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Low-temperature Snoek-type relaxation of hydrogen interstitial atoms in $Nb_{0.8}Mo_{0.2}$

B. Leu[a,*], H. Wipf[a], B. Coluzzi[b], A. Biscarini[b], G. Mazzolai[b], F.M. Mazzolai[b], V.V. Sumin[c]

[a]*Institut für Festkörperphysik, Technische Universität Darmstadt, Hochschulstraße 6, 64289 Darmstadt, Germany*
[b]*NFM-UDR of Perugia, Physics Department, University of Perugia, Perugia, Italy*
[c]*Frank Laboratory of Neutron Physics, JINR, 141980, Dubna, Russia*

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Abstract

Neutron spectroscopy on H-doped b.c.c. $Nb_{0.8}Mo_{0.2}$ alloys demonstrated recently (i) a complete suppression of low-temperature H precipitation up to 5 at.% H, and (ii) an exclusive H occupation of tetrahedral interstitial sites, like pure b.c.c. Nb. We studied by mechanical spectroscopy $Nb_{0.8}Mo_{0.2}$ alloys containing 0.85 and 3 at.% H and found a H-induced low-temperature relaxation at 2 kHz around 80 K. Activation energy and reciprocal pre-exponential relaxation time are ~0.054 eV and $\sim 2.8 \cdot 10^{7}$ s^{-1}, respectively. The relaxation peak is about 80% broader than for an ideal Debye relaxation, which reveals a spectrum of relaxation times. The height of the relaxation (Q^{-1}) peaks is approximately linear to H concentration, thus indicating a Snoek-type relaxation of single H atoms. The heights of the peaks yield a tetragonality $|\lambda_1 - \lambda_2|$ of about 0.04, which is an order of magnitude smaller than that of the Snoek effect of O in Nb. The results suggest that the observed relaxation reflects low-temperature diffusive jumps of single H atoms between tetrahedral interstitial sites, with a jump rate above $\sim 1.2 \cdot 10^{4}$ s^{-1} at 80 K.

Keywords: Snoek type relaxation; Hydrogen; Interstitial atoms; $Nb_{0.8}Mo_{0.2}$ alloys; Relaxation time

1. Introduction

Tunneling and generally all quantum effects of hydrogen diffusion in metals are more prominent at low temperatures so that, for their investigation, low-temperature studies are particularly interesting [1–3]. However, a common problem in low-temperature studies on hydrogen interstitials in pure metals is precipitation where the hydrogen interstitials accumulate in an ordered high-concentration hydride phase in which they become essentially immobile. One way to overcome precipitation is hydrogen trapping by impurity atoms like O, N, C or Ti in Nb or Fe in Pd (see Refs. [1,3] and references therein). A second possibility is studies of hydrogen diffusion in disordered alloys in which the solubility limit is generally much larger than in pure metals, sometimes to an extent that precipitation is completely suppressed down to the lowest temperatures (an example is a mechanical spectroscopy study on the alloy $Nb_{0.5}V_{0.5}$ [4]). The increase of the solubility limit (or suppression of precipitation) is understood by the fact that interstitial sites in a disordered alloy have, in contrast to pure metals, different metallic neighborhoods, so that the energy of a hydrogen interstitial varies from site to site. At low concentrations, the hydrogen atoms can preferentially occupy the energetically most favorable sites, whereas more and more unfavorable sites must be occupied at higher concentrations. Therefore, the energy of the hydrogen interstitials in a high-concentration (hydride) phase shows an increase against the energy of the hydrogen interstitials in (low-concentration) solid solution, an increase not observed in pure metals. As a consequence, precipitation is less favorable in disordered alloys, which increases the solubility limit against pure metals. A more formal analysis of this behavior is given in Ref. [5].

The present paper reports on a mechanical spectroscopy study of H diffusion in disordered $Nb_{0.8}Mo_{0.2}$ alloys with H concentrations up to 3 at.% (H and D refer to the respective hydrogen isotope, whereas hydrogen holds for both isotopes). Neutron spectroscopy [6] demonstrated that the H solubility limit in such alloys exceeds 5 at.% at least down to 10 K, which means the absence of precipitation

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*Corresponding author.
E-mail address: boris.leu@physik.tu-darmstadt.de (B. Leu).

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effects and a pure solid solution of the H interstitials in the present measurements. The neutron experiments demonstrated also a sole H occupation of tetrahedral interstitial sites, in contrast to the previous mechanical spectroscopy study on $Nb_{0.5}V_{0.5}$ [4] where H can occupy both tetrahedral and octahedral sites [7]. The chief results of the present measurements is a high H diffusion at low temperatures, with H jump rates that exceed $\sim 1.2 \cdot 10^4$ s^{-1} at 80 K.

