ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 454–457

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Muon localization along a six-fold ring-shaped site and muon quantum hopping in $GdNi_5$

A.M. Mulders[a,*], P.C.M. Gubbens[b], C.T. Kaiser[b], A. Amato[c], F.N. Gygax[d], A. Schenck[d], P. Dalmas de Réotier[e], A. Yaouanc[e], K.H.J. Buschow[f], F. Kayzel[f], A.A. Menovsky[f]

[a]*School of Physics and Materials Engineering, Monash University, Clayton, Victoria 3800, Australia*
[b]*Interfaculty Reactor Institute, Technical University, Delft, The Netherlands*
[c]*Laboratory for Muon-Spin Spectroscopy, Paul Scherrer Institute, Zurich, Switzerland*
[d]*Institute for Particle Physics, ETH, Zurich, Switzerland*
[e]*Commissariat à l'Energie Atomique, DRFMC, F-38054 Grenoble Cedex 9, France*
[f]*Van der Waals–Zeeman Instituut, University of Amsterdam, Amsterdam, The Netherlands*

Abstract

In $GdNi_5$, the muon localizes at the 3*f* interstitial site and below ~80 K a second muon site becomes populated, either at the 6*m* or 6*k* site. These latter sites are located in a ring surrounding the (0, 0, $\frac{1}{2}$) site and the muon occupies all six sites within the time range of the experiment (10^{-9} s). This ring site is metastable and the muon hops to the preferred 3*f* site. We determine the mean time of stay of the muon in the ring site and show that it is governed by a multi-phonon quantum diffusion process. The coincidence energy is measured to be $E_a = 272$ (10) K and the tunneling matrix element $J = 0.11$ (2) meV.

Keywords: Muon diffusion; Muon spin rotation and relaxation

PACS: 66.35.+a; 76.75.+i

1. Introduction

The magnetic properties of the hexagonal compound (*P6/mmm*) $GdNi_5$ have been studied intensively and are well understood. The Gd 4*f* shell is spherical and therefore its magnetic moment is insensitive to crystal field effects. The magnetic interaction is strong compared to other rare earth atoms (de Gennes scaling) and governs the second order magnetic phase transition at $T_C = 30.85$ K. $GdNi_5$ is a ferrimagnet with a Gd moment of 7 μ_B and an induced Ni moment of 0.16 μ_B. The moments are preferentially aligned along the *c*-axis and this anisotropy is caused by the dipolar interaction [1].

In general, the muon localizes interstitially inside its host and this may lead to a distortion of its near neighbour environment. Because of its positive charge, it acts as a light proton, i.e. it can be considered as a hydrogen like particle. At elevated temperatures the muon will diffuse through the lattice of its host and motional narrowing is commonly observed.

Two non equivalent muon sites become populated below 80 K in $GdNi_5$ [2]. One stable site, the 3*f* site, which is also occupied by the muons at temperatures above 80 K, and a metastable site, the 6*k* or 6*m* site, both located in a ring surrounding the 1*b* site (Fig. 1) and further referred to as 6_{ring}. The muon occupies the six 6_{ring} sites simultaneously within the time range of the μSR experiment

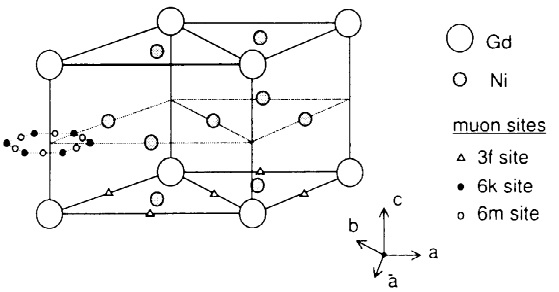

Fig. 1. Unit cell of $GdNi_5$ (hexagonal crystal structure, space group *P*6/*mmm*). The muon localizes at the 3*f* site in the whole temperature range and also below ~80 K in either the 6*m* (0.13, 0.26, $\frac{1}{2}$) or 6*k* (0.225, 0, $\frac{1}{2}$) sites. The muon occupies all six sites within the time range of the experiment [2,4]. Similar work on UNi_2Al_3 [3] suggests that the muon forms an extended localized ring-shaped orbit. We refer to this site as the 6_{ring} site.

*Corresponding author.

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01592-4

(10^{-9} s), forming either a local coherent tunneling state or exhibiting fast hopping along the ring. An equivalent muon localization has been observed recently in the isostructural compound UNi_2Al_3 [3], where the authors show that the muon actually forms an extended state over the six ring sites. In this paper we report on the muon hopping from the metastable 6_{ring} site to the $3f$ site which occurs between 35 and 80 K. Below 35 K we also discuss the analogue with hybrides and deuterides of $LaNi_5$. This work is a continuation of the research in Refs. [4] and [5].

