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THE EFFECT OF Ni REPLACEMENT WITH Ge ON THE MAGNETIC PROPERTIES OF $LaNi_5$ ALLOY

Dam Nhan Ba
Hung Yen University of Technology and Education

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Abstract:

In this paper, we present the results of the study on the magnetic properties of $LaNi_{5-x}Ge_x$ (x = 0.1 - 0.5) alloys based on extending the Langevin's classical theory of paramagnetism. The calculation results show that the number of magnetic particles decreases and the size of magnetic particles increases as the concentration of Ge in $LaNi_5$ alloy increases. The $LaNi_{5-x}Ge_x$ alloy after charge/discharge changes from paramagnetic to super paramagnetic. The calculated data is verified by making joints by the Langevin's function according to the M-H data at room temperature, the results of matching between the theoretical line and the experimental data are over 99%. This study gives us a better understanding of the processes that occur when Ni-MH rechargeable battery is charged/discharged.

Keywords: *Absorption of hydrogen, $LaNi_5$, Ni-MH rechargeable battery, Magnetic properties.*

1. Introduction

The intermetallic compound (IMC) $LaNi_5$ is well known for its ability to store hydrogen reversibly at pressures and temperatures of interest for applications close to ambient conditions [1, 2]. However, long-term cycling leads to severe degradation of the material [3, 4]. To overcome this problem, substitutions have been performed on the Ni sites, leading to pseudo-binary compounds $LaNi_{5-x}M_x$ (M = Al, Sn, Mg, Fe, Co) with improved resistance towards degradation [5-9]. The most important result of alloy substitution for the extension of cycle life is thought to be a reduction in volume expansion upon hydride formation. Co substitution for Ni has been identified as one of the most effective solutes in this respect and results in a greatly reduced tendency toward fragmentation and corrosion leading to batteries with long lifetimes [10, 11]. Unfortunately, cobalt is an expensive element, and the specific role of Co is not well understood. Particularly, it has been shown that Sn significantly enhances the stability of the hydride during temperature cycling [12, 13]. Meli [14] has speculated that Si and Al substitutions inhibit corrosion during electrochemical cycling through the formation of passivating oxide films on the surfaces. However, photoelectron spectroscopy studies "0" on cycled powder electrodes of both $LaNi_{5-x}Si_x$ and $LaNi_{5-x}Al_x$ did not indicate the presence of these solute-enriched surface oxide films. However, good cycling properties are also obtained with Ge-substituted compounds [15]. When doped Ge into $LaNi_5$ alloy, the current density is increased by 10 times compared to the original $LaNi_5$ alloy and other doped elements, meaning that the maximum current capacity of the battery increases by 10 times. This is interesting because Ge is a semiconductor element (group IV in the periodic table).

In this study, we use the Langevin's classical theory of paramagnetism to calculate the concentration of magnetic particles, the size of the magnetic particles and the paramagnetic shell. Consequently, it serves as a reference compound to understand the physical and chemical phenomena influencing the hydrogenation properties.

2. Theory

First we have to look back at Langevin's classical theory of paramagnetism [16]. Langevin (1905) considered the system of N atoms to have a magnetic moment μ placed far enough apart to

not interact with each other. It is known that the magnetization M of the system and the free energy F are related by the Formula:

$$M = -\frac{\partial F}{\partial H} \quad (1)$$

Here

$$F = -Nk_B T \ln Z \quad (2)$$

For a statistical Z value:

$$Z = \sum e^{-\frac{E_i}{k_B T}} \quad (3)$$

The potential U of each atom in the magnetic field H is determined by the Formula:

$$U = -\vec{\mu}.\vec{H} = -\mu H \cos\theta \quad (4)$$

Whereas θ is the angle between $\vec{\mu}$ and $\vec{H}$.

