ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 376–380

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Magnetism in β-DyD_{2+x} and β-HoD_{2+x} studied with positive muons

F.N. Gygax[a,*], P. Vajda[b], D. Andreica[a], M. Pinkpank[a], A. Schenck[a]

[a] *Institute for Particle Physics of ETH Zürich, CH-5232 Villigen PSI, Switzerland*

[b] *Laboratoire des Solides Irradiés, Ecole Polytechnique, F-91128 Palaiseau Cedex, France*

Abstract

We have examined by μSR spectroscopy the four polycrystalline samples β-$HoD_{2.0}$, β-$HoD_{2+0.12}$, β-$DyD_{2.0}$, and β-$DyD_{2+0.135}$, specially to probe their magnetic short-range order (SRO) configurations. The temperature dependencies of the muon-spin relaxation rates for $HoD_{2.0}$, $HoD_{2.12}$, and $DyD_{2.0}$ show similar behavior. For each compound *i* one can define a 'critical' temperature T_{ci} (around 5–8 K) at which the relaxation rate λ_i is maximum. In the extended critical region T_{ci}–$4T_{ci}$ the rate $\lambda_i(T)$ can be fitted by the trial function $\lambda_i = \alpha_i[(T - T_{ci})/T_{ci}]^{-\nu_i}$. The critical exponents ν_i are compared to theoretical predictions. $DyD_{2.135}$ shows different features. With decreasing temperature, starting at 300 K, an increasing fraction of the initial μ^+ polarization is lost, due to the increasing proportion of random local fields fluctuating with rates of 10^8–10^9 s^{-1} at the μ^+ site. Below 10 K a spontaneous Larmor precession signal, corresponding to a field of 0.66 T, is observed. Model calculations of the local field at the μ^+ are performed, assuming commensurate or incommensurate magnetic structures. One infers that a commensurate SRO is likely to develop below 10 K in $DyD_{2.135}$.

Keywords: Rare-earth deuterides; Magnetism; Muon spin relaxation

1. Introduction

The pure rare-earths (R) Dy and Ho crystallize in the hcp structure, which is conserved when H (or D) is added to form the metallic solid solution phases (α or α* phase), RH_y. In general, the equally metallic dihydride β-phase R-compounds, i.e. β-RH_2, possess the CaF_2-type structure: the R atoms form a fcc unit cell, in which the H atoms occupy ideally all *tetrahedral* interstitial sites. This structure is also preserved when additional H atoms are inserted on *octahedral* interstices, giving the superstoichiometric compounds β-RH_{2+x}, with $0 \le x \le 0.23$ for DyH_{2+x} and $0 \le x \le 0.19$ for HoH_{2+x}. The insulating trihydride or γ phase (ideally $RH_{3.0}$) crystallizes in the hexagonal so-called HoD_3 structure. In that case both tetrahedral sites and the one octahedral site are filled up by H or D. A general review of the R-H systems is found in [1], the β-DyD_{2+x} and β-HoD_{2+x} compounds with their magnetic features are particularly treated in Refs. [2–5].

In β-$DyD_{2.0}$ one observes, below $T_2 = 5.0(2)$ K, two sinusoidally modulated magnetic configurations, one for $T \le T_1 \approx 2.5$–3.5 K, the other for $T_1 \le T \le T_2$, with a partial overlap of about 0.5 K between them [4]. The magnetic structure below T_1 is nearly commensurate, with $\boldsymbol{k}_1$ close to (1/4, 1/4, 3/4), that between T_1 and T_2 is more incommensurate, with $\boldsymbol{k}_2 = (0.275, 0.275, 0.750)$. For β-$HoD_{2.0}$, below the Néel temperature $T_2 = 6.3$ K, the magnetic structure is that of a modulated incommensurate antiferromagnet (AF), with a slightly temperature-dependent propagation vector [5]. From $T_1 \sim 3$–4 K on and down to 1.4 K, it is coexistent with a commensurate AF configuration, modulated with $\boldsymbol{k}_1 = (1/4, 1/4, 3/4)$. The transition at T_1 is strongly hysteretic for both configurations. Magnetic fluctuations [short-range order (SRO) magnetism] are observed for $T > T_1$, and up to 45 K.

