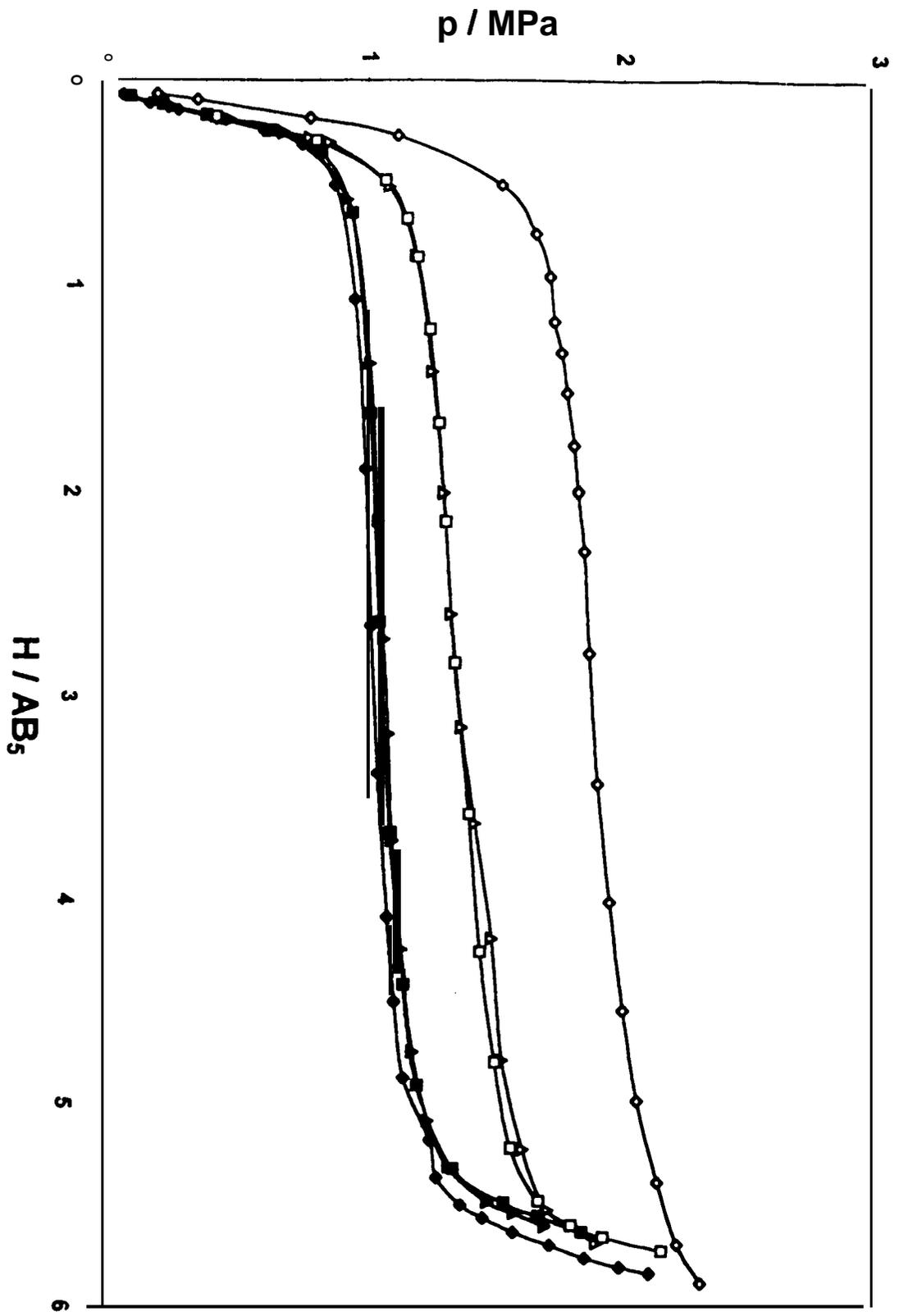


Fig. 7

$\text{LaNi}_{4.8}\text{Sn}_{0.2} - \text{H}$ 373 K



$\text{LaNi}_{4.9}\