2. Experimental

A $GdNi_5$ single crystal was prepared by the Czochralski method in Amsterdam from starting materials of at least 99.99% purity. The sample was shaped into a sphere (diameter of 5.5 mm) with spark erosion in order to avoid demagnetisation corrections [2]. The μ^+SR transverse field measurements took place at the πM3 beamline of PSI and the data presented here were taken with the *a* or *c* axes parallel to $\mathbf{B}_{ext}$ ($B_{ext}=0.6$ T) between 35 and 80 K. In this temperature region the muon hopping from the 6_{ring} to the $3f$ site is prominent. Below 35 K the muon remains at the 6_{ring} site during its lifetime when implanted, whereas above 80 K the muon does not populate the 6_{ring} site in the time window of the experiment (longer than $\sim$1 ns).

In the paramagnetic state of $GdNi_5$, the depolarization of the implanted muon ensemble is mainly caused by the Gd spin fluctuations. The coupling between the muon spin and the Gd spins is primarily due to the dipolar interaction and its strong angular dependence makes the damping rate depend on the muon site and the initial direction of the muon spin with respect to the crystal axes. The muon precession frequency is also muon site specific for the same reasons.

Including the muon hopping, the total polarization function of the muon ensemble writes [6]:

$$P_X(t) = f_{3f}\, e^{-\lambda_X^{(3f)}t}\cos\left(\omega_\mu^{(3f)}t\right) + f_{\text{ring}}\left\{e^{-\check{\lambda}_X^{(\text{ring})}t}\cos(\omega_\mu^{(\text{ring})}t) + \frac{e^{-\lambda_X^{(3f)}t}\cos(\omega_\mu^{(3f)}t+\theta_m) - e^{-\check{\lambda}_X^{(\text{ring})}t}\cos(\omega_\mu^{(\text{ring})}t+\theta_m)}{\tau_{\text{ring}}\sqrt{(\check{\lambda}_X^{(\text{ring})}-\lambda_X^{(3f)})^2 + 4(\delta\omega_\mu)^2}}\right\} \quad (1)$$

with

$$\check{\lambda}_X^{(\text{ring})} = \lambda_X^{(\text{ring})} + \frac{1}{\tau_{\text{ring}}},$$

$$\delta\omega_\mu = \frac{\omega_\mu^{(\text{ring})} - \omega_\mu^{(3f)}}{2} \text{ and } \tan\theta_m = \frac{2\,\delta\omega_\mu}{\check{\lambda}_X^{(\text{ring})} - \lambda_X^{(3f)}}$$

f_{ring}, f_{3f}, $\lambda_X^{(ring)}$, $\lambda_X^{(3f)}$, $\omega_\mu^{(ring)}$, $\omega_\mu^{(3f)}$ are the relative weight factors ($f_{ring}+f_{3f}=1$), damping rates and precession frequencies of the muon at the specific sites.

We analyzed our spectra with Eq. (1) and a fixed ratio $f_{3f}/f_{ring}=1/2$. It is difficult to separate $\lambda_X^{(ring)}$ and τ_{ring} since the fit is mostly sensitive to the sum of both, $\check{\lambda}_X^{(ring)} = \lambda_X^{(ring)} + 1/\tau_{ring}$. Therefore we have calculated $\lambda_X^{(ring)}$ and used this in our fits to extract τ_{ring}. This calculation is based on the experimental damping rates of the $3f$ site which resolve the magnetic Gd fluctuations (for general theory see for example Ref. [7]). It is briefly described in Ref. [5] and further details will be presented in a paper which is in preparation.

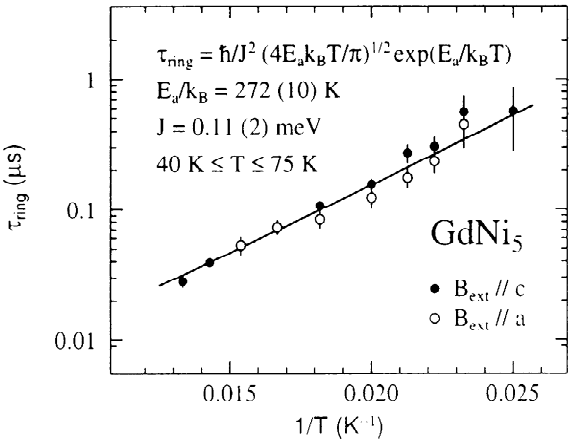

Fig. 2. Temperature dependence of the muon residence time at the 6_{ring} site. The orientation of the external field $\mathbf{B}_{ext}$ is indicated in the figure. The solid line is a fit to Eq. (2) but an Arrhenius law gives a similar result as discussed in the text. At $T=60$ and 65 K where only an open dot is visible, τ_{ring} is equal for both directions of $\mathbf{B}_{ext}$.

