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Coherency stresses and deuterium diffusion in $NbD_{0.33}$

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Abstract

Concentration fluctuations of impurity atoms in solids, such as hydrogen in metals, are accompanied by coherency stresses if the impurity atoms expand or contract the lattice. The coherency stresses raise the elastic energy which accelerates the diffusive decay of the fluctuations and increases, therefore, the value of a diffusion coefficient defined according to Fick's law. We studied the influence of coherency stresses on deuterium diffusion in $NbD_{0.33}$ by neutron spectroscopy, separating coherent and incoherent scattering by neutron spin analysis. The diffusion coefficient D_{bulk} of the deuterium interstitials, obtained from the coherent scattering intensity, was found up to 30 times larger than the diffusion coefficient D_{chem} reported from Gorsky effect measurements [H.C. Bauer, J. Völkl, T. Tretkowski, G. Alefeld, Z. Physik B29 (1978) 17] on the same system, in spite of the fact that both diffusion coefficients describe deuterium diffusion according to Fick's law. We demonstrate that the large differences between D_{bulk} and D_{chem} reflect a dissimilar influence of coherency stresses on these two quantities, and that the differences can quantitatively be described within the elasticity-theoretical concept of Wagner and Horner.

Keywords: Hydrogen in metals; Metal-hydrides; Diffusion; Neutron spectroscopy

1. Introduction

The diffusion behavior of impurity atoms in solid materials – such as hydrogen in metals – is crucially influenced by coherency stresses. The coherency stresses arise in the presence of concentration fluctuations of the impurity atoms if these atoms expand or contract the crystal lattice. The coherency stresses raise the elastic energy which speeds up the diffusive decay of the fluctuations and increases, therefore, the value of a diffusion coefficient defined according to Fick's law.

In this paper, we report on a quasi-elastic neutron scattering study on a $NbD_{0.33}$ crystal which, together with Gorsky effect measurements of Bauer et al. [1], show clearly the influence of coherency stresses on the value of a diffusion coefficient of the deuterium atoms that is defined according to Fick's law. We shall demonstrate that the influence of the coherency stresses can quantitatively be described within the elasticity-theoretical concept of Wagner and Horner [2,3] (see also Refs. [4,5]).

2. Sample and coherent neutron scattering

Our experiments were carried out on a $NbD_{0.33}$ single crystal (length, 89 mm; diameter, 12 mm; crystal axis in [110] direction). The crystal was doped with deuterium at ~600°C in a deuterium gas atmosphere of ~2.8 bar. The deuterium concentration (D/Nb atom ratio 0.33±0.01) was determined from the decrease of the deuterium gas pressure during the doping procedure and from the increase of the sample weight after doping. The doped sample was placed in a sealed Al container to avoid deuterium losses in the course of our neutron scattering experiments.

In a neutron scattering study, the diffusing deuterium interstitials cause a coherent and an incoherent scattering intensity. The relevant intensity here is the coherent one which describes the particle density fluctuations of the deuterium interstitials. In a situation in which the fluctuation dynamics of the deuterium interstitials is characterized by a diffusion coefficient D that is defined according to Fick's law, the coherent scattering law (or intensity) $S(\boldsymbol{Q}, \omega)$ is a Lorentzian line [4,5,10],

$$S(\boldsymbol{Q}, \omega) = \frac{1}{\pi} \cdot \frac{\boldsymbol{Q}^2 D}{\omega^2 + (\boldsymbol{Q}^2 D)^2}, \tag{1}$$

where $\hbar\boldsymbol{Q}$ and $\hbar\omega$ are the momentum and the energy transfer, respectively ($\hbar$ is Planck's constant). The diffusion coefficient D is, thus, obtained from the linewidth $\boldsymbol{Q}^2 D$ of $S(\boldsymbol{Q}, \omega)$. We mention that $S(\boldsymbol{Q}, \omega)$ in (1) is correct

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only for Q values small against π/d, where $d=1.19$ Å [11] is the distance between neighboring tetrahedral sites of the deuterium interstitials. This condition was well fulfilled in the present experiments since the investigated Q values did not exceed 1 Å^{-1}.

The neutron data were taken with the triple axis spectrometer IN 14 at the ILL in Grenoble. This instrument allows discrimination of the coherent from the incoherent scattering intensity by neutron polarization and spin analysis. Spectra were taken at 454, 464 and 504 K (accuracy ±2 K), and with scattering vectors $\boldsymbol{Q}$ in $\langle 111 \rangle$ directions.

