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Dual site occupancy of hydrogen in Sm_2Fe_{17}

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Abstract

The hydrogen absorption properties of the Sm_2Fe_{17} alloy were investigated by measurements of pressure–composition isotherms over the temperature range 423–623 K. The hydrogen atoms occupy not only the octahedral *9e* sites but also the tetrahedral *18g* sites in the rhombohedral Sm_2Fe_{17} lattice. It is believed that the full occupation of the *9e* sites, corresponding to the hydrogen composition $H/Sm_2Fe_{17}=3.0$, is followed by a partial occupation of the *18g* sites. In the present work, however, the partial molar entropy of hydrogen suggests that the *18g* sites start to be occupied even at low hydrogen concentrations. This behavior is followed by drastic changes in the partial thermodynamic properties of hydrogen starting around $H/Sm_2Fe_{17}=2.0$, implying that a large amount of hydrogen can start to enter the *18g* sites before the *9e* sites are completely occupied. This thermodynamic behavior was confirmed by discontinuous changes in the lattice constants and the saturation magnetization of Sm_2Fe_{17} alloy with hydrogen composition. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sm_2Fe_{17} alloy; Pressure–composition isotherms; Lattice parameters; Magnetic properties

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1. Introduction

The Sm_2Fe_{17} compound is one of the high-performance permanent magnet materials. It has been well known that the magnetic properties, i.e. Curie temperature and magnetic anisotropy, drastically change with accommodation of interstitial elements such as carbon, nitrogen and hydrogen [1–5]. In particular, Sm_2Fe_{17} nitride [6,7] is a potential material for a new series of permanent magnet materials with superior magnetic properties exceeding even Nd–Fe–B alloys.

The compound absorbs a large amount of hydrogen with changing magnetic properties [3]. The hydrogenation of the compound is a promising step in the preparation of Sm_2Fe_{17} nitride (HDDR process) [8,9]. Most previous research on the Sm_2Fe_{17}–H system focused on the magnetic properties and the local influence of the interstitial hydrogen in the Sm_2Fe_{17} lattice [10,11] or the characteristics of the reaction between Sm_2Fe_{17} and hydrogen for the HDDR process [9]. From these works, it may be concluded that there are two different interstitial sites available for hydrogen atoms; octahedral *9e* and tetrahedral *18g* sites, in the rhombohedral Th_2Zn_{17} type of crystal structure. It is also believed that the *9e* sites are fully occupied first with hydrogen atoms, corresponding to hydrogen content of $H/Sm_2Fe_{17}=3.0$, and then the *18g* sites start to be occupied. The number of existing *18g* sites is six per formula unit. However, the maximum hydrogen content is $H/Sm_2Fe_{17}=5.0$ so that the *18g* sites are only partially occupied. This dual site occupation phenomenon must be reflected on the thermodynamic behavior of the Sm_2Fe_{17}–H system, but only a few publications on the thermodynamic properties have been reported [12]. In this work, the partial molar quantities of hydrogen were determined from pressure–composition (PC) isotherms. The substantial distribution of the hydrogen atoms over the available interstitial sites in the Sm_2Fe_{17} lattice will be discussed in combination with the variation in lattice parameters and magnetization with hydrogen content.

2. Experimental

The Sm_2Fe_{17} alloy was prepared by arc melting constituent elements of Sm (99.9%) and Fe (99.99%) in an argon atmosphere. The alloy was annealed at 1173 K for 10 h under an argon atmosphere for homogenization. The stoichiometry was confirmed by inductively coupled plasma emission spectroscopy (ICP). The alloy was ground into powders sized <32 μm for pressure–composition (PC) isotherm measurements. The PC isotherms for ab-

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sorption were determined using Sieverts' apparatus from 423 to 623 K. In this study, $Sm_2Fe_{17}H_r$ samples for X-ray diffraction (CuKα) and magnetization measurements were prepared. The Sm_2Fe_{17} powders containing the majority rhombohedral Sm_2Fe_{17} phase and a trace level of Fe, confirmed by XRD, were loaded with hydrogen to a given hydrogen content at temperature higher than 423 K and then the powders were cooled to RT. The reduction in pressure was monitored to calculate the hydrogen uptake during the cooling to RT. The hydrogen content in the Sm_2Fe_{17} alloy powders was unchanged during the XRD and magnetization measurements at RT. The magnetization measurements were carried out using vibrating sample magnetometer (VSM) with the external magnetic field of 15 kOe.

