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Local and long-range hydrogen diffusion in $Nb(OH)_{0.011}$

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Abstract

The quantum diffusion of hydrogen trapped by oxygen interstitials in niobium is well studied in the temperature range below 150 K. The studies demonstrate that the hydrogen is trapped by the oxygen impurity atoms and that the trapped hydrogen performs a rapid local diffusion process between two nearest-neighbour tetrahedral interstitial sites. With temperatures rising above 150 K, the probability that the hydrogen leaves the trap sites increases. The hydrogen dissociates from its original oxygen trapping atom and carries out a long-range diffusional motion before it is trapped again by an oxygen impurity. We studied this situation by neutron scattering in the temperature range from 100 to 300 K. In our experiment we found a continuous transition from local diffusion at low temperatures to a predominantly long-range diffusion at higher temperatures. This behaviour can successfully be described by a two-state model: one state describes the local diffusion of the hydrogen in the trapped state. The other state describes the long-range diffusion process. Each of these states has a characteristic lifetime, which is also a measure for the probability of the hydrogen to be in this state.

Keywords: Diffusion; H in metals; Quasi-elastic neutron scattering

1. Introduction

In the temperature range below ≈150 K the quantum diffusion of trapped hydrogen interstitials in the systems $Nb(OH)_x$, $Nb(NH)_x$ and $Nb(CH)_x$ was intensively studied in a large number of experiments, including neutron spectroscopy (see Refs. [1–5] and references therein). The studies demonstrate that the hydrogen atoms were trapped by the O, N or C interstitial impurities and that the trapped hydrogen performed a rapid local diffusion process between two nearest-neighbour tetrahedral interstitial sites in the niobium bcc lattice.

With temperatures rising above 150 K, the probability increases that the hydrogen atom can leave its trapping sites. The untrapped, free hydrogen atom is then expected to perform a long-range diffusion to another trapping impurity atom, where it is trapped again to carry out a local diffusion process. The aim of this quasi-elastic neutron scattering study is the fast local diffusion of the hydrogen, its detrapping behaviour above ≈150 K and the transition to a mainly long-range diffusion.

The long-range hydrogen diffusion above ≈180 K was already studied by neutron scattering in $Nb(NH)_x$ [6]. However, the high jump rates of the rapid local diffusional motion were not investigated by this study due to the limited energy range of the used instrument (IN10, Institut Laue-Langevin, Grenoble).

2. Sample and experimental details

The measurements were carried out on a $Nb(OH)_x$ single crystal with $x = 0.011$ (12 mm diameter, 65 mm length, crystal axis in [110] direction). Sample preparation and analysis were similar to that described in Ref. [7]. The niobium atoms of the investigated crystal form a bcc lattice, where the O impurities are located on octahedral interstitial sites [8].

The neutron spectra were taken with the time-of-flight spectrometer IN6 at the Institut Laue-Langevin (Grenoble). Vanadium scans were performed to obtain instrument resolution function and detector efficiency. The wavelength of the incident neutrons was $\lambda = 5.12$ Å and the scattering vectors were between $Q = 0.22$ Å^{-1} and $Q = 2.05$ Å^{-1} (for elastic scattering).

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3. Data analysis

3.1. Data reduction

Data reduction was accomplished by the software package INX of the Institut Laue-Langevin [9]. Normalisation to the vanadium spectra was done to take into account the different detector efficiencies. A constant background in the time-of-flight scale was subtracted. The spectra from different scattering angles were grouped to obtain spectra for scattering vectors Q with an approximate equal $\Delta Q/Q$ ratio of about 15%. The conversion from the time-of-flight to the energy scale was performed. The above treatment with INX results in a data set proportional to the measured scattering function $S(Q,\omega)$. To fit a theoretical $S(Q,\omega)$ to this measured $S(Q,\omega)$, one has to consider the instrument resolution by a convolution of the theoretical $S(Q,\omega)$ with the instrument resolution function (as measured by the vanadium scans).