text{Sn}_{0.1} - \text{H}$ 373 K



LaNi_{4.75}Sn_{0.25} - H 373 K

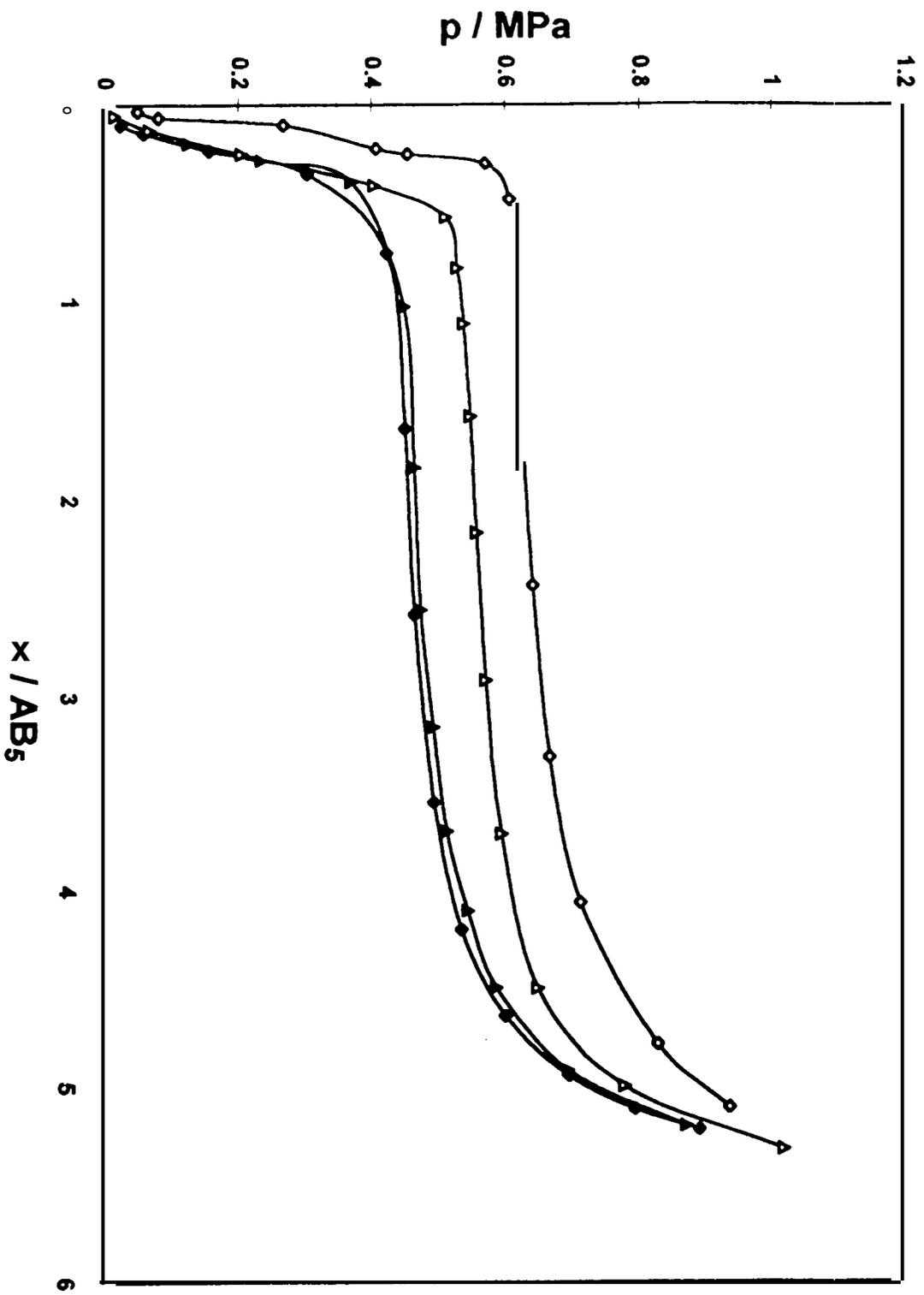


Fig 9