Using Formula (3) to calculate Z, in addition to replacing U from Formula (4) for E_i, we replace the $\sum$ symbol with the $\int$ symbol because in the classical model, the magnetic moment is oriented any θ and φ possible continuous change. We get:

$$Z = \int_0^{2\pi} d\varphi = \int_0^{\pi} e\left(\frac{\mu H \cos\theta}{k_B T}\right) \sin\theta d\theta \quad (5)$$

Add the symbols:

$$a = \frac{\mu H}{k_B T} \text{ and } x = \cos\theta \quad (6)$$

We have:

$$z = 2\pi \int_{-1}^{+1} e^{ax} dx = \frac{4\pi}{a} sha \quad (7)$$

Using the Formulas (1) - (3), we have:

$$F = -Nk_B T \ln\left(\frac{4\pi}{a} sha\right) \quad (8)$$

$$M = Nk_B T \frac{a}{sha}\left(-\frac{1}{a^2} + \frac{1}{a} cha\right)\frac{\partial a}{\partial H}$$

$$M = Nk_B T\left(ctha - \frac{1}{a}\right)\frac{\partial a}{\partial H} \quad (9)$$

Because:

$$\frac{\partial a}{\partial H} = \frac{\mu}{k_B T} \quad (10)$$

So that:

$$M = N\mu L(a) \quad (11)$$

With:

$$L(a) = cth(a) - \frac{1}{a} \quad (12)$$

L(a) is called the Langevin's function.

When $a \to 0, cth(a) \to 1$ and $\frac{1}{a} \to 0$, so that $L(a) \to 1$. Thus, when a is very large, the Langevin's function is asymptotic to the value L(a) = 1.

When $a \ll 1$, $cth(a) \approx \frac{1}{a} + \frac{a}{3}$, so that L(a) $\approx \frac{a}{3}$. Thus, when a is very small, the Langevin's function is a straight line creating an α angle with the horizontal axis.

$$\left(\frac{dL}{da}\right)_{a \ll 1} \equiv \tan\gamma = \frac{1}{3} \quad (13)$$

The experiment is performed at room temperature in the laboratory's normal magnetic field. If taking $\mu \sim 1\mu_B$, H ~ 10^6 A/m = 12600 Oe. We have: $\mu H = \mu_B H = 1.17 \times 10^{-29}$ Wbm x 10^6 A/m = 1.17 x 10^{-23} J. At room temperature corresponds to $k_B T$ = 1.38 x 10^{-23} J/K x 300 K = 4.1 x 10^{-21} J.

Therefore:

$$a = \frac{\mu_B H}{k_B T} = \frac{1.17 \times 10^{-23}}{4.1 \times 10^{-21}} = 2.8 \times 10^{-3} << 1$$

Then we can replace L(a) by a/3. From (11) and (12) equation we get:

$$M = \frac{N\mu^2}{3k_B T} H \quad (14)$$

The maximum magnetic moment is obtained at the maximum magnetic field. From this we know the value of the magnetic moment and from the value of the magnetic moment we calculate χ by the Formula:

$$\chi = \frac{M}{H} = \frac{N\mu^2}{3k_B T} \quad (15)$$

3. Results and discussion

3.1. Calculation of the number of magnetic particles

According to Langevin's classical theory of paramagnetic, we see that at low temperatures, L (a) → 1, (corresponding to large values of a), that is, I has saturation values. We study $LaNi_{5-x}Ge_x$ material, because the material is placed in a magnetic field in the range of -15 kOe 15 kOe, and at room temperature, so the value of a is not large. Moreover, in the Langevin's classical theory of paramagnetic, we consider the atomic N system to be non-interacting. For $LaNi_{5-x}Ge_x$ materials, the size of the material particles is from a few tens of nanometers to hundreds of nanometers, meaning that a single particle can contain thousands to tens of thousands of atoms. So in $a = \frac{\mu H}{k_B T}$ Formula we have to replace μ_B by μ, where μ is worth thousands to tens of thousands of μ_B.