The excess of H in the superstoichiometric dihydrides can change the magnetism drastically, leading sometimes to its total suppression and sometimes to new magnetic transitions at low temperature [1]. β-$DyD_{2.135}$ shows no magnetic long-range order (LRO) but exhibits a broad bump in the cold-neutron diffraction spectrum, appearing for $T < 4$–5 K, attributed to SRO domains [4]. β-$HoD_{2.12}$ exhibits intense SRO magnetism below $T = 8$ K, which seems to be related to that existing for $T > T_1$ in the pure dideuteride HoD_2 [5].

We have examined by μSR spectroscopy the two

*Corresponding author. Tel.: +41-56-310-3225; fax: +41-56-310-4362.

E-mail address: fredy.gygax@psi.ch (F.N. Gygax).

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01541-9

dideuteride systems β-HoD_{2+x} (particularly with $x = 0$ and $x = 0.12$) and β-DyD_{2+x} (particularly with $x = 0$ and $x = 0.135$). It is assumed that in β-RD_{2+x} the implanted positive muons, as the other additional hydrogen isotopes, will occupy some of the free octahedral interstices.

2. $HoD_{2.0}$, $HoD_{2.12}$, and $DyD_{2.0}$

The temperature dependencies of the zero-field (ZF) relaxation data for the three compounds $HoD_{2.0}$, $HoD_{2.12}$, and $DyD_{2.0}$ show similar behavior, and the longitudinal-field (LF) data are identical to the corresponding ZF data, Fig. 1 (for a preliminary report see also Ref. [6]). The transverse-field (TF) measurements carried out at 10 mT in $DyD_{2.0}$ show also a relaxation behavior close to the one of the ZF and LF data. For each compound i one can define a 'critical' temperature T_{ci} (around 5–8 K) at which the relaxation rate λ_i is maximum — for the two Ho compounds λ_i even hits the μSR resolution limit around T_{ci}.

The μSR signals are fitted with an exponential relaxation function, i.e. with a relaxation rate λ_i, associated with an initial asymmetry A_i, in general also a free fit parameter. Above T_{ci} the signal accounts for a constant fraction of 0.8–0.9 of the muons [asymmetries $A_i(T) \approx$ 22–24%]; this fraction drops sharply to about 0.25 below T_{ci}. Hence, a part of the muons is not observed in the signal, particularly below T_{ci}.

Decreasing the temperature towards T_{ci}, one sees clearly the critical behavior. Unfortunately, the experimental conditions (e.g. T gradients in the sample) and particularly the too fast relaxation do not allow a precise study of λ_i in the usually very narrow critical domain with $T - T_{ci} \ll T_{ci}$. Each one of the critical temperatures T_{ci} can be identified with the highest transition temperature detected by bulk methods and/or neutron scattering in that material. For $HoD_{2.0}$ it is close to the Néel temperature $T_2 = 6.3$ K, for $HoD_{2.12}$ near the temperature $T_{SRO} \approx 8$ K below which SRO magnetism is detected [5], and for $DyD_{2.0}$ close to $T_2 = 5.0(2)$ K below which an incommensurate AF configuration is observed [4]. With these T_{ci} values for each sample the parameter $\lambda_i(T)$ can well be fitted by the trial function $\lambda_i = \alpha_i[(T - T_{ci})/T_{Eqs.i}]^{-\nu_i}$ in the 'extended' critical region T_{ci}–$4T_{ci}$, see the fit lines in Fig. 1. For the three compounds the ν_i parameters are very close to 0.5. (The measurements were made on polycrystalline samples, thus one cannot exclude that the observed exponents result possibly from an orientational average over several different values in an anisotropic non-S state system.) The fact that magnetic SRO seems to be present well above T_{ci} is remarkable.

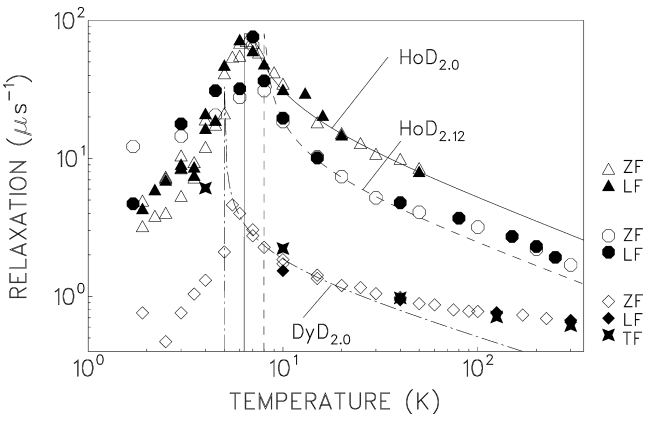

Fig. 1. Temperature dependence of the ZF, LF, and low-TF μSR relaxation rate λ in three β-RD_{2+x} compounds. The lines are functions of the form $\lambda_i = \alpha_i[(T - T_{ci})/T_{ci}]^{-\nu_i}$ fitted to the data in the domains $T_{ci} < T < 4T_{ci}$. The vertical lines indicate T_{ci}.

