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Journal of Alloys and Compounds 356–357 (2003) 186–190

Journal of ALLOYS AND COMPOUNDS

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Theoretical calculation of positron lifetimes for $LaNi_5$–H system

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Received 1 June 2002; accepted 25 October 2002

Abstract

Positron lifetime spectroscopy is a powerful tool for the study of vacancy-type defects in solids. Our positron lifetime measurements have revealed that huge numbers of excess vacancies are formed in addition to dislocations during the first hydrogen absorption process of $LaNi_5$ and excess vacancies becomes mobile and form microvoids by a thermal activation process. For further investigation, theoretical approaches using electronic structure calculations are indispensable. In this work, we have performed theoretical calculations of positron lifetime for $LaNi_5$–H system using first principles electronic structure calculations. By comparison between the theoretical and experimental positron lifetimes, one of the defect components during hydrogen absorption can be ascribed to the annihilation at vacancy-clusters composed of two or three Ni vacancies. The positron lifetime of the vacancy-cluster component increases over 400 ps during isochronal annealing after hydrogen desorption. The vacancy-cluster may contain not only Ni vacancies but also La vacancies, since the vacancy-cluster composed of only Ni vacancies cannot yield such a long positron lifetime.

Keywords: Hydrogen storage materials; Point defects; Electronic states (localized); Positron spectroscopies

1. Introduction

The intermetallic compound $LaNi_5$ is most widely used as hydrogen storage alloy for rechargeable nickel–metal hydride batteries, hydrogen storage vessels, chemical heat compressors and so on. One of the most specific changes during hydrogen absorption of hydrogen storage materials is a large volume expansion. In the case of $LaNi_5$, the lattice constants are expanded by 8% with a large volume increase of 25% by hydrogen absorption [1]. The hydrogen absorption also induces lattice defects. By transmission electron microscopy, dislocations introduced during the initial hydriding in $LaNi_5$ have been observed [2–6]. Shirai et al. have reported that not only dislocations but also vacancies and vacancy clusters are formed during the initial hydriding by using positron annihilation spectroscopy [7].

Positron annihilation spectroscopy is a sensitive tool for vacancy-type defects in solids. In a perfect crystal, the positron wave function is delocalized in the interstitial region because of the repulsion from the ion cores. If vacancy-type defects exist in solids, the positron wave function is localized at the defects where the electron density is lower than in the other regions. The localization of the positron at the defects results in a longer lifetime of the positron compared to the bulk lifetime because the positron lifetime is inversely proportional to the electron density where the positron annihilated. However, interpretation of the experimental positron lifetime for intermetallic compounds such as $LaNi_5$ is more complicated than for pure metals, because several types of vacancies may exist in intermetallic compounds. The different types of vacancies may yield different positron lifetimes. In order to characterise measured positron lifetimes in intermetallic compounds, a theoretical analysis is indispensable. However, little theoretical work has been done for intermetallic compounds.

In this work, we have performed theoretical calculations

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doi:10.1016/S0925-8388(02)01229-X

of positron lifetimes for the bulk and vacancy states in $LaNi_5$ and $LaNi_5$–H systems based on first-principles electronic structure calculations. The calculated results are compared with the experimental positron lifetimes in order to identify lattice defects formed during hydrogen absorption and during isochronal annealing after hydrogen desorption in $LaNi_5$–H system.

2. Method

In order to obtain the electron density and potential, the discrete-variational (DV)-Xα cluster method using a program code SCAT [8,9] is employed. In this first-principles calculation, the molecular-orbital wave function is expressed by a linear combination of atomic orbitals (LCAO). For the electronic structure calculations, we employ spherical model clusters whose radius is about 8 Å. The number of atoms in the model clusters for $LaNi_5$ and $LaNi_5$–H is about 70 and 150, respectively. The three-dimensional potential $V_+(r)$ sensed by the positron is constructed as a sum of the electron static potential $V_C(r)$ due to the nuclei and the electrons, and a correlation potential $V_{corr}(n_-(r))$ describing the electron-positron correlation:

$$V_+(r) = V_C(r) + V_{corr}(n_-(r)), \tag{1}$$

where $n_-(r)$ is the electron density. For the density dependence of $V_{corr}(n_-(r))$ we have used the interpolation formula of Broński and Nieminen [10] based on the result of many-body calculation [11]. The Schrödinger equation for the positron is solved by the finite-difference method [12] employing the periodic boundary conditions for delocalized positron wave function in the bulk state. In the case of the localized positron at the vacancy, the boundary conditions are the vanishing of the positron wave function on the surface of a large polyhedron.