2. Sample preparation and experimental details

$Nb_{0.8}Mo_{0.2}$ alloys were prepared by arc-melting from high purity Nb and Mo. The investigated samples were thin plates (15 to 40 mm long, 4 to 6 mm wide and 0.2 to 0.5 mm thick) cut from the alloys by a diamond saw. The samples were then annealed under ultra-high-vacuum conditions at 2100 °C to reduce the amount of interstitial O and N. Fusion analysis after annealing yielded a total content of O, N and C of about 0.1 at.%. The samples were doped with H by high-temperature exposure to H_2 gas (0.85 at.% H) or electrolytically (3 at.% H). The H concentrations were determined from the amount of absorbed H_2 gas (H_2 gas doping) or by vacuum extraction after the measurements (electrolytic doping).

Mechanical spectroscopy data were taken between 523 to 6580 Hz. Frequencies below and above 2000 Hz were studied with the vibrating reed technique and by free flexural vibrations, respectively. In both cases, vibrational excitation and monitoring of the vibrational amplitudes was accomplished with the help of a capacitor formed by the sample and a counterelectrode [8].

3. Experimental results and discussion

The energy dissipation Q^{-1} of samples measured with the vibrating reed technique is given in Fig. 1 as a function of reciprocal temperature. Fig. 2 similarly presents Q^{-1} values determined from free flexural vibrations. Both figures demonstrate clearly identifiable relaxation peaks with maxima in the temperature range between 70 and 95 K. For an analysis of the temperature dependence of the relaxation process, Fig. 3 compiles in an Arrhenius plot the angular vibrational frequencies $2\pi f$ as a function of the reciprocal temperatures at the maxima of the respective relaxation peaks. In the case of an ideal Debye relaxation process, the reciprocal relaxation time τ, i.e. the relaxation rate $1/\tau$, can directly be identified with $2\pi f$ [8]. Fig. 3 shows that, in such a case, the data points for isotope H are well described by an Arrhenius relation $1/\tau = 1/\tau_0 \cdot \exp[-E/(kT)]$, given by the solid line, where the pre-exponential factor is $1/\tau_0 = (2.8 \pm 1.4) \cdot 10^7$ s^{-1} and the activation energy is $E = (54 \pm 4)$ meV (kT is the thermal energy). However, it should be pointed out that experimental accuracy and limited temperature range of the present

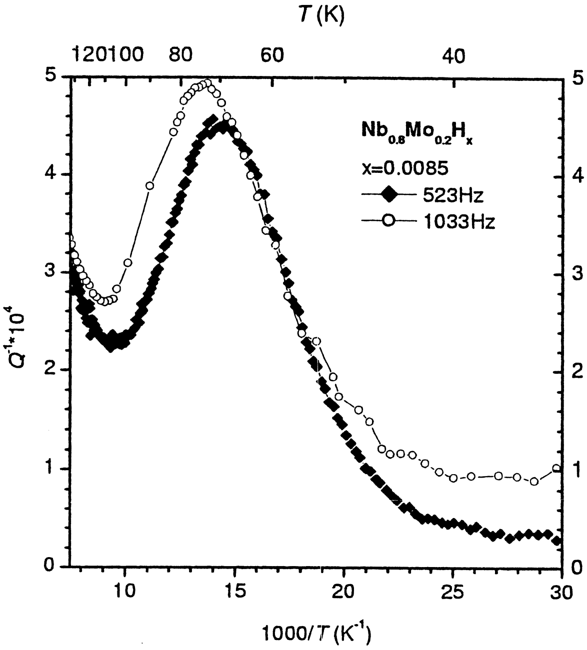

Fig. 1. Energy dissipation of a $Nb_{0.8}Mo_{0.2}$ sample doped with 0.85 at.% H in a plot versus reciprocal temperature (the upper abscissa shows the temperature). The inset indicates the vibrational frequencies. The data were taken with the vibrational reed technique.