Assuming $\mu = 10^3 \mu_B$, infer a = 2.8. According

to the Formulas (11) and (12) we have:

$$N = \frac{M}{\mu(ctha - 1/a)} \quad (16)$$

Plug the values for $a = \frac{\mu H}{k_B T}$ and $M = \chi H$ into the Formula (16) we have:

$$N = \frac{\chi H}{\mu\left(cth\left(\frac{\mu H}{k_B T}\right) - \frac{k_B T}{\mu H}\right)} \quad (17)$$

We take H value from the laboratory's magnetic field, H = 12600 Oe ≈ 10^6 A/m. For $LaNi_5$ materials, in Table 1 we have $\chi = 3.7 \times 10^{-6}$.

Therefore, M = 3.7 A/m. Plug these values into the Formula (17) we have:

$$N = \frac{3.7 A/m}{1.17 \times 10^{-26} Wbm \times (cth2.8 - 1/2.8)}$$

$$N = 61 \times 10^{19} (\text{particles}/m^3)$$

Table 1: The number of N-magnetic particles depends on the concentration of Ge in $LaNi_{5-x}Ge_x$ alloys

No.	Samples	χ (10^{-6})	N x 10^{19} (particles/m^3)
1	$LaNi_5$	3,700	61
2	$LaNi_{4.9}Ge_{0.1}$	2,819	46
3	$LaNi_{4.8}Ge_{0.2}$	2,530	42
4	$LaNi_{4.7}Ge_{0.3}$	2,147	35
5	$LaNi_{4.6}Ge_{0.4}$	1,724	28
6	$LaNi_{4.5}Ge_{0.5}$	1,409	23

Similarly, the values of χ for the material $LaNi_{5-x}Ge_x$ (x = 0.1 - 0.5), we also obtained the values of N, the results are shown in Table 1.

Table 1 shows that if Ge element is doped into $LaNi_5$ alloy, the number of magnetic particles will decrease.

Because element Ge belongs to group IV of the periodic table (non-magnetic element), when doped, it will replace Ni particles (ferromagnetic element), and reduce the number of Ni magnetic particles.

According to Equation (17), we see that N is linearly dependent on χ and the number of magnetic particles is inversely proportional to the concentration of Ge element added. As the number of magnetic particles decreases, the magnetic moment of the sample also decreases.

3.2. Calculate the paramagnetic shell size of the particles

As above, we have calculated the number of magnetic particles per unit volume. We assume that the particle has a spherical shape, lying close together. We can then consider the total volume of all particles per 1 volume unit to be equal to 1 volume unit.

Because the number of particles is measured in units of particles/m^3, so we have:

$$\frac{4}{3}\pi R^3 = \frac{1}{N} \quad (18)$$

Inferred:

$$R = \sqrt[3]{\frac{3}{4\pi N}} \quad (19)$$

With the N values in Table 1 and as calculated by Formula (19), we get the magnetic particle radius of the alloys as follows:

Table 2: Dependence of R particle size on Ge concentration in $LaNi_{5-x}Ge_x$ alloys

No.	Samples	N x 10^{19} (particles/m^3)	R(nm)
1	$LaNi_5$	61	73,1
2	$LaNi_{4.9}Ge_{0.1}$	46	80,3
3	$LaNi_{4.8}Ge_{0.2}$	42	82,8
4	$LaNi_{4.7}Ge_{0.3}$	35	88,0
5	$LaNi_{4.6}Ge_{0.4}$	28	94,8
6	$LaNi_{4.5}Ge_{0.5}$	23	101,2

The results in Table 2 show that when doped Ge is added to $LaNi_5$ alloy, the size of magnetic particles increases.

We have assumed above: $\mu = 10^3 \mu_B$, that is, we assume that the particle has a magnetic moment 1,000 times the atomic magnetic moment. So if the particle is about 10 atomic dimensions, that is, the particle contains about 10^3 atoms, then the magnetic moments of the atom in that particle must be arranged in parallel. That is, the particle then has the structure of a single domain.

We know that for a nanoparticle with a diameter of 5 nm, the number of atoms that it contains is 4,000 atoms. However, as the results have calculated, it is found that the size of the particle is very large, so each particle can contain

up to tens of thousands of atoms. So why does the particle have only magnetic moments equal to 10^3 atomic magnetic moments?

