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Trap identification and impurity-induced localization of muons in Nb

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We present new muon-spin-rotation (μSR) results on extremely purified and very well characterized niobium samples with defined minute amounts of Ta or N. This allows us to separate the influence of substitutional and interstitial impurities on the μSR spectra. The purest sample shows a low but nonzero μSR linewidth from 0.1 to 70 K, while Ta doping gives rise to a high linewidth below 20 K. Pure N doping creates the broad maximum between 30 and 70 K, but also a considerable linewidth below 20 K. The results are interpreted in terms of a model where initial localization is partly catalyzed by impurities and where some muons do not form small-polaron states.

INTRODUCTION

Muon-spin-rotation (μSR) experiments in Nb show a temperature-dependent motional narrowing of the dipolar linewidth which gives information about the state of motion of the positive muon, a light ($m_\mu/m_p \approx \frac{1}{9}$) hydrogen "isotope."

Moderately pure Nb samples (with several hundred at. ppm of impurities) yield[1,2] a μSR linewidth $\sigma(T)$ with a "two plateau" temperature dependence: a low-temperature plateau (from the superconducting transition temperature at 9 K to approximately 16 K) is separated from the high-temperature plateau (30–60 K) by a dramatic dip in the linewidth at 20 K. High-purity Nb samples (with a few impurity at. ppm) show[3–5] a single plateau extending from 4 to 60 K with a strongly reduced linewidth, occasionally with a superimposed complicated structure.

The two-plateau structure in impure Nb can be well described[2] by a two-trap model. Below 16 K the μ^+ rapidly finds an extended shallow trap and stays there during the time of observation (~ 10 μs). As the temperature is increased to 20 K the μ^+ can thermally detrap and become free to roam the sample. At slightly higher temperatures, the μ^+ moves fast enough to find a deeper and more localized second type of trap. The localization at this deep trap produces line broadening up to 60 K, above which temperature the μ^+ can leave the deep traps. This trapping-detrapping behavior has recently been confirmed by zero-field μSR.[6]

A large amount of μSR work has been done with the aim of identifying the nature of these two types of traps. Experiments with nitrogen-doped Nb demonstrated[2] that an increased concentration of this interstitial impurity gave a higher trapping rate and an increased linewidth value for the high-temperature plateau. Introducing interstitial oxygen[4] had less of an effect. It is known[7] that interestitial nitrogen and oxygen trap hydrogen in Nb.

Substitutional vanadium in Nb is also known[8,9] to trap hydrogen, and a μSR experiment with V-doped Nb (Ref. 3) appeared to affect the low-temperature plateau slightly. However, this sample, like many of the other samples studied, also contained Ta impurities. Although substitutional Ta is believed[9] not to trap hydrogen, the μSR experiments suggest[3,4,10] that it could be a shallow trap for muons. The evidence up to date thus indicates that the high- and low-temperature plateaus in the linewidth are associated with interstitial (N,O) and substitutional (V,Ta) impurities, respectively, but an unambiguous demonstration of this has not yet been made.

Other important questions which need to be addressed are: How do muons behave at very low temperatures where interesting phenomena appear in Al and Cu (Refs. 11 and 12) and why are muons in Nb so extremely sensitive to impurities?

In this study we try to answer these questions by μSR measurements on very pure Nb samples and samples doped with Ta or N impurities. In discussing the results we consider the recent idea that muons may remain in metastable states in metals[13,14] and not always form the small-polaron state hitherto assumed. The concept of polaron formation catalyzed by impurities appears particularly well suited for describing μ^+ in Nb.

SAMPLES

Most of the new measurements presented here were made on Nb samples derived from five single-crystal rods prepared by electron-beam float zone melting under UHV at the Max-Planck-Institut, Stuttgart.[15] The residual resistivity ratios ($\mathcal{R}$) of the rods ranged from $\mathcal{R}=7500$ (indicating interstitial impurities C,N,O = 1.5 at. ppm) to $\mathcal{R}=11\,600$ for the purest crystal (C,N,O below 1 at. ppm). These rods were cut in either three or four pieces to yield 19 pieces 4 mm in diameter and 30 mm long. All 19 pieces together formed the "ultrapure" sample which was measured down to 4 K in Ref. 3. Our new zero-field measurement down to 0.1 K used 15 of these pieces. The two center pieces of the $\mathcal{R}=11\,600$ crystal were selected to form a very pure sample, "middle pieces." Two pieces of the $\mathcal{R}=7500$ crystals were selected for doping with nitrogen. Their nitrogen content after doping was 15 at. ppm, and the $\mathcal{R}$ was approximately 1700.[16]

A Ta-doped sample was produced by doping another extremely pure Nb single crystal with original Ta concentration 0.5 at. ppm with a Ta-containing (4360 at. ppm) Nb master alloy by electron-beam float zone leveling under UHV. The Ta concentration was finally determined by neutron-activation analysis to be 53 at. ppm, and the concentration of other metallic impurities was far below the ppm level.[17] The $\mathcal{R}$ of this sample was 11 630.

