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MUON DIFFUSION IN NIOBIUM IN THE PRESENCE OF TRAPS<sup>+</sup>

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ABSTRACT

We have investigated muon diffusion in niobium with controlled amounts of interstitial impurities. The polarization decay was interpreted in terms of a two-state model where the muon is alternatively in a state of free diffusion or in traps. A good fit of all data was obtained, yielding correlation times for the jump motion, as well as capture and release rates of the traps. The muons are found to be mobile in Nb down to 14 K.

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In this work we investigate the diffusion of positive muons in samples of niobium with controlled amounts of impurities and develop a model which makes it possible to understand and analyse the diffusion of muons in the presence of traps. The influence of defects must be better understood before the elementary diffusion processes in ideal lattices can be discussed. This influence is also a phenomenon of interest in itself. The problem is especially interesting for group Vb bcc metals, where extensive data on hydrogen diffusion are available for comparison<sup>1)</sup>. In these metals the muon spin rotation ( $\mu$ SR) results of different groups<sup>2,3)</sup> have so far been inconsistent, probably owing to differences in sample preparation and impurity content. It is known from diffusion studies of H in Nb-N samples that immobile interstitials (N) act as traps for the diffusing species (H) such that the diffusion is strongly affected<sup>4,5)</sup>.

Diffusion of muons in solids has already been studied in a number of cases and the principles of  $\mu$ SR experiments are by now well known from review articles<sup>6)</sup>. In this work the interesting parameter is the depolarization function  $P(t)$ , which determines the decay of the average muon polarization during the observation time of the muon spin precession. The decay is due to the dephasing of the individual muon precession by the randomly directed dipole fields from surrounding nuclei, and the formula developed for  $T_2$  relaxation in NMR should apply. We have, in the case of diffusion in a homogeneous crystal<sup>7)</sup>,

$$P_1(t) = \exp \left\{ - \sigma_f^2 \tau_c^2 \left[ \exp(-t/\tau_c) - 1 + t/\tau_c \right] \right\}, \quad (1)$$

where  $\sigma_f^2$  is the second moment of the frequency distribution due to the internal fields, and  $\tau_c$  is the average time during which correlations between the frequencies exists;  $\tau_c$  is proportional to the mean residence time  $\tau$  of the muons at interstitial sites. For a frozen-in muon we have  $\sigma^2 \tau^2 \gg 1$  and the damping is Gaussian,  $P_G(t) = \exp[-\sigma_f^2 t^2/2]$ , whereas for a diffusing muon with  $\sigma_f^2 \tau_c^2 \ll 1$  we expect  $P_L(t) = \exp[-\sigma_f^2 \tau_c t]$  (Lorentzian damping).

Here we will consider the depolarization for muon diffusion in a crystal with randomly distributed traps. We treat this case by introducing a two-state model

which describes repeated capture and release processes<sup>8</sup>). In this model a muon may either diffuse in the undisturbed lattice or it may be trapped at an impurity. A muon which diffuses in the undisturbed lattice is caught by a trap on the average after a time  $\tau_1$ ; a muon in a trap escapes after an average time  $\tau_0$ . The two states have different polarization decay. The polarization decay of the free state  $P_1(t)$  is given by Eq. (1) in the case of infinite lifetime of this state,  $\tau_1 \rightarrow \infty$ . The polarization decay of the trapped state is governed by an analogous expression  $P_0(t)$ , where  $\sigma_f^2$  is replaced by  $\sigma_t^2$ , the second moment of the frequency distribution in the traps, and  $\tau_c$  is replaced by  $\tau_{ct}$ , the correlation time determined by the motion of the muon in the traps. If there is no internal motion of the muon,  $\tau_{ct}$  is limited by the lifetime of the state of trapping,  $\tau_0$ . We postulate the following equations for  $P_1(t)$ ,  $P_0(t)$ :

$$\begin{aligned} \frac{dP_1(t)}{dt} &= \sigma_f^2 \tau_c \left[ e^{-t/\tau_c} - 1 \right] P_1(t) - \frac{1}{\tau_1} P_1(t) + \frac{1}{\tau_0} P_0(t) \\ \frac{dP_0(t)}{dt} &= \sigma_t^2 \tau_{ct} \left[ e^{-t/\tau_{ct}} - 1 \right] P_0(t) - \frac{1}{\tau_0} P_0(t) + \frac{1}{\tau_1} P_1(t) . \end{aligned} \quad (2)$$