This can be explained logically if the particle is made up of two components, the kernel and the shell. The kernel includes the magnetic moment of atoms arranged in parallel with each other, while the shell consists of chaotic atoms. In other words, the magnetic moment in the kernel arranges the same as that of ferromagnet, while the magnetic moment in the shell is arranged like in paramagnetic. Because the magnetic moment in the shell is chaotic, it creates a demagnetizing field that reduces the magnetization of the particle.

Because the size of the particle we calculate is about 50nm, the size of the kernel cannot be larger than 25nm, that is, it cannot be greater than ½ of the particle size, because if the nucleus is larger than ½ of the particle size, then that particle will have a fairly large magnetic moment. If the demagnetization field of the paramagnetic shell is taken into account, the size of the nucleus can be estimated from 5nm to 25nm.

In the Langevin's classical theory of paramagnetism, we must consider a system of N atoms that do not interact with each other. In order to apply the Langevin's classical theory of paramagnetism in this case, the two particles must not interact with each other. Because the magnetic moment of a particle is determined by the kernels, the interaction between the two particles as well as the decision of the kernels. Because the kernel size is small compared to the particle size, even if we assume that the particles are close together, the distance between the two kernels will be greater than or equal to the particle size, then the interaction between particles is negligible.

3.3. Checking the paramagnetic properties by the Langevin's function

When the sample was in the superparamagnetic state, the magnetization curve consistent with the Langevin's function was corrected for high-temperature induction [17].

$$M(T,H) = A.M_S\left(\coth(x) - \frac{1}{x}\right) + \chi H \qquad (20)$$

With:

$$x = \frac{M_S \rho\pi\left(d_{mag}^3/6\right)H}{k_B T} \qquad (21)$$

Here:

M_S is the saturation magnetic moment in units of emu/g

$\pi\left(d_{mag}^3/6\right)$ is the average volume of magnetic particles

χ is the linear magnetic susceptibility showing the distribution of diamagnetism, magnetic impurities and chaotic spins at the particle surface causing the signal in the high magnetic field to be distorted

ρ is the mass density of particles

Mass density is determined by the formula:

$$\rho = \frac{8M}{N_A a^3}$$

With: M is the molar mass measured by grams; a is the lattice constant; N_A is the Avogadro constant.

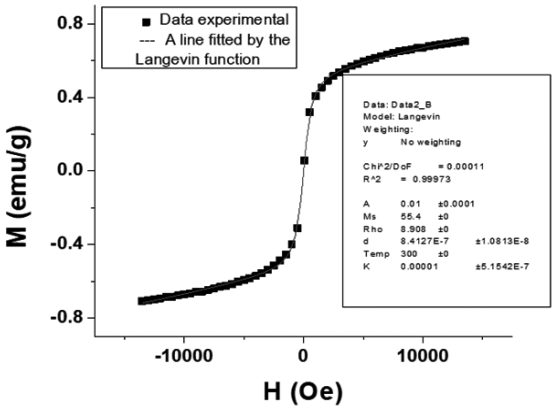

Figure 1. The magnetization curve of the sample $LaNi_5$ after 10 charge/discharge cycles is matched according to the Langevin's function

Figure 1 shows the magnetization curves of samples $LaNi_5$ be fitted in the Langevin's function (symbol ■ represents an experimental data line, —— represents a line fitted by the Langevin's function). The data shown in Figure 1 shows the experimental and fitting lines of Langevin's function with a joints above 99%. This result confirms that the samples were in powder state and the samples were charge/discharge after 10 cycles in superparamagnetic states. The concentration of magnetic particles and the size of the magnetic particles are determined based on the experimental curve fitted according to Langevin's function according to Formula (20),

their values are shown in Figure 2 and Figure 3.

