REVERSIBLE ROOM-TEMPERATURE ABSORPTION OF LARGE QUANTITIES OF HYDROGEN BY INTERMETALLIC COMPOUNDS

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Abstract

Some hexagonal intermetallic compounds of the composition \( \text{AB}_5 \), where A represents a rare-earth metal and B nickel or cobalt, are reported to absorb and desorb easily large quantities of hydrogen gas under relatively small pressures at room temperature. For some selected compounds, viz. \( \text{LaNi}_5 \) and \( \text{SmCo}_5 \), absorption isotherms and X-ray data are given. Also data are given for the quasi-binary compounds \( \text{La}_{1-x}\text{Ce}_x\text{Ni}_5 \). The compound \( \text{LaNi}_5 \) forms the hydride \( \text{LaNi}_5\text{H}_{6.7} \) at room temperature under 2.5 atm of hydrogen pressure. Its unit cell expands 25 vol.\% and seems to retain its hexagonal symmetry. \( \text{SmCo}_5 \) forms the hydride \( \text{SmCo}_5\text{H}_3 \) at room temperature under 4.5 atm of hydrogen pressure, while its unit cell expands 10 vol.\% and becomes orthorhombic. For both hydrides the heat of reaction is found to be about 7 kcal/mol \( \text{H}_2 \).

1. Introduction

Many metals and intermetallic compounds are known to form hydrides. A review was given recently by Westbrook 1). Some of these hydrides find application in the form of getters and as sources of pure hydrogen. Compared to these the family of intermetallic compounds described in this paper is exceptional in that they absorb hydrogen at room temperature quickly and reversibly, dependent only on hydrogen-gas pressure. This behaviour was recently discovered for the compound \( \text{SmCo}_5 \) by Zijlstra and Westendorp 3). The family may be described in general as having the formula \( \text{AB}_5 \) and being of the hexagonal \( \text{CaCu}_5 \) type of structure; A stands for a metal of the lanthanide series, calcium or thorium, and B represents nickel or cobalt.

2. Experimental

The intermetallic compounds were prepared by arc-melting under argon, using commercially pure components. After homogenizing, they were crushed in an agate mortar to grains with a mean size of 50 \( \mu \text{m} \). Samples of about 1.5 grammes were enclosed in small brass containers, provided with a valve and a pressure gauge and connected to a hydrogen cylinder via a thin stainless-steel capillary tube. After exposing the metal powder to hydrogen gas at a certain pressure for some time the amount of absorbed hydrogen could be measured by disconnecting the tube from the cylinder and by allowing the hydrogen to flow out under water into a gas burette. Experiments not carried out at room...
temperature were done by submerging the sample container in a water bath at the desired temperature. X-ray data were obtained by using a Philips diffractometer PW 1310/1330 supplied with a crystal monochromator and a special sample holder designed for exposing powders under gas pressures up to 50 atm. The exposures were done mostly with MoKα and sometimes with CuKα radiation.

LaNi₅

The dimensions of the hexagonal unit cell are \( a = 5.0172 \, \text{Å}, \ c = 3.9816 \, \text{Å}, \ c/a = 0.794, \ V = 86.80 \, \text{Å}^3 \). The conversion to a hydride was effected by exposing freshly crushed powder for some hours to a pressure of 50 atm of hydrogen. In this state the unit cell appears to be still hexagonal but with dimensions \( a = 5.440 \, \text{Å}, \ c = 4.310 \, \text{Å}, \ c/a = 0.792, \ V = 110.5 \, \text{Å}^3 \), which means a volumetric expansion of about 25%. Kinetically this first absorption process is strongly autocatalytic in character. While expanding, the brittle material breaks up into finer particles and thus a large uncontaminated and highly active surface is formed. On decreasing the hydrogen pressure on the hydrided powder to 1 atm the hydrogen starts to be given off and the cell dimensions regain their initial values. The amount of hydrogen evolved from the metal points to the hydride composition LaNi₅H₆.7. This composition is somewhat dependent on pressure and temperature. This is shown in the set of isotherms of fig. 1. From these isotherms it is possible to deduce a value of the heat of reaction of about 7.2 kcal/mol H₂. This heat of reaction is the cause of a considerable rise of temperature when the active LaNi₅ powder is reloaded (which takes place in a few seconds.