How is this behavior explained by the theory? It is of course hazardous to compare the exponents ν_i obtained for a very large T range above T_{ci} to critical exponents given by theories usually only valid in a rather small domain of the reduced temperature $t \equiv (T - T_{ci})/T_{ci}$, e.g. $t < 10^{-2}$. Let us however mention three cases.

(a) For an isotropic antiferromagnet in the critical regime just above $T_{ci} = T_N$, calculations [7,8] give $\lambda \propto \xi^{1/2}$, where $\xi = \xi_0[(T - T_N)/T_N]^{-\nu}$ is the correlation length of the spin clusters near T_N. Since $\nu = 0.705$, one expects $\lambda \propto [(T - T_n)/T_N]^{-0.35}$.

(b) For an uniaxial antiferromagnet in the same T regime, Ref. [7] obtains $\lambda \propto \xi$.

(c) Considering spin lattice relaxations induced by paramagnetic fluctuations far above any critical region, Hartmann et al. [9] determine $\lambda \propto \tau_c = (\tau_{ff}^{-1} + \tau_{fk}^{-1})^{-1}$. τ_c is a local correlation time associated with the ionic moments; it is composed of a T-independent term, τ_{ff}, stemming from the RKKY interaction, and the term τ_{fk}, proportional to T^{-1}, induced by the Korringa mechanism. With such additional components for λ_i one could clearly improve the fit for the higher temperatures, see Fig. 1. However, lacking additional input, the description of the data will remain phenomenological.

On the low-temperature side of T_{ci} a sharp increase of λ_i is also observed when T approaches T_{ci}. However, the data show unusual scattering and the exact dependencies could not be determined precisely, so far, because of two reasons: (i) only a reduced fraction of the muons is visible in the signal ($A_i = 3$–8%, varying), and (ii) hysteretic behavior is encountered in part of the measurements, as also observed by neutron scattering and resistivity studies, and possibly related to the presence of two overlapping AF phases [4,5].

3. $DyD_{2.135}$

The temperature dependence of the μ^+-spin relaxation measured in $DyD_{2.135}$ contrasts with the results obtained in the three other samples. It starts with the difficulty to find adequate fitting functions for the spectra of the different

measurement series (except for the high-TF runs, $B \geq 0.2$ T, taken above 150 K). The problem, first reported in Ref. [6], arises from the fact that with decreasing temperature, starting at 300 K, an increasing fraction of the initial μ^+ polarization is lost, most probably due to the increasing proportion of random local fields fluctuating with rates of the order of 10^8–10^9 s^{-1} at the μ^+ site — fast enough to prevent direct observation of the polarization decay. Fields fluctuating at such rates would have to show a strength of the order of 0.6 T to produce the observed depolarization. Indeed, below 10 K a spontaneous Larmor precession signal, corresponding to a field of 0.66 T at the μ^+, is directly observed.

3.1. ZF, LF and low-TF measurements above 10 K

The most satisfying spectrum description of the ZF and LF measurement series is phenomenological. It is obtained by a stretched exponential relaxation function, $\propto \exp[-(\lambda t)^{\beta}]$, with temperature independent asymmetry, and must reflect the peculiar distribution of random fluctuating-field rates. The low-TF (10 mT) calibration measurements can be fitted by a signal oscillating at the Larmor frequency, again relaxing with a stretched exponential function. The associated λ and β parameters are shown in Fig. 2.