The result for $\tau_{ring}(T)$ is plotted in Fig. 2. The consistency between $\tau_{ring}(T)$ for $\mathbf{B}_{ext}\|c$ and $\mathbf{B}_{ext}\perp c$ supports the validity of our whole method of analysis.

3. Muon hopping analysis

The functional form of the temperature dependence of the mean muon residence time at the 6_{ring} site will be determined by the hopping mechanism [8]. The temperature dependence of τ_{ring} (Fig. 2) suggests either a multi-phonon assisted tunneling process is at play or simply a muon jumping over the energy barrier between two interstitial sites. In the first process, multi-phonon processes equalize for an extremely short time (of the order of 10^{-13} s) the local energy levels of the potential well where the muon is localized and where it likes to jump. When this occurs the muon tunnels through the energy barrier between the two sites. Within the framework of the small polaron theory [8,9]:

$$\tau_{\mathrm{ring}} = \frac{\hbar}{J^2}\sqrt{\frac{4E_a k_B T}{\pi}}\exp\left(\frac{E_a}{k_B T}\right) \quad (2)$$

where E_a is an energy necessary to get the coincidence configuration of both sites and J the tunneling matrix element. From Fig. 2 we obtain $E_a = 272(10)$ K and $J = 0.11(2)$ meV. The jumping mechanism over the energy barrier is described by an Arrhenius law. The data of Fig. 2 are equally well described by this law with $E_a = 244(10)$ K and $\tau_0 = 1.2(2)$ ns. $1/\tau_0$ is the attempt frequency. But, referring to the discussion of Karlsson [10], the anomalous low value of τ_0 indicates that the muon mobility is governed by the multi-phonon assisted tunneling process.

Multi-phonon assisted muon tunneling has been reported before [11,12] in Al and Cu and the spread in J is large: ~1 meV for Al and 36 μeV for Cu. Our value of 0.12 meV for $GdNi_5$ seems consistent with these results. Note that the uncertainty for Al is relatively large [10], in contrast to $GdNi_5$. The value of E_a for Al (32 meV [10]) and $GdNi_5$ (23 meV) are in the same range.

For comparison we mention recent results obtained on $PrIn_3$ [13] and $CuInSe_2$ [14]. The muon hopping is observed at higher temperature, between 150 and 250 K, and analyzed with an Arrhenius law. The energy barrier for the muon hopping in these compounds is substantially higher, 3260 and 2552 K, respectively.

It is interesting to compare the present results with those obtained on hydrides (deuterides) of $LaNi_5$. The relevant hydride phase in this respect is the so-called α-phase in which the hydrogen concentration is comparatively small. From results of powder neutron diffraction studies, Soubeyroux et al. [15] concluded that the D atoms occupy primarily the 12*n* interstitial position near the basal plane. Although their refinement does not exclude occupation of the 3*f* basal plane position, these authors consider occupation of the latter site less likely because of hole size considerations. The low D content and the associated low experimental accuracy does, furthermore not exclude D occupation of also the 6m site. Hempelmann et al. [16] used inelastic neutron scattering to study the localized vibrations of H atoms in the α-phase. The conclusion of these authors is that the H atoms occupy the 3*f* site, although they also found evidence for the occupation of a second interstitial site, 6*m*. Summarizing these results, it can be stated that H(D) atoms tend to primarily occupy interstitial positions located in (or near) the basal plane. Of the 3*f* and 12*n* positions the former (octahedral) site is energetically more attractive in view of the fact that it is coordinated by four Ni atoms and 2 La atoms. The (tetrahedral) 12*n* site is coordinated by 3 Ni atoms but only a single La atom. Therefore, it is reasonable to expect that the 3*f* site is preferred, in agreement with our experiments.

As for the muon localization in isostructural compounds, a range of muon sites have been reported. In $PrNi_5$ the 6*i* site is occupied [17], in UPd_2Al_3 it is the 1*b* site [18] and in UNi_2Al_3, besides the 6_{ring} site similar as in $GdNi_5$, the 2*d* site [3] is occupied at low temperatures.