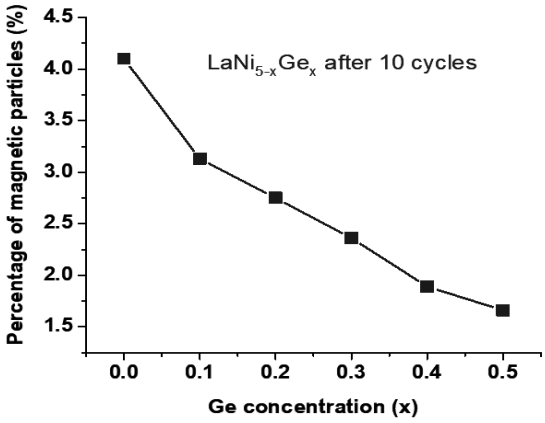

Figure 2. Percentage of magnetic particles of $LaNi_{5-x}Ge_x$ system

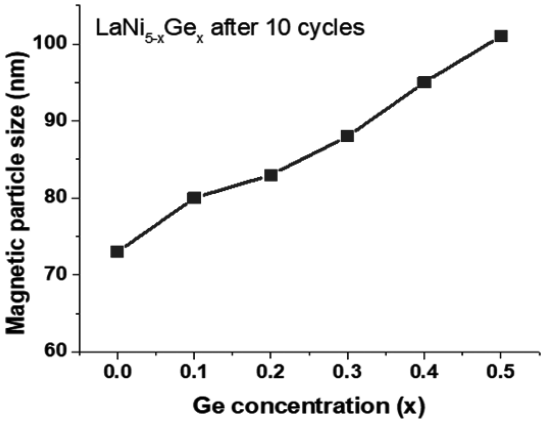

Figure 3. Magnetic particle size of $LaNi_{5-x}Ge_x$ system

As Figure 2 and Figure 3 show, with the concentration of Ge doping increases, the percentage of magnetic particles decreases and the particle size increases. This result is consistent with the results calculated by the classical Langevin's function theory presented above.

4. Conclusion

We have determined the number of magnetic particles, the size of the magnetic particles after charge/discharge and the thickness of the paramagnetic shell of the magnetic particles. On the basis of extending the concept of paramagnetic and paramagnetic, we have assumed the structure of a magnetic particle consisting of two parts of ferromagnetic core and paramagnetic shell. As a result, when the concentration of Ge element instead of Ni increases, the number of magnetic particles decreases, the size of magnetic particles increases. The process of matching experimental data according to the classical Langevin's function theory gives results over 99%. This articulation again confirms the material's magnetic state transition. Thus, it can be considered that the magnetic measurement method is a highly sensitive analytical method to evaluate the quality of electrodes through surveys and comparison with standard samples. This is also a new contribution of research into this field of study.

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ẢNH HƯỞNG CỦA VIỆC THAY THẾ MỘT PHẦN Ni BẰNG Ge LÊN TÍNH CHẤT TỪ CỦA HỢP KIM $LaNi_5$

Tóm tắt:

Trong bài báo này, chúng tôi trình bày những kết quả nghiên cứu về tính chất từ của hệ vật liệu $LaNi_{5-x}Ge_x$ (x = 0,1 ÷ 0,5) trên cơ sở mở rộng lý thuyết thuận từ của Langevin. Các kết quả tính toán cho thấy rằng số hạt từ giảm còn kích thước hạt từ tăng khi nồng độ Ge trong hợp kim $LaNi_5$ tăng. Vật liệu $LaNi_{5-x}Ge_x$ sau phóng/nạp chuyển từ trạng thái thuận từ sang trạng thái siêu thuận từ. Số liệu tính toán được kiểm lại bằng cách làm khớp bằng hàm Langevin theo số liệu M-H tại nhiệt độ phòng, kết quả làm khớp giữa đường lý thuyết và số liệu thực nghiệm đạt trên 99%. Nghiên cứu này giúp ta hiểu sâu sắc hơn các quá trình xảy ra khi phóng/nạp của pin nạp lại Ni-MH.

Từ khóa: *Hấp thụ Hiđrô, $LaNi_5$, pin nạp lại Ni-MH, tính chất từ.*