

Quasielastic neutron scattering study of hydrogen motion in $\text{NbC}_{0.71}\text{H}_{0.28}$

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Abstract

In order to study the mechanism and parameters of H jump motion in the nonstoichiometric Nb carbides, we have performed quasielastic neutron scattering (QENS) measurements for $\text{NbC}_{0.71}\text{H}_{0.28}$ over the temperature range 11–475 K. Our results indicate that about 30% of H atoms in this system participate in a fast diffusive motion. The temperature dependence of the corresponding H jump rate in the range 298–475 K follows the Arrhenius law with an activation energy of 328 ± 9 meV. The Q dependence of the QENS data suggests that the observed jump motion corresponds to long-range diffusion of H atoms along chains of the off-centre sites in carbon vacancies.

1. Introduction

Cubic transition-metal carbides MC_{1-y} are known to retain their stability up to high concentrations y of structural vacancies in the carbon sublattice [1, 2]. Nonstoichiometric carbides MC_{1-y} having the metallic properties and NaCl-type structure can absorb hydrogen from the gas phase, forming ternary compounds $\text{MC}_{1-y}\text{H}_x$. Neutron diffraction studies of these compounds [3–7] have shown that hydrogen atoms occupy mainly the vacancies in the carbon sublattice (octahedral sites). The cubic niobium carbides NbC_{1-y} are stable in the y range from 0 to 0.30; at higher y , the Nb carbides adopt a hexagonal structure.

A nuclear magnetic resonance (NMR) study of the cubic $\text{NbC}_{1-y}\text{H}_x$ ($0.01 \leq y \leq 0.29$) [8] has revealed that the hydrogen mobility in this system strongly depends on the concentration of carbon vacancies. For samples with $y \leq 0.24$, no significant motional contributions to the proton spin-lattice relaxation rate R_1 have been found up to 420 K. On the other hand, for $\text{NbC}_{0.71}\text{H}_{0.28}$ the measured $R_1(T)$ exhibits a frequency-dependent peak near 300 K [8]. Such a peak is a characteristic feature of the motional contribution to R_1 ; it occurs at the temperature at which the hydrogen jump rate τ_d^{-1} becomes approximately equal to the NMR frequency. The NMR results [8] also suggest that only a fraction of hydrogen

atoms in $\text{NbC}_{0.71}\text{H}_{0.28}$ participate in the fast jump motion. However, NMR measurements cannot give direct information on spatial aspects of hydrogen motion. In particular, it is not clear whether the observed $R_1(T)$ peak is due to long-range H diffusion or to localized H jump motion. Recent neutron diffraction measurements [9] have shown that hydrogen atoms in $\text{NbC}_{0.71}\text{H}_{0.28}$ occupy the sites displaced from the centres of carbon vacancies; the existence of such off-centre H sites may be related to the enhanced H mobility in this compound. The aim of the present work is to study the microscopic picture and the parameters of H jump motion in $\text{NbC}_{0.71}\text{H}_{0.28}$ using the quasielastic neutron scattering (QENS) technique [10, 11], which can probe both the frequency and spatial scales of atomic motion. To the best of our knowledge, this is the first application of QENS to studies of H motion in hydrogenated transition-metal carbides. We have measured QENS spectra for $\text{NbC}_{0.71}\text{H}_{0.28}$ over the temperature range 11–475 K using two neutron spectrometers with high and medium energy resolution.

2. Experimental details

The preparation of $\text{NbC}_{0.71}\text{H}_{0.28}$ was described in [8]. X-ray diffraction analysis has shown that, in addition to the main

NaCl-type phase with the lattice parameter $a = 4.437 \text{ \AA}$, this sample also contains a small amount ($\sim 5 \text{ wt\%}$) of the hexagonal Nb_2C phase. The presence of the hexagonal phase may be related to the fact that the composition of $\text{NbC}_{0.71}$ is close to the boundary of the homogeneity range of the cubic NbC_{1-y} phase ($0 \leq y \leq 0.30$).