Fig. 1. Isotherms of hydrogen gas (pressure \( p \) atm) in equilibrium with absorbed hydrogen in LaNi₅ (concentration: H atoms/LaNi₅).
at a pressure of 30 atm hydrogen). Since the sorption rate is a function of pressure as well as of temperature and since it is simplest to keep the external pressure constant, we measured the desorption rate as a function of temperature, while the external pressure was 1 atm. The sample of LaNi$_5$ had already been subjected to a loading-delading cycle 10 times previously, so that it might be considered as having a constant active surface. No special precautions were made to measure isothermally. Figure 2 shows some desorption curves for temperatures from 18°C to 49°C. The activation energy for the reaction is determined from the initial slopes and is thus roughly estimated to be 12 kcal/mol H$_2$ (0.25 eV/atom H).

SmCo$_5$

This is the intermetallic compound from which permanent magnets have recently been made with record (BH)$_{max}$ values$^2$). Analogous to LaNi$_5$ it shows a room-temperature absorptivity for hydrogen gas. Freshly crushed SmCo$_5$ powder at room temperature under 100 atm hydrogen pressure needs about 48 h to become saturated with hydrogen (first loading). It desorbs against 1 atm hydrogen in about $\frac{1}{2}$ h and, without exposing the powder to air, it may be reloaded in less than 1 min under 50 atm hydrogen. A typical set of absorption isotherms, measured under equilibrium conditions is shown in fig. 3. There was no marked difference in plateau pressures (hysteresis) when absorbing or desorbing the hydrogen. At room temperature the horizontal part occurs at a pressure of 4 atm and the maximum amount of hydrogen absorbed at 10 atm is about 3·0 H atoms/SmCo$_5$. In this state the unit cell of SmCo$_5$, which normally has the hexagonal CaCu$_5$ structure with $a = 4·995$ Å, $c =$
3.965 Å, \( c/a = 0.794 \), \( V = 85.67 \, \text{Å}^3 \), has lost its hexagonal symmetry by anisotropic expansion. The new unit cell can be described as orthorhombic with \( a = 8.848 \, \text{Å}, \ b = 5.272 \, \text{Å}, \ c = 4.050 \, \text{Å} \) and \( V = 188.9 \, \text{Å}^3 \) (see the schematic figure 4). This means a volumetric expansion of about 10%. The

![Graph](image)

**Fig. 3.** Isotherms of hydrogen gas (pressure \( p \) atm) in equilibrium with absorbed hydrogen in SmCo\(_5\) (concentration: H atoms/SmCo\(_5\)).

![Diagram](image)

**Fig. 4.** Anisotropic expansion of the basal plane of SmCo\(_5\) due to the absorption of 3.0 H atoms per unit cell. Elongation \( \parallel a_{\text{hex}}: 4.8\% \); elongation \( \perp a_{\text{hex}}: 1.6\% \).
anisotropy of the expansion seems to be a general feature of the RCo$_5$ compounds; it has also been observed in e.g. PrCo$_5$.

Form the isotherms of fig. 3 the heat of solution in the half-saturated condition was determined to be 7.4 kcal/mol H$_2$, which is about the same as in the case of LaNi$_5$. The behaviour of the principal magnetic properties as a function of hydrogen content has been investigated by Zijlstra and Westendorp 3).