The positron lifetime τ is calculated as the reciprocal value of the positron annihilation rate λ by

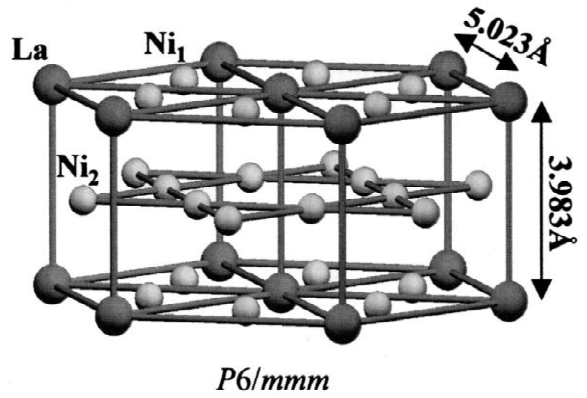
$$\lambda = \pi r_0^2 c \int n_+(r) n_-(r) \gamma(r) \mathrm{d}r \tag{2}$$

where r_0 is the classical electron radius, c is the speed of light, $n_+(r)$ is the positron density and $\gamma(r)$ is the enhancement factor describing the short-range pileup of the electron at the positron. For the enhancement factor, we have used the interpolation formula by Puska et al. [10] based on Lantto's data [13]. Partial annihilation rates are obtained using the results of the Mulliken population analysis [14].

3. The structure of $LaNi_5$ and $LaNi_5H_7$

The intermetallic compound $LaNi_5$ crystallises in the hexagonal $CaCu_5$-type structure which belongs to the space group $P6/mmm$, with $a = 5.0228$ Å and $c = 3.9826$ Å [15] as shown in Fig. 1. La atoms occupy the 1*a* site and there are two different sites for Ni atoms: the 2*c* and 3*g* sites. The structure of $LaNi_5$ consists of stacking of two types of layers: one is composed of La on the 1*a* site and Ni on the 2*c* site, the other is composed of only Ni on the 3*g* site. The hydrogen absorption of $LaNi_5$ leads to a reduction of symmetry and to a doubling of the *c*-axis of the hexagonal unit cell accompanying a large lattice expansion. Lartigue et al. [16] reported that the structure of $LaNi_5H_7$, which is a hypothetically ordered full hydride, is described in the space group $P6_3mc$ as well as the space group $P31c$ with five types of interstitial sites. Recently, Tatsumi et al. [17] have performed first-principles calculations on phases in the $LaNi_5$–H system with full geometry optimization and found that the lowest energy structure is

(a) $LaNi_5$



(b) $LaNi_5H_7$

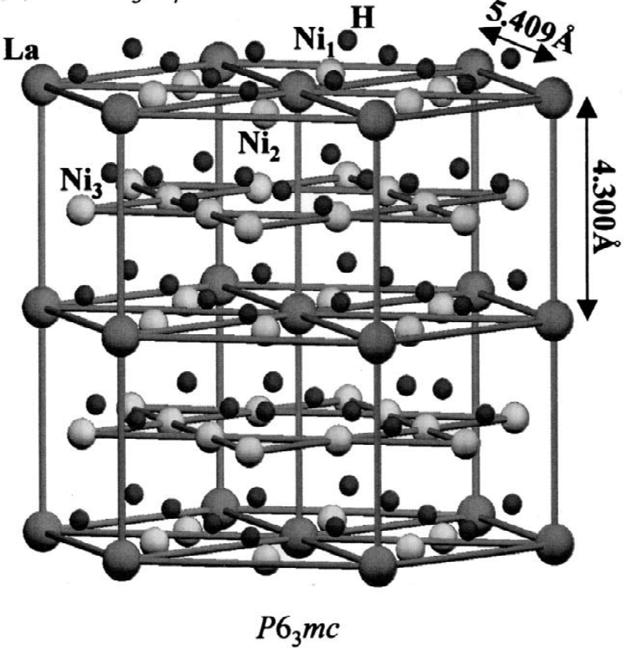


Fig. 1. The structure of (a) $LaNi_5$ and (b) $LaNi_5H_{7-}$.

close to the model analyzed with the space group of $P6_3mc$ by Lartigue et al. Thus, we employ the structure described in the space group $P6_3mc$ with $a=5.0228$ Å and $c=3.9826$ Å by Lartigue et al. for LaNi$_5$H$_7$ [16]. The Ni$_1$ site in LaNi$_5$ turns into two different sites, Ni$_1$ and Ni$_2$, in LaNi$_5$H$_7$ because of the lowering of symmetry.