QENS measurements were performed on the high-resolution backscattering spectrometer IN10 (Institute Laue–Langevin (ILL), Grenoble) and on the disc-chopper time-of-flight spectrometer DCS (NIST Center for Neutron Research, Gaithersburg, MD). These two spectrometers complement each other with respect to the resolution and the accessible range of energy transfers, enabling one to probe H motion over a range of jump rates from 10^8 to 10^{12} s^{-1} . In our experiments the incident neutron wavelengths were 6.27 \AA (IN10) and 4.8 \AA (DCS), the ranges of energy transfers $\hbar\omega$ studied were $\pm 14 \text{ \mu eV}$ (IN10) and $\pm 1.2 \text{ meV}$ (DCS), and the energy resolution full widths at half-maximum (FWHMs) were 1.0 \mu eV (IN10) and 120 \mu eV (DCS). The ranges of elastic momentum transfers $\hbar Q$ studied corresponded to Q ranges of $0.50\text{--}1.96 \text{ \AA}^{-1}$ (IN10) and $0.60\text{--}2.32 \text{ \AA}^{-1}$ (DCS). For measurements on IN10, the powdered $\text{NbC}_{0.71}\text{H}_{0.28}$ sample was placed in a flat Al container oriented nearly perpendicular to the incident beam, and for measurements on DCS it was placed in an annular Al container. In both cases, the sample thickness was 0.3 mm . In order to determine the temperature range where the effects of quasielastic line broadening become observable on the energy scale of the backscattering spectrometer, we used a special fixed-window operation mode of IN10. In this mode, the Doppler drive is stopped (so that the energy transfer is zero) and the elastic scattering intensity at different Q values is recorded as a function of temperature. For such an elastic scan, the sample temperature was swept from 39 to 430 K at a rate of 0.6 K min^{-1} . QENS spectra were recorded at $T = 11, 298, 328$ and 351 K on IN10 and at $T = 250, 425, 450$ and 475 K on DCS. The scattering angles corresponding to the Bragg reflections were shielded by cadmium (IN10) or excluded from the analysis (DCS). The raw experimental data were corrected for absorption and self-shielding using the standard ILL or NIST programs. For both spectrometers, the instrumental resolution functions were determined from the measured QENS spectra of $\text{NbC}_{0.71}\text{H}_{0.28}$ at low temperatures (11 K for IN10 and 250 K for DCS).

3. Results and discussion

Figure 1 shows the temperature dependences of the elastic scattering intensities measured at two Q values using the fixed-window operation mode of IN10. For both Q values, the results of the elastic scan exhibit a characteristic step in the range 270–340 K. The amplitude of the observed changes in the relative elastic scattering intensity considerably exceeds that expected for the temperature dependence of the Debye–Waller factor. Therefore, the elastic intensity drop in the range 270–340 K can be related to quasielastic line broadening due to the onset of H jump motion on the timescale corresponding to the IN10 resolution. These results suggest that the changes in QENS

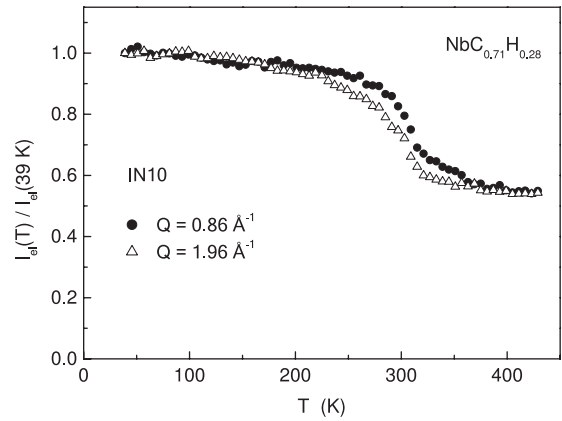


Figure 1. The temperature dependences of the elastic neutron scattering intensities for $\text{NbC}_{0.71}\text{H}_{0.28}$ obtained using the fixed-window operation mode of IN10 at $Q = 0.86$ and 1.96 \AA^{-1} . The intensities are normalized to their corresponding values at 39 K.