**The system (La$_{1-x}$Ce$_x$)Ni$_5$**

The study of this system was undertaken because the two compounds LaNi$_5$ and CeNi$_5$ behave quite differently with respect to hydrogen: LaNi$_5$ absorbs large quantities of hydrogen at room temperature at relatively low (e.g. 4.5 atm) pressures, while 150 atm is not sufficient to activate and load CeNi$_5$. Cerium, which is a neighbouring element of lanthanum in the lanthanide series differs from this in two respects, viz. its radius is somewhat smaller and it has, next to the trivalency of most of the lanthanides, the possibility of becoming tetravalent. To investigate which of the two possibilities (or both) might be responsible for the difference in the hydrogen-absorption behaviour, we studied the influence of a gradual substitution of La by Ce in LaNi$_5$ on the stability of the hydrided material. The results, together with the change of the $a$- and $c$-axes are shown in fig. 5. In contrast to the monotonic decrease of the $a$-axis with Ce content, the $c$-axis becomes constant at about $x = 0.5$. It is presumed

![Fig. 5. Pressure at the horizontal part in the room-temperature pressure vs H-content curves (indicating the stability of the hydride) as a function of $x$ in the La$_{1-x}$Ce$_x$Ni$_5$ system. Lower part: lattice parameters of the hexagonal unit cell of La$_{1-x}$Ce$_x$Ni$_5$.](image-url)
that this behaviour is connected with a change of valency of cerium at this concentration.

3. Discussion

The three examples reported are representative of the group of intermetallic compounds under investigation in their behaviour with respect to hydrogen. The most striking property of these compounds is their ability to absorb and desorb large amounts of hydrogen at room temperature. The density of hydrogen in e.g. LaNi₅ under 2.5 atm at room temperature is 6.7 atoms per LaNi₅ or 7.6·10⁻²² atoms/cm³, i.e. nearly twice as high as in liquid hydrogen. This number can still be increased somewhat by a partial substitution of La by Ce, e.g. the alloy Ce₀.₃ La₀.₇ Ni₅ can dissolve 7 hydrogen atoms per formula unit. Combined with the high reaction rate at room temperature these compounds seem promising in view of technical applications, especially if it is taken into account that one can expect the hydrogen desorbed to be of a high degree of purity.

Compared to the hydrogen-binding capacity of their pure elements the amount of absorbed hydrogen in these intermetallic compounds is surprisingly high. The La compound that is richest in hydrogen is LaH₃, whereas under equilibrium conditions pure nickel can dissolve only negligibly small quantities of hydrogen. A similar behaviour has been found for the compound ZrNi. While ZrH₂ is the highest hydride known of Zr, ZrNi can be hydrided up to ZrNiH₂.₈₈. It rather appears (the more so in the nickel-rich LaNi₅) as if the element with the strong affinity for hydrogen induces nickel to become also a hydrogen-binding element. In this connection it is noteworthy that by electrolytically charging nickel films an unstable hydride phase is formed with concentrations as high as 0.7 hydrogen atoms/nickel. Also it seems that the well-known catalytic properties of the nickel surface in hydrogenating reactions must be related to the phenomenon discussed here. A similar influence of nickel or nickel compounds on reaction kinetics was recently found in the formation of MgH₂. While the reaction of pure magnesium with hydrogen proceeds rather slowly, an addition of only 5% nickel is sufficient to get excellent kinetics (at 260 °C).

The sorption capacity of SmCo₅ is less than half that of LaNi₅, which is not surprising considering that cobalt is not known to form hydrides, neither in bulk nor at its surface as a catalyst. However, it has been found that e.g. HfCo also can bind more hydrogen, viz. HfCoH₂.₉₈, than the pure constituents. In this case hafnium and perhaps samarium also seem to induce the Co atom to behave as a hydrogen-binding element.

Changes in the ability to take up hydrogen within the given conditions can be caused in principle by factors of geometrical or electronic nature. In the geometrical factor we include the crystallographic structure and the number,
shape and size of the interstices. The electronic factor is determined by the valency of the elements. From preliminary experiments we learned that the stability of the hydrides decreases with increasing atom number of R. This is shown by the values in table I, where the equilibrium pressures at room temperature are given for a number of compounds in the series RNi₅ and RCo₅ (in which R is a rigorously trivalent metal).