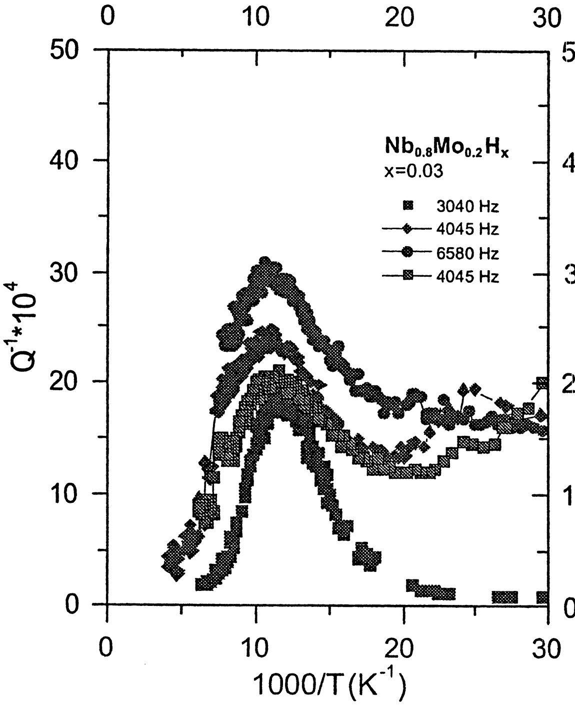

Fig. 2. Energy dissipation of a $Nb_{0.8}Mo_{0.2}$ sample doped with 3 at.% H in a plot versus reciprocal temperature. The inset indicates the vibrational frequencies. The data were taken from free flexural vibrations.

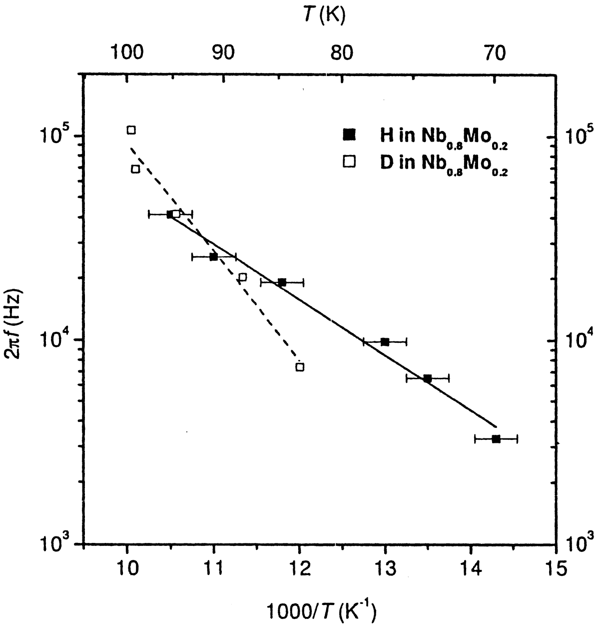

Fig. 3. Angular frequency $2\pi f$ in an Arrhenius plot versus the reciprocal temperature at the maxima of the relaxation peaks (the upper abscissa indicates the temperature). The figure shows the present data for H and previous ones for D [9]. For an ideal Debye relaxation, $2\pi f$ is the relaxation rate.

data certainly cannot exclude the possibility of other functional temperature dependencies of $1/\tau$.

The measured relaxation peaks are about 80% broader than what is expected for an ideal Debye relaxation. This indicates a spectrum of relaxation rates, centered essentially around the values given above.

A straightforward interpretation of the present results is a Snoek-type relaxation due to diffusive jumps of single H atoms between tetrahedral interstitial sites. This interpretation is supported by the essentially linear dependence of the relaxation strength on H concentration indicated by the spectra in Figs. 1 and 2. In contrast to Snoek relaxation in pure b.c.c. metals, a more complex relaxation mechanism is expected in disordered $Nb_{0.8}Mo_{0.2}$. First, applied stresses will differently modify the energy of H interstitial atoms on differently oriented sites, such as in the conventional Snoek effect [8]. However, stresses can also modify the energy of H interstitials on sites with different metallic neighborhoods, even if these sites are identically oriented. Another fact to consider is that the energy of H interstitials will principally vary from site to site, with the additional consequence that H jump rates depend on between which sites jumps occur. All these effects do not allow giving a quantitative relationship between relaxation rate $1/\tau$ and H jump rates, in contrast to the conventional Snoek effect [8]. However, $1/\tau$ will certainly characterize these jump rates.

From the height of the relaxation peaks in Figs. 1 and 2, the tetragonality $|\lambda_1-\lambda_2|$ of the involved λ tensors can be estimated to be about 0.04, thus being about 14 times smaller than for the Snoek effect of O in Nb [8]. This estimate is very rough (i) because of the complex relaxation mechanisms and (ii) because the present samples were polycrystalline.

Before discussing our results in more detail, we mention recent mechanical spectroscopy data for the relaxation rate of D interstitials in $Nb_{0.8}Mo_{0.2}$ [9]. These data are also presented in Fig. 3.