A preliminary evaluation indicates: (i) At 300 K λ increases from 1.3 μs^{-1} in ZF to ~2.0 μs^{-1} in TF (10 mT), then to 3.6 μs^{-1} in LF (25 and 50 mT); the β parameters are scattered around 0.45. (ii) With decreasing temperature all λ values increase, the trend becomes dramatic below 150 K, and the three $\lambda(T)$ dependencies seem to peak at the resolution limit around 80–90 K. The indicated decrease of λ with further decreasing T is not necessarily real, but probably a consequence of the stretched exponential fit. It reflects the important loss of polarization of a growing muon fraction, finally evident below 40 K, where the data can no longer be fitted because of missing initial asymmetry. (iii) The positive difference $\lambda_{LF} - \lambda_{ZF}$ increases with decreasing T. This difference suggests the existence of a *static* random field component, but from the ensemble of observations one concludes that the main part of the μ^+-spin relaxation is of *dynamic* origin. (For a discussion of the effect of static vs. dynamic random fields on muon-spin relaxation and the recourse to stretched exponential relaxation functions see, e.g. Ref. [10]).

3.2. Spontaneous precession signal

At temperatures below 10 K a rapidly attenuated spontaneous oscillation at a frequency of ~90 MHz is found in the ZF data, e.g. Fig. 3. This signal is well fitted by an exponential relaxation with a temperature independent asymmetry of the order of 5–6%. In addition, a small non-oscillating signal with exponential decay is also

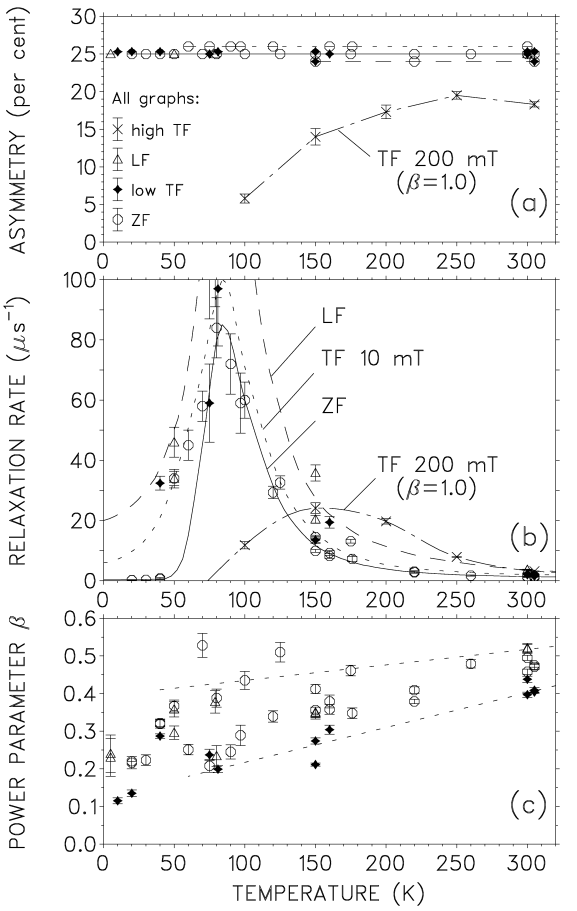

Fig. 2. ZF, LF and TF measurements in $DyD_{2.135}$ as a function of temperature. The μ^+ spin-relaxation signal is fitted with a stretched exponential function. For ZF, LF and low-TF data series the asymmetries (a) are assumed temperature independent, close to maximum, whereas λ (b) and β (c) are free fit parameters. For high-TF measurements ($B \geq 0.2$ T) the relaxing polarization is simply exponential ($\beta = 1.0$), whereas the asymmetries and λ are free parameters. The lines are only meant to indicate the trends.

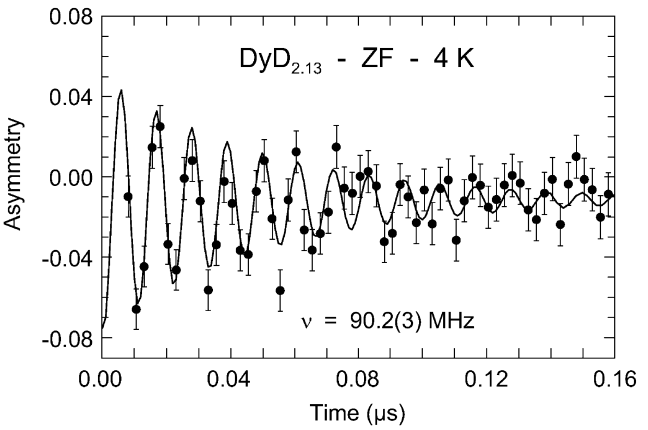

Fig. 3. $DyD_{2.135}$, ZF measurement at 4 K. A spontaneous 90.2(3) MHz precession is visible at the beginning of the spectrum.