4. Results and discussion

4.1. Positron lifetimes for LaNi$_5$

In order to evaluate the reliability of the positron lifetime calculation, the calculated positron lifetimes are compared to the experimental data for LaNi$_5$. The experimental positron lifetimes, listed in Table 1, for the bulk and vacancy states in LaNi$_5$ are obtained by measuring the well-annealed and electron-irradiated specimens [7], respectively. The calculated positron lifetime for the bulk state is in very good agreement with the experimental value. In the case of the vacancy state, the calculated positron lifetimes for the Ni vacancy are close to the experimental value for the electron-irradiated specimen. Because the inward relaxation around the vacancy is not taken into account in our calculations, it is reasonable that the calculated positron lifetimes are slightly larger than the experimental ones. The calculated positron lifetimes, therefore, well reproduce the experimental data.

4.2. Positron lifetimes for LaNi$_5$H$_7$

The lattice constants of LaNi$_5$ are expanded up to 8% by hydrogen absorption. Generally, positron lifetimes for bulk states increase with the expansion of lattice constants. On the other hand, the hydrogen atoms absorbed in the interstitial sites of LaNi$_5$ enhance the positron annihilation. Because of these opposite effects, the positron lifetime of the bulk state for LaNi$_5$H$_7$ cannot be estimated from the measured positron lifetime of LaNi$_5$. The calculated positron lifetimes and annihilation rates of LaNi$_5$ and LaNi$_5$H$_7$ are listed in Table 2. The positron annihilation rates of Ni and La atoms in LaNi$_5$H$_7$ decrease because of the expansion of the lattice constants. Despite the positron annihilation of absorbed hydrogen atoms, the positron lifetime of the bulk state for LaNi$_5$H$_7$ is slightly longer than that for LaNi$_5$ owing to the decrease in the positron annihilation rates of La and Ni induced by the lattice expansion.

Table 1
Positron lifetimes for bulk and monovacancy state in LaNi$_5$.

	Positron lifetime (ps)	
	Calc.	Exp.
Bulk	125	122
Defect		160
La Vacancy	241	
Ni$_1$ Vacancy	166	
Ni$_2$ Vacancy	177	

Table 2
Positron lifetimes and annihilation rates for bulk state in LaNi$_5$ and LaNi$_5$H$_7$.

	Lifetimes (ps)	Annihilation rate (ns^{-1})		
		La	Ni	H
LaNi$_5$	125	1.650	6.381	
La	130	1.193	5.156	1.379

It has been previously observed that the mean positron lifetime increases from the bulk lifetime up to 180 ps during hydrogen absorption in LaNi$_5$ [7]. The component analysis for the positron lifetime spectra has revealed that the positron lifetime for the lattice defects formed during hydrogen absorption is 180–190 ps (K. Sakaki, H. Araki, Y. Shirai, unpublished data). In order to estimate the structure of the lattice defects, we have performed positron lifetime calculations for various monovacancies and divacancies in LaNi$_5$H$_7$. The configuration of the hydrogen atoms around the vacancy is important for the construction of the model clusters on vacancies, because the hydrogen atoms around the vacancy affect the positron lifetime. After hydrogen desorption, a small amount of hydrogen still remains in LaNi$_5$. The hydrogen release temperature of the residual hydrogen was examined by a quadrupole mass spectrometer for the isochronally annealed LaNi$_5$ after hydrogen desorption [18]. The release temperature was found to coincide with the vacancy migration temperature. This result indicates that the residual hydrogen is mainly trapped at vacancies and vacancy clusters. Thus, when constructing model clusters for the vacancy states of LaNi$_5$H$_7$, the hydrogen atoms around the vacancy are not removed. The positron lifetime for La vacancy in LaNi$_5$, 241 ps, is longer than that of the experimental values of 180–190 ps. The result indicates that La vacancies are not included in the lattice defects formed during hydrogen absorption. Thus, La site is not taken into account as vacancy site. In the case of Ni site, there are three different sites in LaNi$_5$H$_7$. In the present work, the positron lifetimes were calculated for Ni$_1$–Ni$_2$, Ni$_1$–Ni$_3$, Ni$_2$–Ni$_3$ and Ni$_3$–Ni$_3$ divacancies which are the nearest-neighbor pairs. On Ni$_3$–Ni$_3$ divacancy, two types of Ni$_3$–Ni$_3$ pair are taken into account, because the second nearest length of Ni$_3$–Ni$_3$, 2.7061 Å, is close to the first nearest length, 2.7029 Å. The calculated positron lifetimes for Ni monovacancies and divacancies are given in Table 3. Although the lattice constants of LaNi$_5$H$_7$ are longer than those of LaNi$_5$, the positron lifetimes for the Ni monovacancies in LaNi$_5$H$_7$ are close to those in LaNi$_5$. This is because the hydrogen atoms around the Ni monovacancies in LaNi$_5$H$_7$ contribute to the positron annihilation. The Ni divacancies show various positron lifetimes ranging from 173 to 201