3. Results and discussion

The PC isotherms for Sm_2Fe_{17}–H system show no plateau region due to the stoichiometric hydride formation (Fig. 1), implying that the $Sm_2Fe_{17}H_r$ can be considered as a single solid solution over the experimental temperatures and hydrogen concentrations. This was confirmed by the fact that no hysteresis was observed on the isotherms because the hysteresis is caused by the existence of the different phase boundaries during the hydride formation and decomposition processes.

Relative partial molar thermodynamic quantities have been determined from the thermodynamic relation

$$\Delta\mu_H = 1/2RT \ln P_{H_2} = \Delta H_H - T\,\Delta S_H$$

where $\Delta\mu_H$ is the relative chemical potential of hydrogen, and ΔH_H and ΔS_H are the relative molar enthalpy and entropy, respectively. Fig. 2 shows the relative molar enthalpy of hydrogen, ΔH_H. The partial enthalpy is rather constant at lower hydrogen concentrations but it increases sharply from $H/Sm_2Fe_{17} = r = 2.0$.

The relative partial molar entropy, ΔS_H, was also determined from the isotherms, as shown in Fig. 3. The partial entropy decreases steadily with increasing hydrogen concentration until $r = 2.0$ and then starts increasing drastically with increasing r, reaching a maximum value at approximately $r = 3.25$. When the hydrogen concentration further increases, the entropy value again decreases with increasing r. The drastic change in the thermodynamic quantities can be explained in relation to the dual site occupancy phenomenon of hydrogen atoms in the rhombohedral Sm_2Fe_{17} lattice.

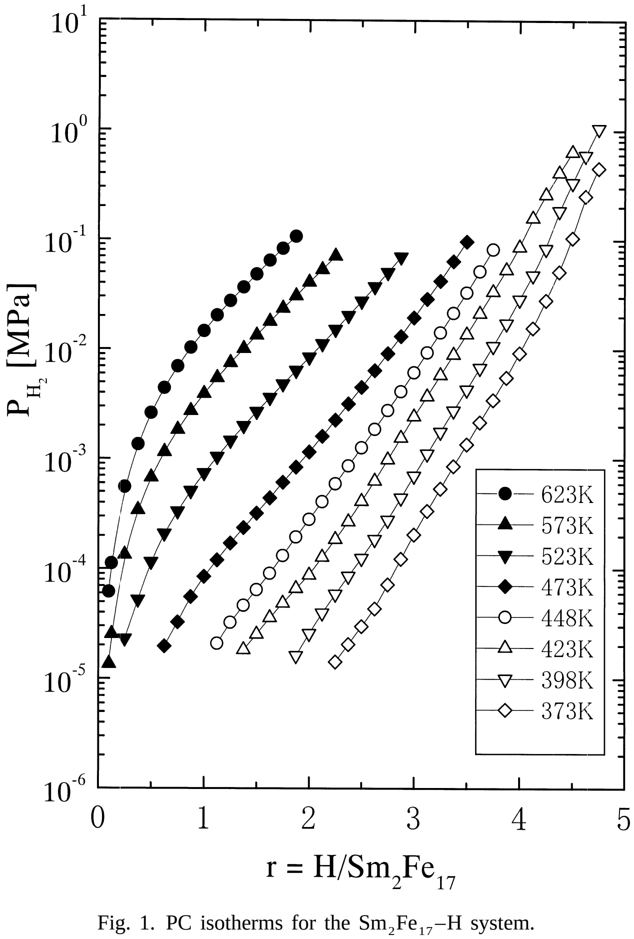

Fig. 1. PC isotherms for the Sm_2Fe_{17}–H system.