RESULTS

The main part of the data presented here was obtained at SIN where very small samples (8×4-mm^2 cross section, thickness $\gtrsim 100\ \mu$m) can be measured using the low momentum surface muon beam and a transverse field setup. The measurement down to 0.1 K was made at CERN using a ^{3}He-^{4}He dilution refrigerator and a zero-field setup, in order to avoid inhomogeneous broadening from the flux lines in superconducting Nb. The data were corrected for a cryostat background determined by measuring a stainless-steel dummy sample which gives no μSR signal below 25 K. All linewidth data presented here were evaluated by fitting a Gaussian damping function $P(t)=P(0)\exp(-\sigma^2t^2)$ to the corrected spectra. This means that we always use σ as a one-parameter description of the damping rate, although the real line shape may be far from Gaussian when muons are mobile.

The results of the zero-field measurement down to 0.1 K are shown in Fig. 1 together with earlier 1100-G transverse field data from Ref. 3. The zero-field damping rate was divided by $2^{1/2}$ in order to allow comparison with the transverse field linewidth. This factor is given in Ref. 18, and the validity of the procedure was checked by measuring at 11 K (above T_C) with both methods. The two sets of data join smoothly onto one another, and it appears that below 5 K, σ increases slightly towards a plateau below 1 K. The plateau value is, however, far below the expected $\sigma_0=0.4-0.5\ \mu\text{s}^{-1}$ for immobile pointlike muons at interstitial sites in Nb.[19] The structure in σ above 30 K may be attributed to remaining traces of impurities.

The influence of impurities on the linewidth in Nb is demonstrated in Fig. 2, where the results of the new measurements are compared with the typical two-plateau structure obtained in impure samples [Fig. 2(b)]. The data in Fig. 2(b) were obtained from a sample with 10–20 ppm N and 80–100 ppm Ta, and although the results were given in Refs. 2 and 3 we include them here for comparison. It should be noted that the plateaus are not really flat and that the low-temperature plateau in reality reaches a maximum at 12–15 K. In niobium the measured σ are almost field independent up to 500 G,[1] but decrease at higher fields.

The purest Nb sample [middle pieces in Fig. 2(a)] shows a small plateau from 10 to 70 K with a much reduced σ value. The complex behavior seen by other authors[3–5] in highly pure samples is absent, but a slight indication of the dip at 20 K is still noticeable.

The influence of the two kinds of impurities can be separately seen in Figs. 2(c) and 2(d). Figure 2(c) very clearly demonstrates that the plateau below 20 K

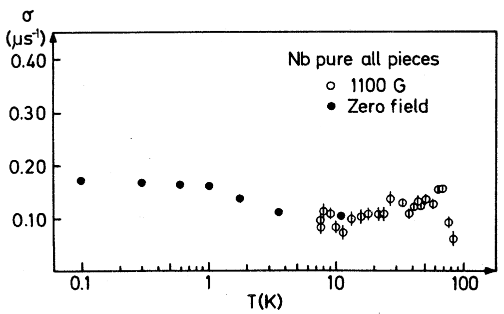

FIG. 1. Damping rate (linewidth) for muon precession in niobium as function of temperature. The σ values measured in zero magnetic field have been reduced by a factor of $2^{1/2}$.

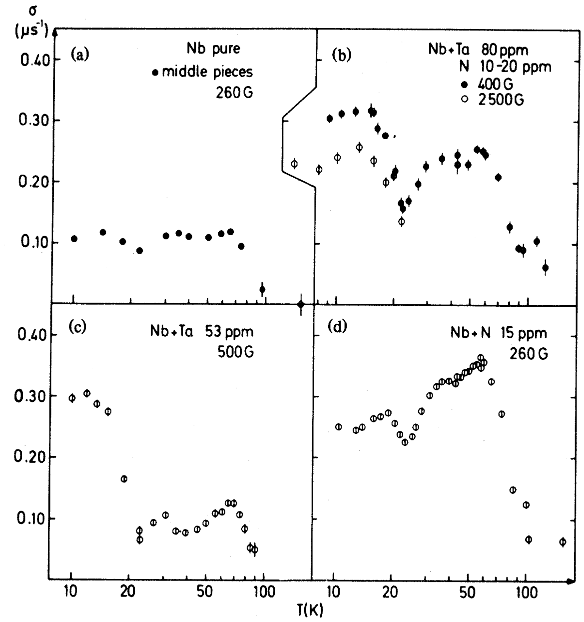

FIG. 2. Damping rates as functions of temperature in niobium samples with varying contents of impurities. The "middle pieces" sample in (a) is the purest measured, with $\mathcal{R} = 11\,600$, and the effects of doping with Ta or N impurities can be seen in (b)–(d).

is created by Ta impurities (substitutional) while only a very small part of the high-temperature plateau remains. The activation energy for escape from the shallow Ta traps is ~220 K. Doping with N impurities (interstitial) alone, however, gave a less clear result [Fig. 2(d)]. The deep high-temperature trap (30–60 K) is present as expected (activation energy for escape ~550 K), but a considerable linewidth also remains below 20 K.