TABLE I
Equilibrium pressures (at room temperature) for some AB₅ compounds at halfway saturation with hydrogen

<table>
<thead>
<tr>
<th>compound</th>
<th>pressure (atm)</th>
<th>compound</th>
<th>pressure (atm)</th>
</tr>
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<tbody>
<tr>
<td>PrCo₅</td>
<td>0.6</td>
<td>LaNi₅</td>
<td>2.5</td>
</tr>
<tr>
<td>NdCo₅</td>
<td>0.8</td>
<td>PrNi₅</td>
<td>12</td>
</tr>
<tr>
<td>SmCo₅</td>
<td>4.0</td>
<td>NdNi₅</td>
<td>20</td>
</tr>
<tr>
<td>GdCo₅</td>
<td>2.0</td>
<td>SmNi₅</td>
<td>&gt;60</td>
</tr>
</tbody>
</table>

The only change in the series being the decrease of R radius we must attribute the change in stability in this case to geometrical factors. The radius ratio R/Ni in the series RNi₅ does not reach Dwight’s critical limit 1.30, below which the hexagonal CaCu₅ type is not stable and where the cubic AuBe₅ type is formed. In view of the data in table I we must assume that at this point the transformation pressure will be very high, so it is not surprising that ZrNi₅ (radius ratio 1.28, cubic) could not be hydrogenated. A conclusion that the hexagonal structure is necessary in this respect is therefore not justified.

The above limit of 1.30 does not seem to be critical in the sense that cubic structures are not stable at larger values. Recently Buschow et al. found six RCo₅ compounds with radius ratio up to 1.42 to have the cubic AuBe₅ type of structure.

The hydrogen-sorption capacity remains rather large in YbNi₅ and CaNi₅ (with divalent metals), contrary to that of ThNi₅ and ZrNi₅ (with tetravalent metals). Taking into account that the radius is also affected in these cases this still seems to indicate that the sorption capacity is larger at lower electron concentrations.

The reaction of metals with gaseous hydrogen at room temperature is not exceptional. A first step in the reaction may be assumed to be the splitting up of a hydrogen molecule, likely preceded by an adsorption of H₂ at the metal surface. Although the incubation time at the first loading might lead us to believe that the surface reaction controls the process, we now assume that the penetration of the hydrogen by diffusion into the bulk is rate-determining. This is
sustained by an electrolysis experiment, in which an abundance of hydrogen ions is discharged at the metal surface. In this case the hydrogenation does not proceed essentially faster. If the chemical bond metal-hydrogen is already formed at the surface we may wonder whether the hydrogen diffuses as a positively charged particle (a proton) or as a negatively charged $H^-$ ion (like H is bound in LiH or CaH$_2$).

X-ray measurements show that regions which are completely hydrogenated may exist in equilibrium with regions having very small hydrogen content. It is concluded that the hydrogen does not fill gradually and randomly the available interstices and it follows that there is a positive interaction between the hydrogen atoms possibly by means of a strain that accompanies the filling of an interstitial hole. A hydrogen atom may induce thus another atom to occupy a neighbouring site. Which sites are preferred by the hydrogen atoms is not yet known. This will be investigated by neutron diffraction in the near future. At the moment we can only make a suggestion based on the geometry of the elementary cell. The two kinds of holes which can accommodate the largest spheres are both neighbouring rare-earth atoms. One is situated at $(x, 2x, z)$ with $x = 0.21, z = 0.27$, the other at $(x, 0, z)$ with $x = 0.43, z = 0.12$. They can accommodate spheres with diameter of 0.35 Å and 0.32 Å respectively (in the undistorted lattice). From the symmetry of the space-group ($P6/mmm$) it follows that both kinds of holes are 12-fold.

In the $\text{RCO}_5$ compounds the orthorhombic deformation might be caused by a less symmetrical filling of the same holes as in $\text{LaNi}_5$, which then implies a greater interaction between the hydrogen atoms, possibly accompanied by a smaller mobility.

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REFERENCES