If we let  $\tau_0, \tau_1 \rightarrow \infty$ , we have two uncoupled equations for  $P_1(t)$  and  $P_0(t)$  whose solutions are of the type (1). The terms proportional to  $\tau_1^{-1}$  and  $\tau_0^{-1}$  describe the changes of  $P_1$  or  $P_0$  by transitions between the two states. The total polarization decay is given by the sum of both contributions  $P(t) = P_1(t) + P_0(t)$ . We assume random stopping sites of the muons in the crystal and choose as initial conditions  $P_1(t=0) = 1$ ,  $P_0(t=0) = 0$ . This is a good approximation for small defect concentrations. The differential equations have been solved using a Runge-Kutta-Merson procedure. The results and the parameters used will be discussed below.

The experiments were performed at the 600 MeV Synchro-cyclotron at CERN. The temperatures were kept constant within 0.1 K. Separate runs on dummy samples of known performance were done to obtain the corrections for the background.

The samples were originally prepared for hydrogen diffusion studies; their preparation is described in detail elsewhere<sup>9</sup>). From the resistivity ratios, a

maximum content of O, N, or C of 60 ppm for the starting material of samples I and II, and of 10-20 ppm for sample III, could be estimated (Table 1). Mass spectroscopy measurements showed an over-all concentration of substitutional impurities (mainly Fe, Cr, and Ta) of less than a total of 100 ppm. Sample I (3700 ppm N) was doped with nitrogen and sample III (1000 ppm H) with hydrogen. In the temperature region of interest, the hydrogen atoms are completely precipitated. Measurements of residual resistivity and electron microscope inspection showed no substantial nitrogen clustering in the doped sample I.

The damping parameters  $\Lambda$  <sup>10)</sup> were obtained from the experimental spectra as inverse times for decay of the polarization to 1/e. Here Eq. (1) was used, assuming a low temperature line-width  $\sigma_f = 0.33 \mu\text{sec}^{-1}$ . Figures 1a to 1c show the parameter  $\Lambda$  obtained for samples I, II, and III as a function of temperature. It is evident that the muon diffusion is strongly influenced by the presence of nitrogen. The dip in  $\Lambda(T)$  at about 18 K is most pronounced for sample III with the lowest content of interstitials such as N, O, and C, whereas this dip is almost absent for the impure sample I. For this sample, the drop after the broad maximum at 40-50 K is also shifted to higher temperatures by about 10 K, and is steeper.

In a preliminary qualitative interpretation, we assume that the muon is frozen in at 10 K. Then the first drop can be ascribed to the onset of free diffusion, i.e. not influenced by the nitrogen traps. The increase of damping above 18 K is then due to capture by the traps. In the broad maximum the muons experience the dipolar fields in the traps for most of their lifetime. The sharp drop above about 50 K indicates the beginning of release processes from the traps and the resulting motional narrowing, owing to repeated capture and release processes. In at least one of the samples there are indications of a still deeper type of trap at  $\sim 150$  K. In the fits of Eqs. (2) to the data, we have assumed Arrhenius laws for the different times:

$$\begin{aligned}\tau_c^{-1} &= \Gamma_c \exp(-E_c/T) , \\ \tau_1^{-1} &= \Gamma_1 \exp(-E_1/T) , \\ \tau_0^{-1} &= \Gamma_0 \exp(-E_0/T) .\end{aligned}\tag{3}$$

The fit was made by using the Harwell routine VA05AD, and was performed simultaneously for the different samples. The parameters  $E_c$ ,  $\Gamma_c$ ,  $E_0$ ,  $\Gamma_0$ , and  $\sigma_f$ , which represent local properties of the jump processes and hence should not depend on the impurity concentration, were taken equal for all samples, while  $E_1$ ,  $\Gamma_1$ , and  $\sigma_t$  were allowed to vary independently for each sample. The values obtained are given in Table 1 and plotted in Figs 1a to 1c. A good over-all fit of the three samples has been achieved.