At 80 K, the present measurements yield a relaxation rate $1/\tau=1.2\cdot10^4\ s^{-1}$ which we shall, for reasons of simplicity, first identify with a typical H jump rate. For H in pure Nb, the H jump rate at 80 K, extrapolated from temperatures above 120 K, is $\sim2\cdot10^8\ s^{-1}$, and even higher jump rates above $10^{10}\ s^{-1}$ are found at 80 K by neutron spectroscopy for H interstitials that are trapped in Nb by O or N impurities [1,3]. In both cases, H jumps occur between tetrahedral interstitial sites, as in the present situation. The difference of more than four orders of magnitude must be attributed to the site-to-site variations in H energy in disordered $Nb_{0.8}Mo_{0.2}$. Such energy variations may decrease H jump rates between neighboring sites in the present tunneling-dominated diffusion process [1–3]. However, we must also consider that the H interstitials will essentially occupy only energetically favorable sites, both before and after a stress-induced relaxation process (the stress-induced energy variations are much smaller than site-to-site differences of H energy). Therefore, a relaxation process will solely modify the H occupancy of energetically favorable sites which, in general, will not be nearest-neighbor ones so that the H interstitials must diffuse over longer distances which involves a series of consecutive H jumps. This has two consequences. First, the actual (averaged) H jump rate exceeds the measured relaxation rate $1/\tau$. A second consequence is that any diffusion between energetically favorable sites will, in general, require jump paths over energetically unfavorable sites and, thus, jumps from favorable to unfavorable sites. This will decrease $1/\tau$ even in a completely classical consideration by a factor of roughly $\exp[-\varepsilon/(kT)]$, where ε is the energy difference between the favorable sites and the most unfavorable site along a given jump path. Such a factor becomes plausible by considering two neighboring sites 1 and 2 where the energy of site 2 exceeds that of site 1 by ε so that, at low H concentrations, the occupation probabilities p_1 and p_2 of the two sites have the ratio $p_2/p_1=\exp[-\varepsilon/(kT)]$. Further, ν_1 and ν_2 are the jump rates from site 1 to site 2 and from site 2 to site 1, respectively. Detailed balance requires $p_1\nu_1=p_2\nu_2$ so that the jump rate ν_1 from the low to the high energy site is reduced against ν_2 by $\exp[-\varepsilon/(kT)]$.

The above considerations show (i) that the actual (averaged) jump rates in the present case are in fact larger than $1/\tau$ and (ii) that variations of the H energy from site to site can drastically reduce the relaxation rate. We think that both effects can explain the large difference between the present relaxation rates and the much higher H jump rates [1,3] mentioned above.

Before concluding, we address three further aspects. It is known that the relaxation strength for a process in which an atom can occupy two sites with energy difference ε is reduced by a factor $\exp[-\varepsilon/(kT)]$ [8]. This exponential reduction of relaxation strength for processes involving sites of higher energy corresponds completely to our reasoning that only energetically favorable sites are important for the relaxation process. The second aspect is mechanical spectroscopy measurements for H trapped by O impurities in Nb [10,11] (see also Ref. [3]). At 80 K, the measurements yielded relaxation rates of about $2\cdot10^{3}\ \mathrm{s}^{-1}$, differing by less than a factor of ten from our results. The relaxation observed in these measurements can, similarly as in the present case, be explained by a H occupancy of energetically favorable trap sites, where the diffusive paths between these favorable sites involves passing unfavorable ones (see Ref. [3] for more details). Finally, the mechanical spectroscopy measurements on H-doped $\mathrm{Nb}_{0.5}\mathrm{V}_{0.5}$ [4], mentioned in the introductory section, yielded at 105 K, the lowest temperature of the measurements, a relaxation rate of $\sim3.5\cdot10^{3}\ \mathrm{s}^{-1}$. A low-temperature extrapolation suggests an even 1000 times smaller value at 80 K. Such a small value, four orders of magnitude below the present relaxation rate at 80 K, indicates either extremely large site-to-site differences in H energy, much larger than those in $\mathrm{Nb}_{0.8}\mathrm{Mo}_{0.2}$, or a nearly complete occupation solely of octahedral sites. The latter scenario seems more likely, particularly since the distance between nearest-neighbor octahedral sites in a b.c.c. alloy is $\sqrt{2}$ times larger than the distance between nearest-neighbor tetrahedral sites, so that tunneling becomes less efficient for octahedral occupancies. That the distance between interstitial sites is important is well demonstrated by a comparison between b.c.c. metals with tetrahedral H occupancies and f.c.c. metals with octahedral occupancies. The distance between nearest-neighbor octahedral sites in f.c.c. metals is typically twice as large as the distance between nearest-neighbor sites in b.c.c. metals, a fact that makes H tunneling and, thus, H diffusion at low temperatures in b.c.c. drastically faster than in f.c.c. metals [1,3].

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