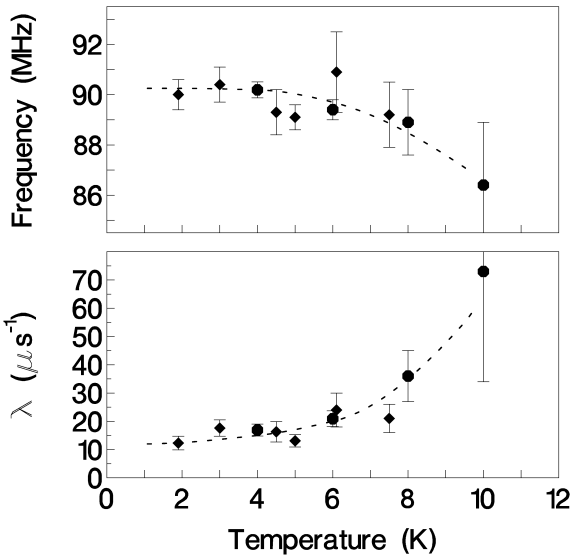

Fig. 4. Temperature dependence of the precession signal in ZF $DyD_{2.135}$. The signal is lost above 10 K.

present. The temperature dependencies of frequency and relaxation rate of the oscillating component are shown in Fig. 4. This component accounts for a fraction of the missing asymmetry in $DyD_{2.135}$ below ~80 K.

The 90 MHz signal is also observed in LF (up to 0.1 T) and low-TF data below 10 K. It is worth pointing out here that by contrast no spontaneous oscillation is detected in the three other β-RD_{2+x} compounds in the studied temperature range 2–300 K. Moreover, very recently performed ZF measurements in newly available samples of β-$DyH_{2.06}$ and β-$DyH_{2.09}$ [11], down to $T = 1.9$ K, do not reveal spontaneous precessions.

This 90 MHz precession signal corresponds to a field of 0.66 T at the μ^+ site. This can only be caused by some magnetic ordering (SRO?) of the Dy-ions moments seen by a noticeable fraction of the muons.

The only indication of magnetic ordering obtained from magnetic susceptibility measurements [3] in $DyH_{2.14}$ (assumed magnetically equivalent to the deuteride with similar x) is a broad χ maximum at $T_M = 10.1$ K, with possibly a shoulder at 13 K. The cold-neutron diffraction study in $DyD_{2.135}$ shows only a broad bump in the spectra appearing for $T < 4$–5 K. Both observations are interpreted as the appearance of SRO domains of ~30 Å correlation length. From the same studies in stoichiometric β-$DyD_{2.0}$ two LRO, sinusoidally modulated configurations, partially overlapping, are detected: the nearly commensurate structure with a propagation vector $\boldsymbol{k}_1 = (0.258, 0.273, 0.750)$, close to (1/4, 1/4, 3/4), below $T_1 \approx 2.5$–3.5 K and the more incommensurate structure with $\boldsymbol{k}_2 = (0.275, 0.275, 0.750)$ below $T_2 = 5.0(2)$ K. These neutron data indicate a magnetic Dy-ion spin oriented along [001].

Without a clear knowledge on the magnetic structure of $DyD_{2.135}$, we have considered two cases for a simple model calculation of the local field at the μ^+ site:

(i) One postulates the *commensurate* structure (1/4, 1/4, 3/4) mentioned above, close to the effective incommensurate modulation seen in $DyD_{2.0}$, around the μ^+. (This structure has to be short-range ordered to stay compatible with the bulk measurements in $DyD_{2.135}$.) The calculation yields a single non-zero field value for one half of the octahedral μ^+ sites, and a field exactly zero for the other half of the sites. The spectral distribution (considering a few reasonable assumptions in addition, i.e. a line broadening) is shown in Fig. 5. ZF data and model calculations agree very well. The magnetic moment on the Dy ion, oriented along [001], would have to be $|\mu| = 1.6\ \mu_B$ to yield the observed μ^+-precession frequency of 90 MHz. This is even more reduced with regard to the estimated $|\mu| = 3.5(5)\ \mu_B$ from neutron diffraction measurements in $DyD_{2.0}$ [4], which was already strongly quenched from the free-ion value of 10 μ_B by the cubic crystal field. A further reduction can be expected, after introduction of octahedral hydrogens, due to the broken symmetry of the cubic environment, leading eventually to a tetragonal deformation of the crystal field, with new levels which are very sensitive to the actual stoichiometry (see e.g. Ref. [1]).