Table 3
Positron lifetimes for monovacancy and divacancy in $LaNi_5H_{7-}$

		Lifetimes (ps)
Experimental lifetime for defects		180–190
Monovacancy	Ni_1	161
	Ni_2	163
	Ni_3	173
Divacancy	Ni_1–Ni_2	173
	Ni_1–Ni_3	184
	Ni_2–Ni_3	183
	Ni_3–Ni_3 (1st NN)	201
	Ni_3–Ni_3 (2st NN)	187

ps. In the case of the Ni_1–Ni_2 divacancy, one hydrogen atom bonded to the Ni_3 atom exists between the Ni_1 and Ni_2 sites. The existence of the hydrogen atom results in the shortest positron lifetime of 173 ps for the Ni_1–Ni_2 divacancy. The Ni_3–Ni_3 divacancy (first NN), which shows the longest positron lifetime, has the largest free volume because the hydrogen atoms bonded to the two Ni_3 atoms is also removed by the forming of the Ni_3–Ni_3 divacancy. The comparison between the calculated positron lifetimes and the experimental data indicates that the major lattice defects introduced during hydrogen absorption are the Ni–Ni divacancies. By taking account of the lattice relaxation around the defects which is ignored in our calculations, the possibility of the formation of triple Ni vacancies is also considered.

4.3. Vacancy clusters in $LaNi_5$

As mentioned above, the lattice defects introduced during hydriding still exist in $LaNi_5$ after hydrogen desorption. Fig. 2 shows the result of the component analysis of the lifetime spectra during isochronal annealing of $LaNi_5$ after hydrogen absorption (K. Sakaki, H. Araki, Y. Shirai, unpublished data). The increase in the positron lifetime of the vacancy clusters in the range from 423 to 673 K indicates that three-dimensional vacancy clusters (voids) are formed by vacancy migration. In order to estimate the size and structure of the vacancy clusters, we have performed positron lifetime calculations for two types of vacancy clusters. One is composed of only Ni vacancies and the other includes Ni and La vacancies. While various geometries of vacancies can be considered for the vacancy clusters, we select the model clusters having a high symmetry because of the limitation of the computer resources. Fig. 3 shows the calculated positron lifetimes for the vacancy clusters as a function of the vacancy cluster size. The positron lifetime increases linearly with the vacancy cluster size up to the five Ni vacancy clusters. The increase in the positron lifetime for the vacancy clusters composed of only Ni atoms saturates to the lifetime of 280 ps which is shorter than the measured lifetime shown in Fig. 2. The vacancy clusters having larger positron lifetime cannot be formed by only Ni vacancies. Thus, the vacancies formed by hydriding may become microvoids composed of Ni and La vacancies in the temperature range of 423–623 K.

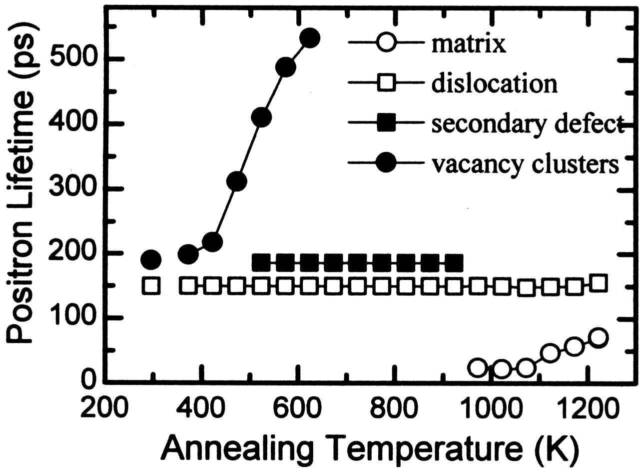


Fig. 2. Change in positron lifetime during the isochronal annealing of $LaNi_5$ after hydrogen desorption.