3. Experimental results and discussion

Fig. 1 shows results for the coherent scattering intensity, measured at 464 K for three different Q values. The solid lines are fit curves to the data, performed with Lorentzian lines convoluted with the experimental resolution. The diffusion coefficients of the deuterium interstitials derived from our fits are presented in Fig. 2 (full circles), together with Gorsky effect results for the diffusion coefficient of deuterium reported by Bauer et al. [1] for the identical system $NbD_{0.33}$ (solid line). It can be seen that the diffusion coefficients obtained by neutron scattering and Gorsky effect differ up to a factor of 30, in spite of the fact that both diffusion coefficients describe deuterium diffusion according to Fick's law. In the following, we shall demonstrate that the differences in the diffusion coefficients result from the dissimilar influence of coherency stresses on the deuterium fluctuations probed by neutron scattering and Gorsky effect.

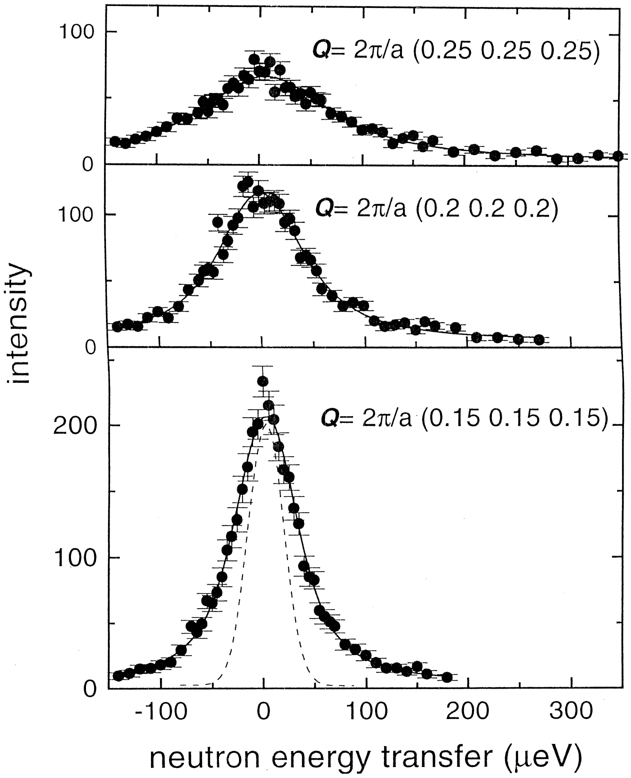

Fig. 1. Neutron spectra of the coherent scattering intensity, taken from our $NbD_{0.33}$ crystal at 464 K. The indicated Q values are 0.81, 0.65 and 0.49 Å^{-1}, from top to bottom ($a=3.36$ Å [12] is the lattice parameter). Solid curves are fits to the data. The broken line in the bottom spectrum represents the experimental resolution.

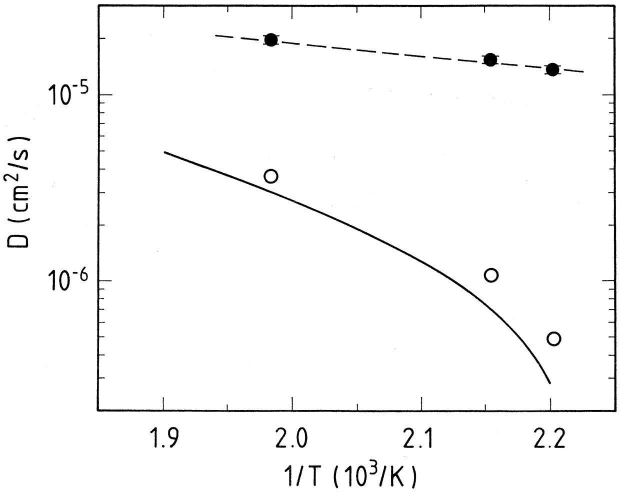

Fig. 2. Arrhenius plot of diffusion coefficients D of deuterium in $NbD_{0.33}$ obtained by the present neutron scattering study (full circles) and in Gorsky effect measurements of Bauer et al. [1] (solid line). The broken line shows an Arrhenius relationship for the present neutron data, yielding an activation energy of 0.15±0.02 eV. The open circles are diffusion coefficients calculated according to (2) from our neutron data (see text).

The influence of coherency stresses on the fluctuation dynamics of impurity atoms – in our case deuterium interstitials – was theoretically discussed by Cahn [6–8], Krivoglaz [9] and Wagner and Horner [2,3] (see also Refs. [4,5]). Latter authors showed specifically that concentration fluctuations in a given sample can be classified in two types of eigenmodes: (i) bulk (or microscopic) modes and (ii) macroscopic modes. The bulk modes, already discussed by Cahn [6–8] and Krivoglaz [9], are (sinusoidal) concentration fluctuations with wavelengths much smaller than the dimensions of a given sample. The macroscopic modes, on the other hand, have characteristic lengths in the range of these dimensions. Their coherency stresses and, therefore, elastic energies are smaller than those of the bulk modes, or they are even zero in some cases. The macroscopic modes differ, further, from the bulk modes in that their properties will, in general, depend on the elastic boundary conditions, i.e. on the shape of the investigated sample.