$\tau_c^{-1}$  should be proportional to the jump rate of a muon in an ideal niobium crystal. Since the muons are light compared to all other interstitials they are good candidates for the quantum-mechanical hopping theory<sup>11)</sup>. However, a direct comparison is difficult, since the free diffusion is prominent only in a small interval (15-20 K) where no simple Arrhenius law should apply. The apparent low value of the activation energy seems reasonable, compared to the calculated value of 300 K for hydrogen at higher temperatures<sup>12)</sup>.

The time  $\tau_1$  decreases as expected with increasing impurity concentration. The disappearance of the dip at larger impurity concentrations is directly related to the shorter lifetime of the state of free diffusion. A serious problem, however, is the explanation of the values for the ratio  $\tau_1/\tau_c$  found by the fit. The value of  $\tau_1/\tau_c$  at 18 K is only about 60 for sample III. In this sample the average distance between two impurities (interstitial defects and substitutional defects, except Ta) can be estimated to be about 18 lattice constants. If the capture process is diffusion-controlled, one expects a ratio  $\tau_1/\tau_c = 18^2 \nu^2$ , where  $\nu$  is the number of steps within a unit cell. An estimate for the correlation time is  $\tau_c = \tau \nu^2$ , since it can be assumed that local correlations do not exist for distances larger than a lattice constant. Similar factors have been found in other situations<sup>13)</sup>. Taking this factor into account we still have a discrepancy of a factor of five between the observed and expected values. One tentative explanation is drift motion, where the muons perform a more or less directed motion towards the traps. If the trapping process is diffusion-controlled, the activation energies  $E_1$  and

$E_c$  should be equal. The fit resulted in activation energies  $E_1 < E_c$ , which decrease with increasing impurity concentration (see Table 1). Such a behaviour can be expected for drift motion.

The shift of the drop of  $\Lambda(T)$  above 50 K (Figs. 1a to 1c) is also explained in our model, since at high impurity concentration a muon is trapped almost immediately after a release process, instead of propagating for some time in the free state.

The activation energy  $E_0$  of about 578 K for the escape process is smaller than that of hydrogen in Nb-N<sup>9)</sup>, which has been found to be about 1940 K ( $E_0$  is the sum of binding and migration energy). The difference in the binding energy can possibly be attributed to differences in the zero-point energies. The small prefactor  $\Gamma_0$  of the escape rate may be due either to small tunnelling matrix elements for this escape process, or to drift motion towards the traps.

We finally comment on the line-widths observed at low temperatures (12-14 K) for the polycrystalline samples. The observed value at 400 G is  $\sigma = 0.33 \mu\text{sec}^{-1}$ , and at 2.74 kG we obtain  $\sigma = 0.24 \mu\text{sec}^{-1}$ . A single-crystal experiment at 25 K<sup>14)</sup> indicated that the electric quadrupole field dominated the interaction of the neighbour nuclei<sup>15)</sup> at 400 G, whereas the magnetic decoupling limit was approached at 2.5 kG. New experiments have shown that this situation is also valid at 11 K. The relative change for the polycrystalline  $\sigma$ -values is therefore in agreement with theory (a 30% decrease expected from the low to the high field limit).

The absolute value  $\sigma = 0.33 \mu\text{sec}^{-1}$  is, however, much lower than expected for tetrahedral or octahedral positions in an undisturbed Nb-lattice (even if a realistic lattice distortion of 3% is taken into account in the theory). One possible explanation is that the muon is in an extended state containing four tetrahedral and four triangular sites as suggested for hydrogen by Birnbaum and Flynn<sup>16)</sup>. A small decrease of  $\sigma$  below 15 K is also evident (Fig. 1c); it might either reflect a shift of muon density towards sites with lower dipole fields or the onset of a coherent quantum propagation.

To summarize, the work presented in this letter has shown that muon depolarization data may produce detailed microscopic information on diffusion processes. Capture and release phenomena associated with trapping centres can be well described by the model developed. In particular, the dip in the depolarization rate at 18 K, which depends on the concentration of interstitials, can be related to the capture probability. The decrease above 50 K and its concentration dependence can be understood as motional narrowing due to repeated release processes. One possible extension of the model is the inclusion of several kinds of traps.