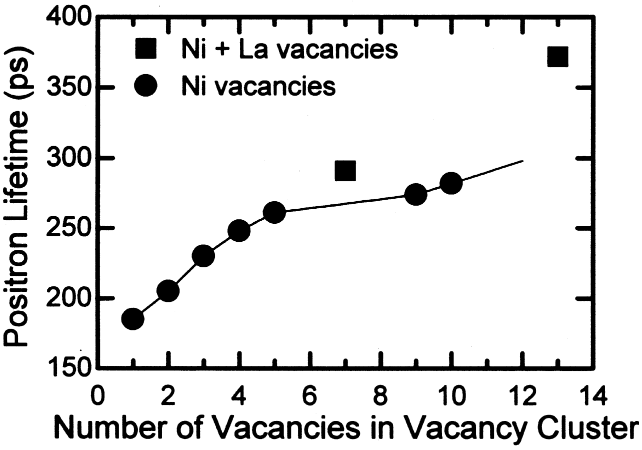


Fig. 3. Calculated positron lifetimes as a function of the number of vacancies in vacancy clusters in La Ni_{5-}.

5. Conclusion

We have performed the theoretical calculations of the positron lifetimes for the bulk and vacancy states of $LaNi_5$ and $LaNi_5H_7$ using first principles electronic structure calculations. The lattice defects in $LaNi_5$ formed during hydrogen absorption and the agglomeration of vacancy clusters after hydrogen desorption by isochronal annealing have been investigated by comparing the calculated positron lifetimes and measured data. The increase in the positron lifetime during hydrogen absorption can be ascribed to the formation of lattice defects composed of two or three Ni vacancies. The residual vacancies after hydrogen desorption become microvoids composed of Ni and La vacancies by isochronal annealing.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. This work was partly carried out at the Strategic Research Base 'Handai Frontier Research Center' supported by the Japanese Government's Special Coordination Fund for Promoting Science and Technology.

References

[1] P. Fischer, A. Furrer, G. Busch, L. Schlapbach, Helv. Phys. Acta 50 (1977) 421.
[2] G. Kim, C. Chun, S. Lee, J. Lee, Acta Metall. Mater. 42 (1994) 3157.
[3] G. Kim, S. Lee, K. Lee, C. Chun, J. Lee, Acta Metall. Mater. 43 (1995) 2233.
[4] H. Inui, T. Yamamoto, M. Yamaguchi, in: Proceedings of the First International Symposium on New Protium Function, Osaka, Japan, September 16, 1999, pp. 28–35.
[5] H. Inui, T. Yamamoto, M. Yamaguchi, in: Abstracts of the Fall Meeting of the Japan Institute of Metals, 1999, p. 126, (in Japanese).
[6] T. Yamamotio, M. Hirota, H. Inui, M. Yamaguchi, Metals Mater. 6 (2000) 609.
[7] Y. Shirai, H. Araki, T. Mori, W. Nakamura, K. Sakaki, J. Alloys Comp. 330–332 (2002) 125.
[8] H. Adachi, M. Tsukada, C. Satoko, J. Phys. Soc. Jpn. 45 (1978) 875.
[9] D.E. Ellis, G.S. Painter, Phys. Rev. B 2 (1970) 2887.
[10] E. Broński, R.M. Nieminen, Phys. Rev. B 34 (1986) 3820.
[11] J. Arponen, E. Pajanne, Ann. Phys. (NY) 121 (1979) 343.
[12] M.J. Puska, R.M. Nieminen, J. Phys. F: Met. Phys. 13 (1983) 333.
[13] L. Lantto, Phys. Rev. B 36 (1987) 5160.
[14] R.S. Mulliken, J. Chem. Phys. 23 (1955) 1833.
[15] P. Thompson, J.J. Reilly, J.M. Hastings, J. Less-Common. Met. 129 (1987) 105.
[16] C. Lartigue, A. Le Bail, A. Percheron-Guégan, J. Less-Common Met. 129 (1987) 65.
[17] K. Tatsumi, I. Tanaka, H. Inui, K. Tanaka, M. Yamagushi, H. Adachi, Phys. Rev. B 64 (2001) 184105.
[18] K. Sakaki, H. Araki, Y. Shirai, in: S. Hanada, Z. Zhong, S.W. Nam, R.N. Wright (Eds.), Proc. Fourth Pacific Rim Int. Conf. on Advanced Materials and Processing (PRICM4), The Japan Institute of Metals, 2001, p. 437.