4. Conclusions

In this paper we have reported on the muon dynamics in $GdNi_5$ between 35 and 80 K and observed clear signatures of the quantum behaviour of the muon. The muon localizes only at the 3*f* interstitial site at elevated temperatures and below ~80 K a second muon site becomes populated. This is the so-called 6_{ring} site and after localization in this ring site, the muon hops to the 3*f* site. The 3*f* site as preferred muon site and the 6*m* site as a second site, is in agreement with the hydrogen sites found in $LaNi_5H_x$.

We have determined the residence time of the muon at the 6_{ring} site in $GdNi_5$ as function of temperature. It is observed that the muon hopping from the 6_{ring} site to the 3*f* site slows down with decreasing temperature and is well described by a multi-phonon assisted tunneling process. We find coincidence energy $E_a = 272(10)$ K and tunneling matrix element $J = 0.11(2)$ meV.

References

[1] A. Yaouanc, P. Dalmas de Réotier, P.C.M. Gubbens, A.M. Mulders, F.E. Kayzel, J.J.M. Franse, Phys. Rev. B 53 (1996) 350.
[2] A.M. Mulders, Complex Magnetic Phenomena in Rare Earth Intermetallic Compounds, Thesis, Chapter 6, Delft University of Technology, 1998.
[3] A. Schenck, N.K. Nato, G. Solt, D. Andreica, F.N. Gygax, M. Pinkpank, A. Amato, Eur. Phys. J. B 13 (2000) 245;
A. Amato, D. Andreica, F.N. Gygax, M. Pinkpank, N.K. Sato, A. Schenck, G. Solt, Physica B 289–290 (2000) 447.
[4] A.M. Mulders, C.T. Kaiser, P.C.M. Gubbens, A. Amato, F.N. Gygax, M. Pinkpank, A. Schenck, P. Dalmas de Réotier, A. Yaouanc, K.H.J. Buschow, F. Kayzel, A. Menovsky, Pysica B 289–290 (2000) 451.
[5] A.M. Mulders, C.T. Kaiser, P.C.M. Gubbens, A. Amato, F.N. Gygax, A. Schenck, P. Dalmas de Réotier, A. Yaouanc, K.H.J. Buschow, F. Kayzel, A. Menovsky, Hyperfine Interact. (2001) accepted for publication.
[6] A. Möslang, H. Graf, G. Balzer, E. Recknagel, A. Weidinger, Th. Wichert, R.I. Grynszpan, Phys. Rev. B 27 (1983) 2674.
[7] A. Yaouanc, P. Dalmas de Réotier, E. Frey, Phys. Rev. B 47 (1993) 796.
[8] V.G. Storchak, N.V. Prokof'ev, Rev. Mod. Phys. 70 (3) (1998) 929.
[9] C.P. Flynn, A.M. Stoneham, Phys. Rev. B 1 (1970) 3966.
[10] E. Karlsson, Hyperfine. Interact. 97/98 (1996) 305.
[11] D. Herlach, in: J. Devreese (Ed.), Recent Developments in Condensed Matter Physics, Vol. 1, Plenum Press, New York, 1981.
[12] R. Kadono, J. Imazato, T. Matsuzaki, K. Nishiyama, K. Nagamine, T. Yamazaki, D. Richter, J.-M. Welter, Phys. Rev. B 39 (1989) 23.
[13] G. Alexandrowicz, T. Tashma, M. Socolovsky, A. Amato, A. Grayevsky, F.N. Gygax, M. Pinkpank, A. Schenck, N. Kaplan, Phys. Rev. Lett. 82 (1999) 1028.
[14] J.M. Gil, P.J. Mendes, L.P. Ferreira, H.V. Alberto, R.C. Vilao, N. Ayres de Campos, A. Weidinger, Y. Tomm, Ch. Niedermayer, M.V. Yakushev, R.D. Tomlinson, S.P. Cottrell, S.F.J. Cox, Phys. Rev. B 59 (1999) 1912.

[15] J.L. Soubeyroux, A. Percheron-Guegan, J.C. Achard, J. Less-Common Metals 129 (1987) 181.
[16] H. Hempelmann, D. Richter, G. Eckold, J.J. Rush, J.M. Rowe, M. Montoya, J. Less-Common Metals 104 (1984) 1.
[17] R. Feyerherm, A. Amato, A. Grayevsky, F.N. Gygax, N. Kaplan, A. Schenck, Z. Phys. B 99 (1995) 3.
[18] R. Feyerherm, A. Amato, F.N. Gygax, A. Schenck, C. Geibel, F. Steglich, N. Sato, T. Komatsubara, Phys. Rev. Lett. 73 (1994) 1849.