The low-temperature region is particularly interesting. Muons have been found to be mobile down to 14 K and, below that, indications of delocalization have been observed. An extension of the experiments to lower temperatures would help to clarify whether at these temperatures the muon changes from a "self-trapped" localized state to an extended "band" state. Furthermore, the role played by the substitutional impurities should be investigated.

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REFERENCES

- 1) J. Völkl and G. Alefeld, *in* Diffusion in solids, recent developments, (Eds. A.S. Nowick and J.J. Burton), (Academic Press, New York, 1975).
- 2) O. Hartmann, E. Karlsson, K. Pernestål, M. Borghini, T.O. Niinikoski and L.O. Norlin, *Phys. Letters*, 61A, 141 (1977).
- 3) Reports at the 4th Internat. Conf. on Hyperfine Interactions, Madison, NY, USA, 1977 (to be published in *Hyperfine Interactions*).
- 4) W. Münzing, J. Völkl, H. Wipf and G. Alefeld, *Scripta Metallurgica* 8, 1327 (1974).
- 5) D. Richter, J. Töpler and T. Springer, *J. Phys. F.* 6, L93 (1976).
- 6) J.H. Brewer, K.M. Crowe, F.N. Gyax and A. Schenck, *in* Muon physics, Vol. III, (Eds. V.W. Hughes and C.S. Wu), (Academic Press, New York, 1975).
- 7) See, for example, A. Abragam, Nuclear magnetism (Oxford Univ. Press, Oxford, 1961).
- 8) Two-state models have been applied to hydrogen diffusion in the presence of traps by D. Richter, K.W. Kehr and T. Springer, Proc. Conf. on Neutron Scattering, Gatlinburg, Tenn., USA, 1976 (Ed. R.M. Moon), Vol. I, p. 568. See also K. Schroeder, *Z. Phys.* B25, 91 (1976).
- 9) D. Richter and T. Springer, Diffusion of hydrogen in niobium in the presence of trapping impurities studied by neutron spectroscopy, to be published in *Phys. Rev. B*.
- 10) I.I. Gurevich, E.A. Mele'shko, I.A. Muratova, B.A. Nikolsky, V.S. Roganov, V.I. Selivanov and B.V. Sokolov, *Phys. Letters* 40A, 143 (1972).
- 11) C.P. Flynn and A.M. Stoneham, *Phys. Rev. B* 1, 3966 (1970).
- 12) K.W. Kehr, Diffusion von Wasserstoff in Metallen, *Berichte der KFA, Jülich*, Jül-1211 (1975).



- 13) A. Heidemann, G. Kaindl, D. Salomon, H. Wipf and G. Wortmann, Phys. Rev. Letters 36, 213 (1976).
- 14) O. Hartmann, E. Karlsson, L.-O. Norlin, K. Pernestål, M. Borghini, T. Niinikoski and E. Walker, Report at the 4th Internat. Conf. on Hyperfine Interactions, Madison, NJ, USA, 1977 (to be published in Hyperfine Interactions).
- 15) O. Hartmann, Phys. Rev. Letters 39, 832 (1977).
- 16) H.K. Birnbaum and C.P. Flynn, Phys. Rev. Letters 37, 25 (1975).

Table 1

Sample characteristics and fitted parameters. The following fitted parameters were assumed equal for all samples:

$$\Gamma_c = 1.36 \times 10^{12} \text{ sec}^{-1}; E_c = 250 \text{ K};$$

$$\Gamma_0 = 8.1 \times 10^8 \text{ sec}^{-1}; E_0 = 580 \text{ K};$$

$$\sigma_f = 3.2 \times 10^5 \text{ sec}^{-1}.$$

	Sample I	Sample II	Sample III
N, O, C content (ppm)	3700	< 60	10-20
H content (ppm)			1000
$\Gamma_1$ (sec <sup>-1</sup> )	$2.9 \times 10^9$	$3.8 \times 10^9$	$1.9 \times 10^9$
E <sub>1</sub> (K)	150	190	205
$\sigma_t$ (sec <sup>-1</sup> )	$3.2 \times 10^5$	$2.7 \times 10^5$	$2.4 \times 10^5$

Figure caption

Fig. 1 The damping parameter  $\Lambda$  as function of temperature, for samples I-III.  
The temperature scale has an uncertainty of  $\pm 1$  K in the 10-30 K range.