3.2. Two-state model

The neutron spectra were analysed with a two-state model [10,11]. One state, state A, describes the rapid local diffusion of the trapped hydrogen atom, i.e. the tunnelling of the hydrogen between two nearest-neighbour sites. The other state, state B, relates to the free, long-range diffusion of the hydrogen atom through the niobium lattice. A hydrogen atom remains for a mean lifetime τ_1 in the trapped state. After having left the trapping impurity, the hydrogen diffuses for a mean lifetime τ_2 through the host lattice until it is captured again by an interstitial impurity atom. The incoherent neutron scattering function $S(Q,\omega)$ for such a two-state model can be calculated as [10,11]

$$S(Q,\omega) = \frac{1}{1+\frac{\tau_2}{\tau_1}} \cdot \frac{A + B\frac{\tau_2}{\tau_1} + \frac{2AB}{\tau_1}}{1 + \frac{AB}{\tau_1 \tau_2}} + cc. \qquad (1)$$

The term A corresponds to the first state, i.e. the trapped hydrogen tunnelling between two interstitial sites:

$$A = \frac{f(Q)}{i\omega + \frac{1}{\tau_1}} + \frac{1 - f(Q)}{i\omega + \frac{1}{\tau_1} + 2\nu} \qquad (2)$$

where ν is the jump rate of the hydrogen between the two nearest-neighbour tetrahedral sites and $f(Q)$ is the elastic incoherent structure factor (EISF) in the case of $\tau_1 \to \infty$. In an orientational average the EISF is given by [1]

$$f(Q) = 1 - \int \mathrm{d}\epsilon\ Z(\epsilon) \left[\frac{1/2 - \sin(Qd)/(2Qd)}{\cosh^2(\epsilon/(2\,k_B T))} \right] \qquad (3)$$

where $Z(\epsilon)$ describes the distribution of energy shifts ϵ between the two nearest-neighbour sites occupied by the trapped hydrogen, d is the distance of these sites and $k_B T$ is the thermal energy. The term B describes the other, long-range diffusion of the hydrogen,

$$B = \frac{1}{i\omega + \frac{1}{\tau_2} + \Delta\omega(Q)} \qquad (4)$$

with the scattering vector dependent width $\Delta\omega(Q)$. For $Q \to 0$, $\Delta\omega(Q) = DQ^2$, where D is the usual self diffusion coefficient. Taking the average over all directions of the scattering vector Q, $\Delta\omega(Q)$ is given by [12]

$$\Delta\omega(Q) = \nu_D \left(1 - \frac{\sin(Ql)}{Ql} \right) \qquad (5)$$

with $\nu_D = 6D/l^2$ for the jump rate of the long-range diffusion and with $l = 1.17$ Å as the distance between neighbouring tetrahedral interstitial sites.

To apply this two-state model to the neutron scattering spectra it is essential to know the parameters of the local diffusion process, namely the asymmetry energy of the sites between local diffusion takes place, and the distance d between these sites. The neutron spectra measured at 100 K were used to obtain this information. The asymmetry energy was already determined in Ref. [1]. In this reference, a Lorentzian distribution was assumed for $Z(\epsilon)$ in Eq. (3) and a width of $\epsilon_0 = 8$ meV was found for $\mathrm{Nb(OH)}_{0.011}$. From the 100 K data the EISF $f(Q)$ was obtained directly by fitting the elastic and quasi-elastic, Lorentzian-shaped, component of the spectra (see Eq. (2)) for $\tau_1 \to \infty$). The ratio between the quasi-elastic intensity and the total scattering intensity gives the quantity $1 - f(Q)$. The distance d between the tunnel sites of the hydrogen in Eq. (3) was adjusted to fit this experimentally obtained EISF $f(Q)$, resulting in $d = 0.93$ Å.

3.3. Fitting

The scattering function $S(Q,\omega)$ from Eq. (1) was fitted to the neutron spectra. The following fit parameters were used: the ratio between the mean lifetimes of each state, τ_2/τ_1, the mean lifetime of the long-range diffusion state, τ_2, the jump rate ν of the trapped hydrogen, the diffusion coefficient D or the jump rate $\nu_D = 6D/l^2$ of the long-range diffusion process, a scaling factor and parameters for a background linear in energy (a constant background in the time-of-flight scale was subtracted during data reduction).

After fitting each spectrum of a certain scattering vector Q for one temperature alone, a set of parameters was chosen that was able to describe all spectra at one temperature together. This parameter set was basically obtained by taking the mean value of all results of one fit parameter for one temperature. The results from larger scattering vectors Q were weighted higher, because they were more reliable and sensitive due to the greater broadening of the spectra.

