ELSEVIER

Journal of Alloys and Compounds 253–254 (1997) 258–259

Journal of ALLOYS AND COMPOUNDS

Structure and microdomain structure of ordered niobium hydrides and deuterides by means of neutron scattering

B. Hauer[a,b,*], R. Hempelmann[b], T.J. Udovic[c], J.J. Rush[c], W. Kockelmann[d], E. Jansen[d], W. Schäfer[d], D. Richter[a]

[a] *Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany*
[b] *Physikalische Chemie, Universität des Saarlandes, 66123 Saarbrücken, Germany*
[c] *National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*
[d] *Institut für Mineralogie der Universität Bonn, Außenstelle Jülich, 52425 Jülich, Germany*

Abstract

Extensive high-resolution vibrational density of states measurements have been performed on ordered niobium hydrides and deuterides by means of neutron vibrational spectroscopy (NVS). The investigations show a splitting of the hydrogen vibrational modes into a two-peak system in the case of the ϵ-phase and a three-peak system in the case of the λ-phase. These different peak systems can be assigned to different hydrogen sites, which is further confirmed by neutron diffraction (ND) data.

Keywords: Niobium; Metal hydrogen system; Neutron vibrational spectroscopy; Neutron diffraction

1. Introduction

The investigation of the hydrogen potential in ordered niobium hydrides by NVS is the basis for understanding these prototype metal hydrogen systems. Therefore, several NVS experiments have been performed on this topic [1–3]. However, until now different vibrational states could not be assigned to different hydrogen sites. Herein we present highly resolved NVS data where a splitting in different peak systems could be detected and, in combination with supporting ND measurements, could be associated with different hydrogen sites within a single phase.

2. Experimental

The starting materials were single crystals and polycrystalline niobium with a purity of at least 99.9%. The hydrogen loading was performed from the gas phase and monitored by weight increase. The NVS and ND experiments were carried out using the high-resolution BT-4 filter spectrometer and the high-resolution BT-1 powder diffractometer, respectively, at NIST.

3. Results

We investigated the vibrational spectra of $NbH(D)_x$ samples in the ϵ-phase ($0.109<x<0.715$).

Due to phase separation at low T in all samples with H(D) concentrations below $x=0.75$, the scattering nearly exclusively originated from the ϵ-phase. The spectrum of $NbH_{0.609}$ measured at 4 K shows a peak splitting at neutron energy transfers near 120 meV and 160 meV (Fig. 1). The intensity ratios of the split components are both 2:1. This result was confirmed by measurements on $NbH_{0.109}$ as well as on deuterides taking into account the peak shift due to the isotopic effect. Spectra measured on samples with isotopic dilution (e.g., $NbD_{0.54}H_{0.06}$) show a linear superposition of the peaks measured on the pure hydrides and deuterides with nearly no additional peak shifts. ND experiments performed on $NbD_{0.715}$ confirm the structure as proposed in [4] but indicate, in addition, a displacement of niobium atoms from their position in the ideal bcc niobium lattice towards intrinsic hydrogen vacancies that exist due to the nonstoichiometry.

The vibrational excitations measured on $NbH(D)_x$ samples with hydrogen concentrations $0.794<x<0.945$ ($T<200$ K) show a splitting into up to three peaks (Fig. 2). The intensity of the peak at 109 meV decreases with larger hydrogen content and vanishes at $x=0.85$. ND data

---

[*] Corresponding author.

0925-8388/97/$17.00
PII S0925-8388(96)02886-1

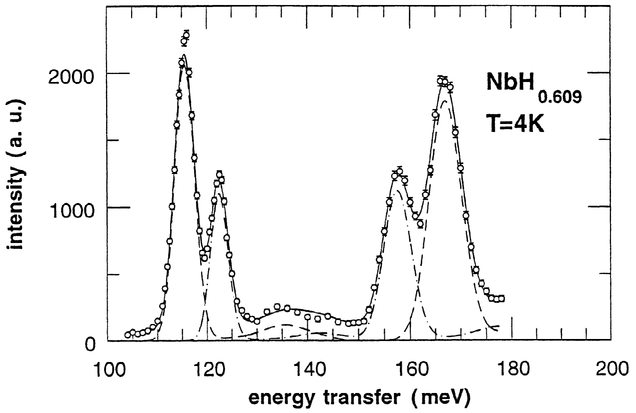

Fig. 1. Neutron vibrational spectrum for $NbH_{0.609}$ at 4 K. The solid line is the result of the fitting procedure; the dashed lines are the contributions of the two different peak systems.

measured on $NbD_{0.788}$, $NbH_{0.794}$ and $NbD_{0.852}$ confirm that the λ-phases consist of microdomains with β-phase structure separated by 180° domain boundaries, as proposed in [5]. At the concentration $x=0.788$, the exclusive existence of domain boundaries with an ordering of the intrinsic hydrogen vacancies in plane layers can be excluded, whereas domain boundaries with a zig-zag structure of the vacancies or the coexistence of both types are both consistent with the data. At $x=0.852$, the data do not allow a distinction between either model.

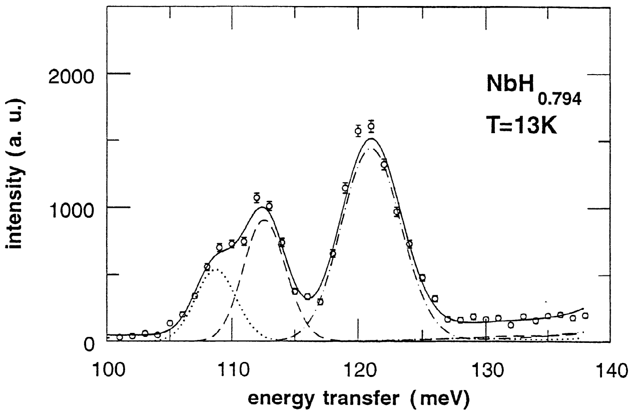

Fig. 2. Neutron vibrational spectrum for $NbH_{0.794}$ at 13 K.

4. Discussion

The spectra of the samples with isotopic dilution prove that the hydrogen atoms are not significantly coupled, since characteristic peak shifts which would be expected in that case are not detectable. Rather, the splitting is caused by distortions of the surrounding niobium tetrahedra, which differ for two different hydrogen sites. These sites show an occupation ratio of 2:1. These distortions of the niobium tetrahedra are confirmed by the ND data.

The peak splitting in case of the λ-phases can be attributed to the existence of three different hydrogen sites, one within the microdomains having β-phase structure and the two others within the two different types of domain boundaries mentioned above. This result is in accordance not only with the ND data but also with the intensity ratios of the NVS peaks, which allow a recalculation of the hydrogen content in the framework of the different models of the domain boundaries. At higher hydrogen concentrations ($x\sim0.85$), only the domain boundary consisting of plane layers of the intrinsic hydrogen vacancies exists.

References

[1] D. Richter and S.M. Shapiro, *Phys. Rev. B*, 24 (1980) 599.
[2] J. Eckert, J.A. Goldstone, D. Tonks and D. Richter, *Phys. Rev. B*, 27 (1983) 1980.
[3] S. Ikeda and N. Watanabe, *J. Phys. Soc. Japan*, 56 (1987) 565.
[4] V.A. Somenkov, V.F. Petrunin, S. Sh. Shil'stein and A.A. Chertkov, *Sov. Phys. Cryst.*, 14 (1970) 522.
[5] B.J. Makenas and H.K. Birnbaum, *Acta Met.*, 30 (1982) 469.