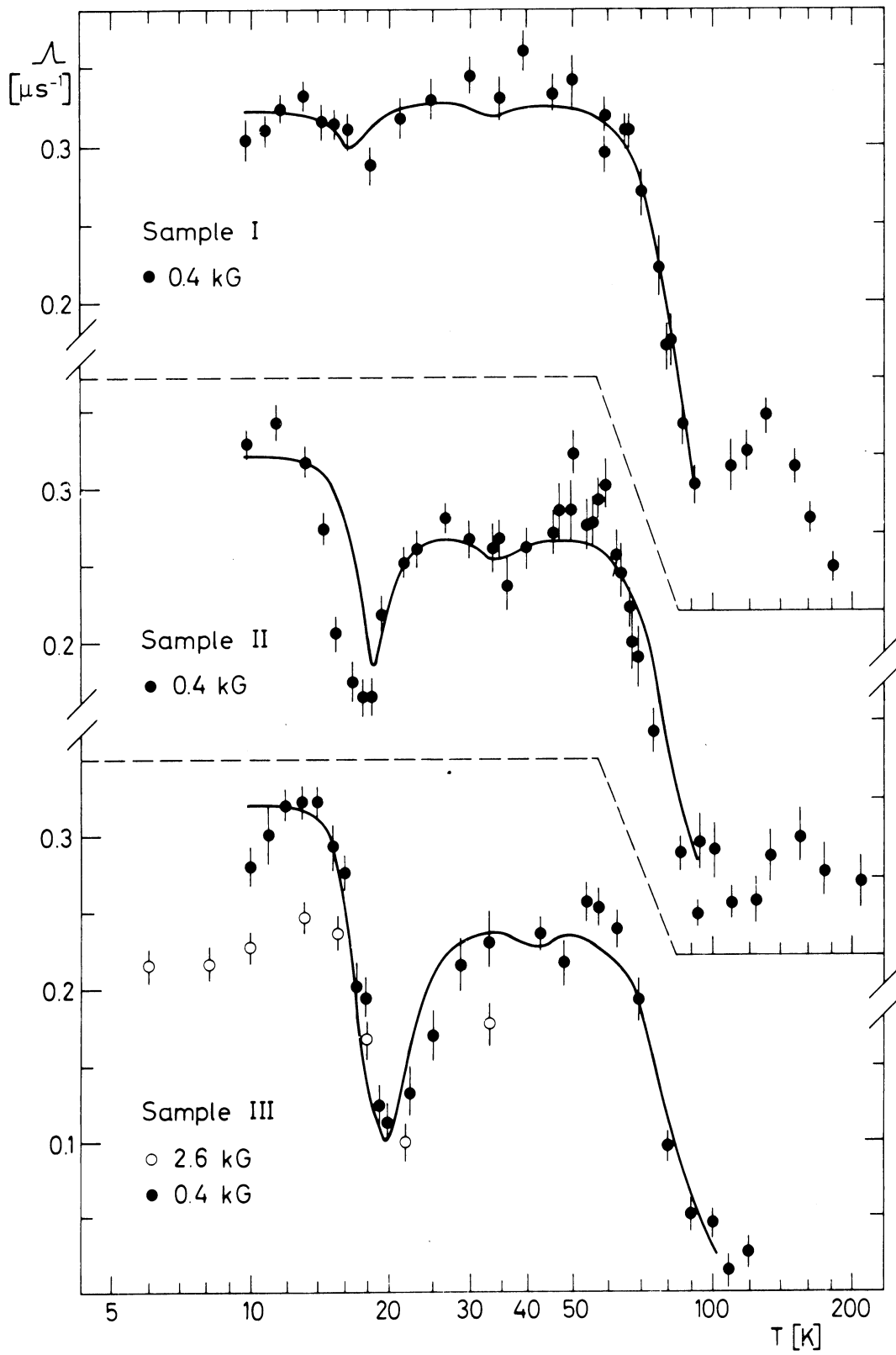


Fig. 1