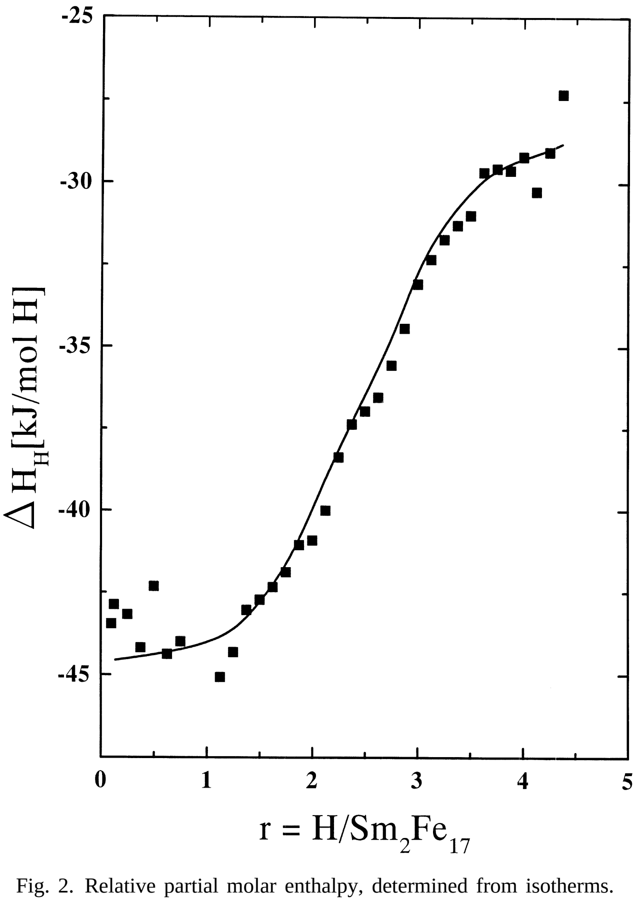

Fig. 2. Relative partial molar enthalpy, determined from isotherms.

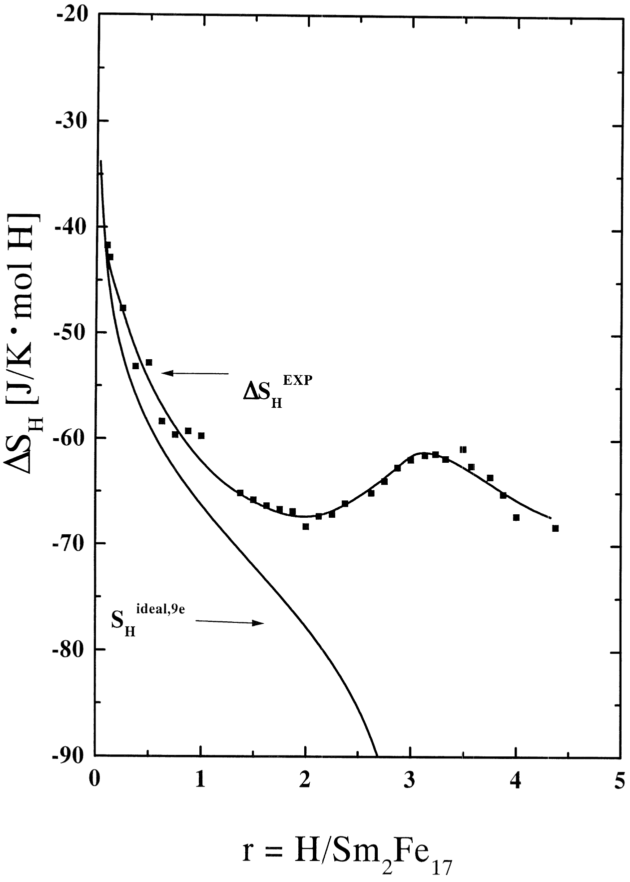

Fig. 3. Relative partial molar entropy, determined from isotherms.

The hydrogen atoms occupy not only the octahedral *9e* but also the tetrahedral *18g* sites. The *9e* octahedron comprises two Sm and four Fe atoms. On the other hand, two Sm and two Fe atoms form the *18g* tetrahedron. From the viewpoint of affinity of the interstitial sites for hydrogen, the *18g* site seems to have a higher affinity for hydrogen than the *9e* site because the mean electronegativity values for the *9e* site is higher than that for the *18g* site. Therefore, if affinity of the interstitial sites is a dominant factor for hydrogen occupation, the *18g* sites should be occupied first instead of the *9e* sites, but the *9e* sites are actually occupied first. According to the recent work done by Christodoulou and Takeshita [3], the calculated sizes of the *9e* and *18g* sites are 2.2 and 1.2 times larger than the hydrogen atom, respectively. It was, therefore, concluded that the hydrogen atoms occupy preferentially the large l*9e* sites first before starting occupation of the small *18g* sites because lower site energy for the *9e* site can be expected [3,11]. For the Sm_2Fe_{17}–H system, the effect of interstitial size seems to be a dominant factor for the hydrogen interstitial occupation. Moreover, the first and second nearest neighbor *18g*–*18g* distances are smaller than 2.1 Å which is the closest distance allowed between interstitial hydrogen atoms, suggested by Switendick [13]. Considering the coordination of the *18g* sublattice in the Sm_2Fe_{17}, it may be concluded that the hydrogen atoms can occupy only one third of the *18g* sites [3]. That is the reason why the maximum hydrogen concentration in Sm_2Fe_{17} is $r = 5.0$. The geometry of the interstitial site in Sm_2Fe_{17} is summarized in Table 1.