The important aspect of the above analysis is that coherent neutron scattering probes the dynamics of deuterium fluctuations with wavelengths $2\pi/Q$ (in our case about 10 Å), i.e. the dynamics of bulk modes [2–5]. The diffusion coefficient of the Gorsky effect measurements characterizes, on the other hand, the dynamics of coherency stress-free macroscopic modes [1–5]. This means that the two experimental techniques measure in fact different diffusion coefficients, D_{bulk} (neutron scattering) and D_{chem} (Gorsky effect), according to the nomenclature of Ref. [4].

In what follows, we shall assume an elastically isotropic material and an isotropic volume expansion due to the deuterium interstitials. In this case, the relationship between D_{bulk} and D_{chem} is given by Refs. [2–4]:

$$\frac{D_{\mathrm{bulk}}}{D_{\mathrm{chem}}} = 1 + \frac{\rho \cdot (E_1 - E_{\mathrm{bulk}})}{k_B T \cdot f_{\mathrm{therm}}}, \tag{2}$$

where $k_B T$ is the thermal energy and ρ is the particle density (number per volume) of the deuterium interstitials. f_{therm} is the thermodynamic factor, given by $\rho \cdot \partial\mu/\partial\rho/k_B T$, where $\partial\mu/\partial\rho$ is the partial derivative of the chemical potential of the deuterium interstitials with respect to their particle density. The difference $E_1 - E_{\mathrm{bulk}}$ can be written as $E_1 - E_{\mathrm{bulk}} = P^2 \cdot (1/B - 1/C_{11}) = P^2 \cdot 4G/\{B \cdot (3B + 4G)\}$, where P is a trace component of the double force tensor of the deuterium interstitials, B is the bulk modulus, G is the shear modulus and C_{11} is one of the elastic moduli in Voigt's notation. Finally, P is given by $P = (B/\rho) \cdot (\Delta V/V)$, where $\Delta V/V$ is the relative volume expansion caused by a deuterium particle density ρ.

With the help of (1), D_{chem} can be calculated from our neutron data for D_{bulk}. Using $\rho = 1.73 \times 10^{28}\ \mathrm{m}^{-3}$ [12], $\Delta V/V = 0.0561$ [12], and elastic moduli $B = 17.1 \times 10^{10}\ \mathrm{J/m^3}$ and $G = 3.92 \times 10^{10}\ \mathrm{J/m^3}$ [13] (G is the mean of Reuss' and Voigt's orientational average [14]), we find $P = 3.5$ eV and $\rho \cdot (E_1 - E_{\mathrm{bulk}}) = 0.045$ eV. The thermodynamic factor f_{therm} was determined in the Gorsky effect measurements of Bauer et al. [1], given there in the parametrized form $f_{\mathrm{therm}} = (T - T_s)/(\alpha \cdot T)$, where $\alpha = 0.51 \pm 0.05$ and $T_s = (444 \pm 2)$ K for the present deuterium concentration. The results for D_{chem}, calculated from the numerical data above and from our neutron data for D_{bulk}, are presented in Fig. 2 (open circles). It is seen that these calculated results agree well with the D_{chem} values of the Gorsky effect measurements, in particular under consideration of the fact that our calculation did not consider any experimental error either in the Gorsky effect results or in the literature data for the elastic moduli. The good agreement shows that the large differences between the diffusion coefficients obtained from our coherent neutron spectra and from the Gorsky effect measurements are caused, and quantitatively describable, by coherency stresses.

We mention, finally, that the present large ratios $D_{\mathrm{bulk}}/D_{\mathrm{chem}}$ are a consequence of the fact that sample composition and investigated temperatures are in a range of the Nb–D phase diagram that is closely above the spinodal temperature $T_s \simeq 444$ K of a miscibility gap [1,11]. This means small values for f_{therm}, so that $D_{\mathrm{bulk}}/D_{\mathrm{chem}}$ in (2) becomes large.

4. Conclusion

The present neutron scattering results demonstrate – together with the Gorsky effect data of Bauer et al. [1] – clearly the influence of coherency stresses on deuterium diffusion in $\mathrm{NbD}_{0.33}$. The different diffusion coefficient values obtained by the two experimental techniques can quantitatively explained within the elasticity-theoretical concept of Wagner and Horner [2–5].

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