$\text{LaNi}_{4.68}\text{Sn}_{0.32} - \text{H}$ 373 K

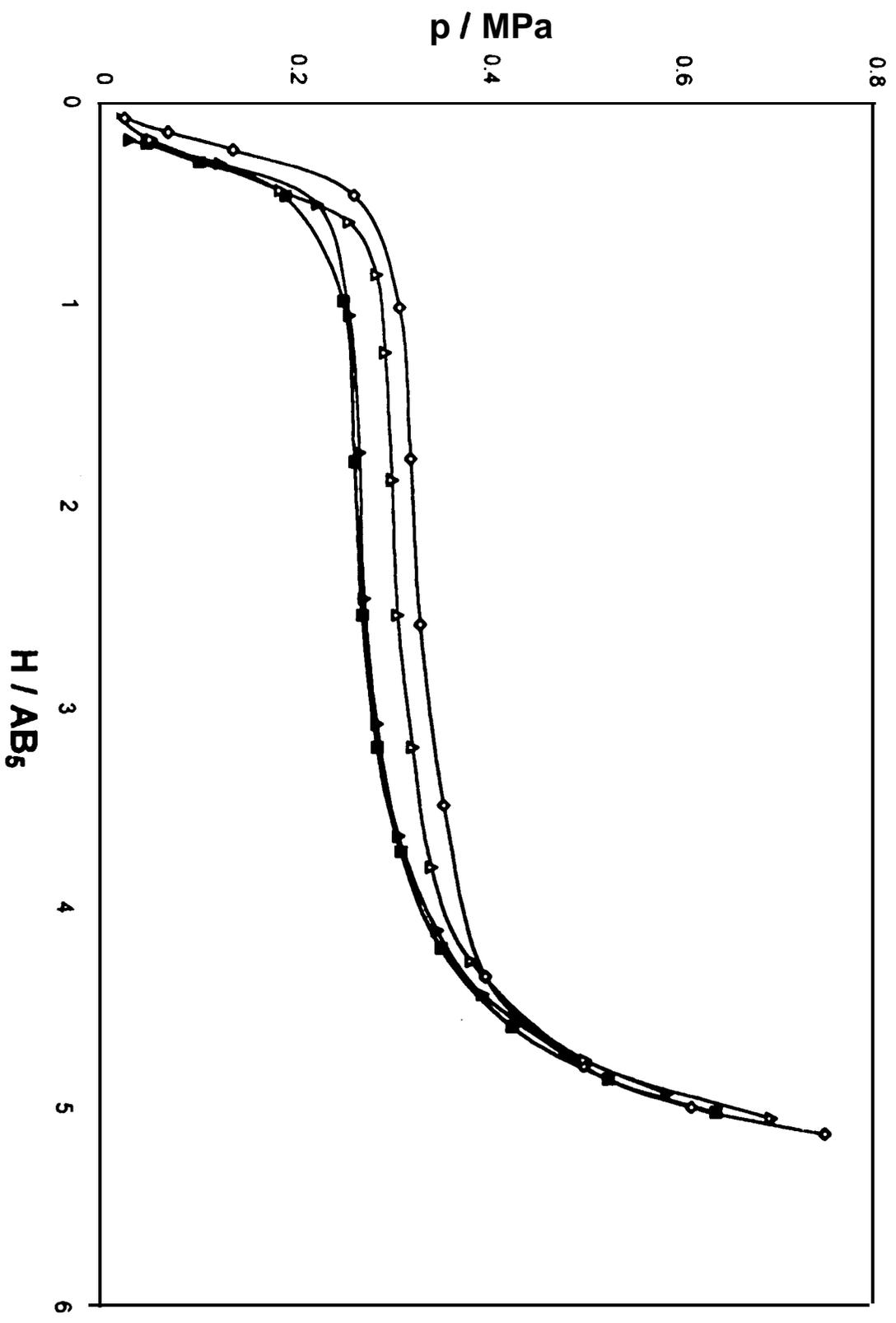


Fig. 10

LaNi_{5-x}Sn_x - H 373 K