Summing up, Fig. 2 positively identifies the linewidth plateau below 20 K with shallow traps created by Ta impurities (substitutional). Similarly, the identification of the high-temperature plateau with deep traps from interstitial impurities (C,N,O) is confirmed, but an unexpected influence on the μSR spectra below 20 K is also revealed.

DISCUSSION

In interpreting these data with the conventional trapping model given in, e.g., Ref. 2, one assumes that the implanted muons reach local thermal equilibrium at random sites. These are then the starting point for the subsequent diffusion. This model, however, fails to explain the occurrence of linewidth significantly lower than that predicted for static μ^+ *and* constant over a wide temperature range. Such a low, extended plateau has been observed with the purest niobium samples [Figs. 1 and 2(a)]. We are therefore led to invoke temperature-independent diffusion or capture processes, and to consider the possibility that muons do not always self-trap immediately at random interstitial sites.[14,20,21]

Self-trapping means that the lattice is expanded locally around the muon such that a new equilibrium is reached for the elastic particle-host and host-host atomic forces. The potential-energy minimum associated with such a small-polaron state is lower than that of an extended "free" state of the particle, but separated from it by an energy barrier.[13,14] The transition from the free to the self-trapped state in a perfect lattice therefore requires assistance in the form of thermal fluctuations. Detailed theories are, however, lacking.

Emin[21] arrived at the result that the dynamic stability of the metastable extended state is governed by an "adiabaticity parameter" $A = B/\hbar\omega_0$, where B is the rigid-lattice bandwidth for the muon and ω_0 the harmonic-oscillator frequency for the vibrations of the surrounding lattice atoms. For small A the lattice can react to the actual muon position and the muon will be self-trapped within a vibrational period $\approx 10^{-12}$ s, while for $A > 1$ self-trapping becomes increasingly difficult. B is given by zJ, and the tunneling matrix element J can be estimated to be ≈ 60 meV for free muons in Nb (this value is comparable with the overlap $J = 43$ meV calculated by Kehr[22] on the basis of a periodic one-dimensional potential which gives rise to the correct hydrogen vibrations in Nb). If we approximate the lattice frequency ω_0 with

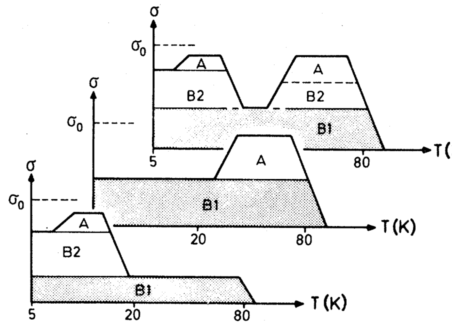

FIG. 3. Schematic picture of the contributions to the linewidth σ in various idealized situations if small-polaron formation is catalyzed by impurities. The bottom picture is the case of Ta doping, where a fraction $B2$ of the muons self trap close to the substitutional Ta impurities, while the fraction A, thermally self-trapped at random positions, must first diffuse to the traps in order to contribute to σ. The fraction $B1$ contains muons self-trapped close to remaining interstitial (C,N,O) impurities. These muons dominate in the middle picture (N doping only), together with A muons which have diffused to the traps. The top figure represents the case when both types of interstitials are present. The total observed linewidth σ does not reach the value σ_0 expected if all muons are localized and static, since, at small impurity levels, some muons always remain in the metastable propagating state.

the Debye frequency ω_D, we arrive at $A \approx 1.8 - 2.5$ for muons in Nb, indicating the possibility of a dynamically stable non-self-trapped state. (A similar estimate, using the free muon bandwidth, gives $A \approx 0.8$ for muons in Al[12].)

However, localization may also be induced by static strains close to impurities.[13] For muons propagating in the extended metastable state, this process would be capture controlled. In analogy with positron trapping, the trapping rate is then proportional to the trap concentration and independent of temperature.[23] These small polarons are then not formed at random interstitial sites but near crystal defects, and can only move if the temperature is high enough to dissociate them from the traps. These muons would therefore give rise to temperature-independent plateaus in σ extending to zero temperature. Additional structure in $\sigma(T)$ originates from muons reaching the small-polaron state by the thermal process before trapping takes place.

There could also be a considerable fraction of muons which never form small polarons, especially in very pure samples. They would not contribute to the μSR linewidth since the motional narrowing in the extended metastable state is complete.

The principal consequences of this model are depicted in Fig. 3, which can be compared to the results in Fig. 2. In the low-temperature region (Fig. 1), we tentatively interpret the increase of σ towards the small plateau as the onset of coherent diffusion below 5 K, in analogy with Al.[12]

CONCLUSION

Summarizing the results presented here, we draw the following conclusions: (i) As in pure Al, the muon diffusion rate is extremely fast in pure Nb, and its temperature dependence has not been observed directly; (ii) very small amounts of impurities have a strong influence on the linewidth pattern; (iii) Ta (substitutional) and N (interstitial) impurities give rise to shallow and deep traps, respectively, each with characteristic features in the μSR spectra; and (iv) self-trapping of muons in Nb is not always achieved thermally, but can evidently be catalyzed by impurities. This means that in sufficiently pure material a fraction of the muons may not reach the equilibrium small-polaron state.

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