The thermodynamic behavior (Figs. 2 and 3) can be understood on the basis of the dual occupation of the hydrogen atoms in Sm_2Fe_{17} as discussed above. The partial molar entropy of hydrogen decreases with increasing r until $r = 2.0$. The decrease in the entropy cannot be described by the approximation that the interstitial hydrogen atoms are randomly distributed only over the *9e* sites. If the hydrogen atoms are distributed randomly over the *9e* sites, the ideal partial configurational entropy of hydrogen can be written as $S_H^{ideal} = -R \ln [r/(\beta - r)]$, where β, the number of available interstitial sites per formula unit, is taken as 3. The deviation of the partial entropy from S_H^{idea} is defined as the excess partial entropy. The excess partial entropy evaluated from Fig. 3 is positive and increases in magnitude with r. It is not realistic for this system that the excess partial entropy is positive. This could be because the definition of the ideal solution is inappropriate. The expression of S_H^{ideal} with $\beta = 3.0$ is no longer reasonable as a ideal solution for Sm_2Fe_{17}–H system.

According to the blocking model, if some of the sites are blocked for occupation by hydrogen atoms, the experimental partial molar entropy should reduce more rapidly with r than S_H^{idea} [14,15]. This is not the case for the Sm_2Fe_{17}–H system at $r < 2.0$. The experimental partial entropy value is more positive than S_H^{idea}. It can be concluded that the blocking model is not a good approach to the interpretation of the present thermodynamic behavior.

A reasonable explanation seems to be that a portion of the *18g* sites may start to be occupied even at relatively low hydrogen concentrations. If this is the case, the experimental partial entropy should always be more positive than S_H^{ideal}. This is the case for the result shown in Fig. 3. In fact, the entropy value starts increasing rapidly at $r = 2.0$. This rapid increase in the entropy corresponds to

Table 1
Interstitial sites for hydrogen in Sm_2Fe_{17}

	9e	*18g*
Interstitial	Octahedron:2Sm4Fe	Tetrahedron:2Sm2Fe
Interstitial size ratio to H atom	2.2	1.2
Existing sites per Sm_2Fe_{17}	3	6
Available sites per Sm_2Fe_{17}	3	2
Distances between neighbors (Å)	>4	1st n.n: 1.14 2nd n.n: 1.95 3rd n.n: 2.28

the process that the *9e* sites become fully occupied and the large number of the *18g* sites start to be occupied. Finally when the *9e* sites are fully occupied at $r = 3.25$, the entropy again starts decreasing because the entropy change is controlled only by the distribution of hydrogen atoms in *18g* sites. The dual occupation behavior should also describe the rapid increase in the partial molar enthalpy shown in Fig. 2. Recently Wirth et al. calculated solution energies for both interstitial sites in Sm_2Fe_{17} at very low hydrogen concentration, i.e. −26 kJ/H for octahedral and −18 kJ/H for tetrahedral sites, and suggested that at high temperature the octahedral *9e* sites only are occupied [16]. More detailed information on the coordination of interstitial site is necessary to determine a fraction of hydrogen atoms on each site at given temperature.

As shown in Fig. 4, at lower hydrogen concentrations the lattice expansion is substantially anisotropic. The lattice expands steadily along the *a* direction but shrinks along the *c* direction. The lattice expansion along the *a* direction can be understood by consideration of the geometry of interstitial sites suggested by Christodoulou and Takeshita [3]. The *9e* site is surrounded with two Sm and four Fe atoms. The Fe–Fe distance along the *c* direction is longer than the Fe–Fe and Sm–Sm distances in the *c* plane so that the *9e* octahedron is expanded anisotropically in the *a* direction by the insertion of hydrogen atom. The *c* parameter should be insensitive to *r* in this sense. The reduction in the *c* parameter could be understood by considering the spontaneous magnetostriction caused by the change in the exchange interaction between Fe atoms. On the other hand, the shape of the *18g* tetrahedron is rather isotropic [3] so that the isotropic expansion of the *18g* tetrahedron can be expected, causing isotropic expansion of Sm_2Fe_{17} lattice as well.

Consequently, the above discussion leads to the conclusion that most hydrogen atoms enter the *9e* sites at relatively lower hydrogen concentrations and the *18g* sites become occupied when more hydrogen is introduced, consistent with the conclusion derived from the thermodynamic behavior. The conclusion is further supported by the magnetic properties of $Sm_2Fe_{17}H_r$ alloys. As shown in Fig. 5, the saturation magnetization increases with increasing *r*. The increase in the magnetization is related to the increase in Curie temperature with *r*. The increase in Fe–Fe distance due to the hydrogen occupation causes a positive contribution to the Fe–Fe exchange interaction, yielding the increases in Curie temperature and magnetization. The contribution of hydrogen atoms on each site to the expansion of lattice parameters (Fe–Fe distance) is different. Therefore, it is understandable that the linearity of magnetization changes at $r = 2.0$, which is coincident with the rapid change in the partial molar quantities shown in Figs. 2 and 3.