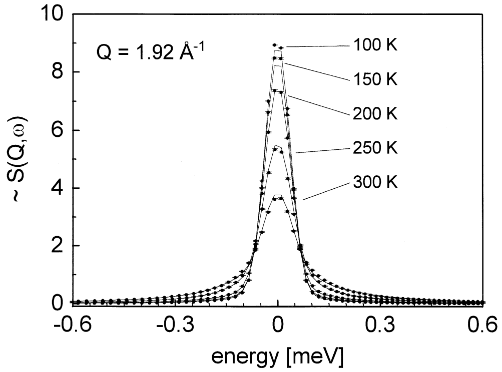

Fig. 1. Quasi-elastic neutron spectra of Nb(OH)$_{0.011}$ taken at different temperatures for the scattering vector $Q = 1.92$ Å^{-1}. The solid lines are curves resulting from the two-state model explained in the text.

4. Results and discussion

The incoherent scattering function of the two-state model (Eq. (1)) is able to describe the measured neutron spectra. Fig. 1 shows the neutron spectra for the highest scattering vector $Q = 1.92$ Å^{-1} after data reduction. The solid lines are theoretical curves from the common parameter set of fit results for each temperature.

The main results are: (i) the jump rates of the local diffusion ν and the long-range diffusion process ν_D, as shown in Fig. 2; and (ii) the ratio between the mean lifetimes τ_2/τ_1, as shown in Fig. 3. The jump rates of the local diffusion process exceed by far the jump rates of the long-range diffusion at lower temperatures. The diffusion coefficient D or the jump rates ν_D of the long-ranged diffusion are close to the values from Gorsky measurements [13].

The fits were not sensitive to the mean lifetime τ_2 of the free, long-range diffusion state as long as τ_2 exceeded $1/\nu_D$ (this is a reasonable condition for a long-range diffusion process). So the ratio τ_2/τ_1, but no absolute values for the mean lifetimes τ_2 and τ_1, were obtained by the fits.

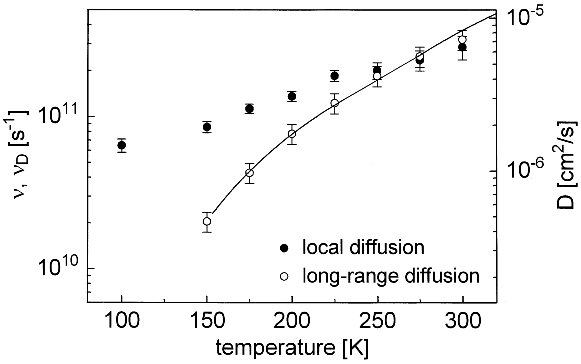

Fig. 2. Jump rates ν and ν_D for the rapid local diffusion of the trapped hydrogen and for its long-range diffusion, respectively. The right scale shows the diffusion coefficient $D = l^2 \cdot \nu_D/6$ of the long-range diffusion process. The solid line represents Gorsky effect data for the long-range diffusion [13].

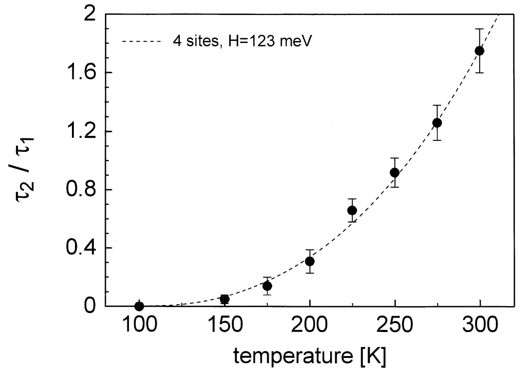

Fig. 3. Temperature dependence of the ratio between the mean lifetime τ_2 of the long-range diffusion state and the mean lifetime τ_1 of the trapped state. The dashed line corresponds to the trapping model explained in the text.

One of the most important results of this study is the ratio τ_2/τ_1 between the mean lifetime τ_2 of the free, long-range diffusion state and the mean lifetime τ_1 of the trapped state of the hydrogen. This ratio is as well the ratio between the concentrations of the hydrogen in the free diffusing and in the trapped state. A trapping model [14] is able to model the temperature-dependent results for τ_2/τ_1, as can be seen in Fig. 3 (dashed line). The trapping model considers interstitial sites for the hydrogen around an interstitial impurity atom with the same binding enthalpy H. It describes the experimental results for τ_2/τ_1 if one trap consists of four possible interstitial sites for the hydrogen and if the binding enthalpy is $H \approx 123$ meV.

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