(ii) Assuming the *incommensurate* structure with $\boldsymbol{k}_1 = (0.258, 0.273, 0.750)$, again with the Dy moment aligned along [001], one calculates the (broadened) spectral distribution shown by the broken line in Fig. 5 [12]. As usual for incommensurate modulations the distribution shows a very asymmetric peak with a non-vanishing low-field tail extending all the way to field zero. To fit a μSR spectrum associated to such a field distribution one needs the Bessel function $J_0(t)$ [12]. We have tried to fit the ZF measurements with such a function, but the results were not satisfying.

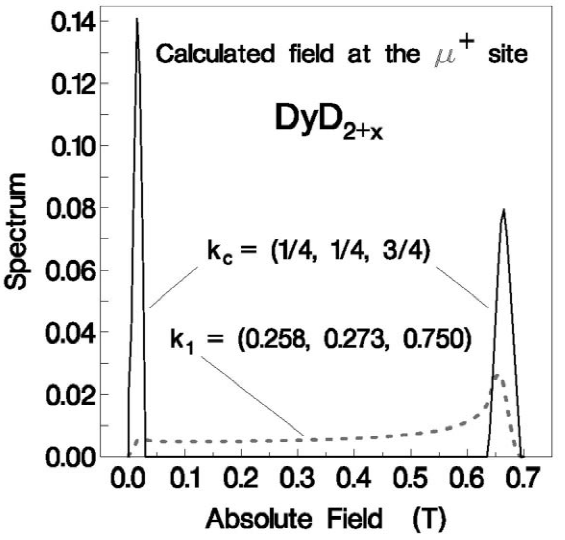

Fig. 5. Local field at the μ^+ site in $DyD_{2.135}$. Calculated spectral distributions for the modulated commensurate structure with $\boldsymbol{k}_c = (1/4, 1/4, 3/4)$, solid line, and the modulated incommensurate structure with $\boldsymbol{k}_1 = (0.258, 0.273, 0.750)$, broken line.

From this crude comparison one infers that a commensurate magnetic structure rather than an incommensurate one is likely to develop below 10 K in $DyD_{2.135}$, as indicated through resistivity measurements [1], and possibly related to octahedral-hydrogen lattice ordering in this system.

References

[1] P. Vajda, in: K.A. Gschneidner, Jr., L. Eyring (Eds.), Hydrogen in Rare-Earth Metals, Including RH_{2+x}, Handbook on the Physics and Chemistry of Rare Earths, Vol. 20, Elsevier, New York, 1995, p. 207.
[2] P. Vajda, J.N. Daou, Phys. Rev. B 45 (1992) 9749.
[3] A. Boukraa, P. Vajda, J.N. Daou, Z. Phys. Chem. 179 (1993) 413.
[4] P. Vajda, G. André, J. Hammann, Phys. Rev. B 55 (1997) 3028.
[5] P. Vajda, G. André, O.J. Zogal, Phys. Rev. B 57 (1998) 5830.
[6] F.N. Gygax, P. Vajda, D. Andreica, M. Pinkpank, A. Schenck, Physica B 289–290 (2000) 273.
[7] S.W. Lovesey, Hyperfine Interact. 72 (1992) 389.
[8] A. Schenck, F.N. Gygax, in: K.H.J. Buschow (Ed.), Magnetic Materials Studied by Muon Spin Rotation Spectroscopy, Handbook of Magnetic Materials, Vol. 9, Elsevier, Amsterdam, 1995, p. 57.
[9] O. Hartmann, E. Karlsson, R. Wäppling, J. Chappert, A. Yaouanc, L. Asch, G.M. Kalvius, J. Phys. F: Met. Phys. 16 (1986) 1593.
[10] Y.J. Uemura, Muon Science, in: S.L. Lee, S.H. Kilcoyne, R. Cywinsky (Eds.), SUSSP Publications and Institute of Physics Publishing, Bristol, 1999, p. 85.
[11] We are grateful to O.J. Zogal (Wroclaw) for the preparation of the Dy hydride samples.
[12] A. Schenck, in: S.L. Lee, S.H. Kilcoyne, R. Cywinsky (Eds.), Muon Science, SUSSP Publications and Institute of Physics Publishing, Bristol, 1999, p. 39.