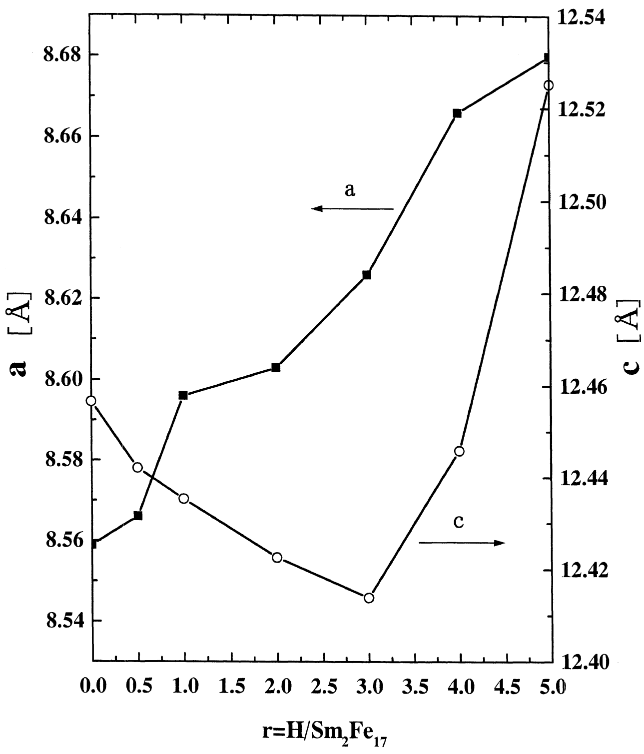

Fig. 4. Variation in lattice parameters with hydrogen concentration.

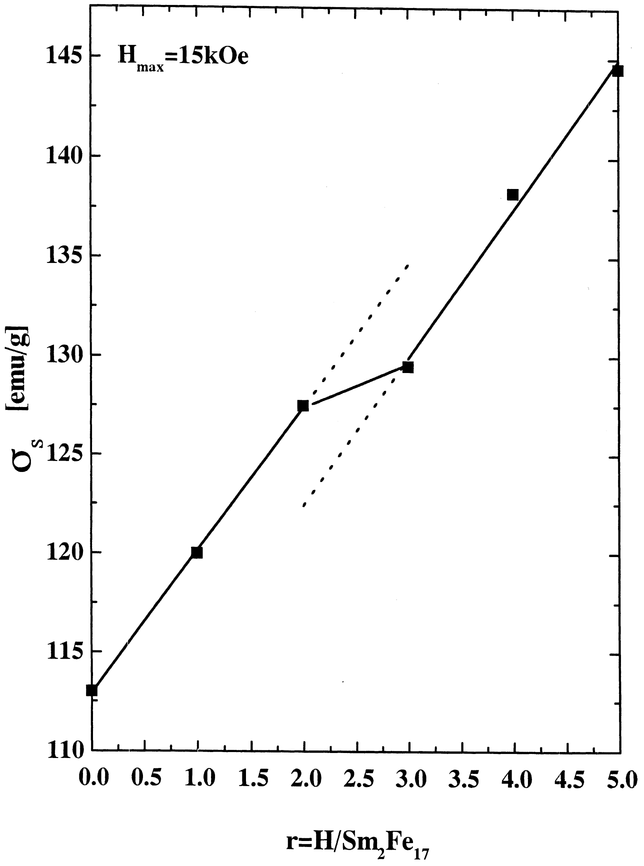

Fig. 5. Variation in magnetization with hydrogen concentration.

4. Conclusions

In this study we have derived partial thermodynamic quantities of hydrogen from PC isotherms of the Sm_2Fe_{17}–H system. The variation in partial molar entropy and enthalpy with hydrogen concentration in Sm_2Fe_{17} implies that even at low hydrogen concentration the *18g* site starts to be occupied. When more hydrogen was introduced, a drastic change in the partial molar entropy and enthalpy with increasing hydrogen concentration occurred, implying that a large amount of hydrogen starts to occupy the *18g* sites. The thermodynamic behavior was confirmed by the discontinuous change in the lattice constants and the saturation magnetization of Sm_2Fe_{17} with hydrogen concentration.

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