spectra measured by IN10 should be most pronounced in the T range of the step. As the temperature increases further, the rate of the jump motion responsible for the step becomes higher than the width of the frequency ‘window’ of IN10 and the measured elastic intensity should exhibit a new plateau. Such a plateau can be seen in figure 1 at $T > 360 \text{ K}$. For a spatially confined (localized) jump motion, the plateau level is expected to be Q -dependent, reflecting the Q dependence of the elastic incoherent structure factor (EISF) [10, 11]. However, comparison of the measured elastic intensities at $Q = 0.86$ and 1.96 \AA^{-1} (figure 1) shows that, while there is a shift of the T range of the step, the level of the high- T plateau is nearly the same for both Q values. The same is also true for the other Q values (not shown). Thus, the results of the elastic scan are *not* consistent with the picture of localized H motion. It is natural to assume that the jump process responsible for the observed step is associated with long-range H diffusion. The value of the high- T plateau suggests that only a fraction of all H atoms participate in this diffusion, the remaining H atoms being static on the timescale determined by the IN10 resolution. This interpretation is supported by the measurements of QENS spectra to be discussed below.

QENS spectra for $\text{NbC}_{0.71}\text{H}_{0.28}$ measured on both IN10 ($T = 298, 328$ and 351 K) and DCS ($T = 425, 450$ and 475 K) can be satisfactorily described by a sum of two components: a narrow ‘elastic’ line represented by the spectrometer resolution function $R(Q, \omega)$ and a resolution-broadened Lorentzian ‘quasielastic’ line. As an example of the data, figure 2 shows the QENS spectrum measured on DCS at $T = 475 \text{ K}$ and $Q = 2.32 \text{ \AA}^{-1}$. The spectra have been fitted with the model incoherent scattering function

$$S_{\text{inc}}(Q, \omega) = A_0(Q)\delta(\omega) + [1 - A_0(Q)]L(\omega, \Gamma) \quad (1)$$

convoluted with $R(Q, \omega)$. Here $\delta(\omega)$ is the ‘elastic’ δ function, $L(\omega, \Gamma)$ is the ‘quasielastic’ Lorentzian function with the half-width at half-maximum (HWHM) Γ and A_0 is the weight of the ‘elastic’ component. The solid curve in figure 2 shows the fit of this two-component model to the data and the broken

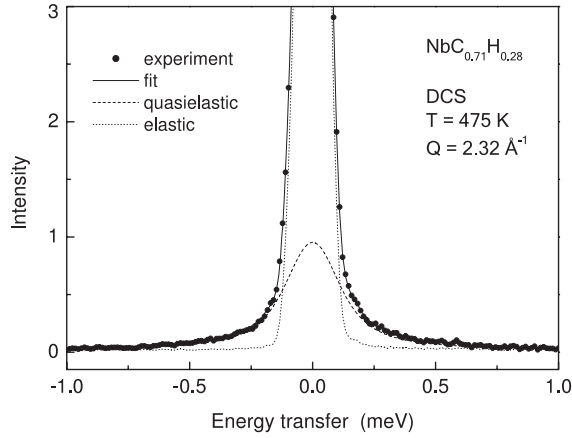


Figure 2. The QENS spectrum for $\text{NbC}_{0.71}\text{H}_{0.28}$ measured on DCS at $T = 475$ K and $Q = 2.32 \text{ \AA}^{-1}$. The full curve shows the fit of the two-component model equation (1) to the data. The dotted curve represents the elastic component (the spectrometer resolution function) and the dashed curve shows the Lorentzian quasielastic component.

curves represent contributions of the two components. As the first step of the analysis, we have used the model function (1) with A_0 and Γ being independent fitting parameters. The half-width Γ is found to increase with increasing Q , reaching a saturation at $Q > 1.7 \text{ \AA}^{-1}$. At any fixed Q value, the value of Γ strongly increases with increasing temperature. Such a behaviour of Γ is typical of the case of jump motion leading to long-range diffusion [10, 11]. The weight A_0 is found to be nearly Q - and T -independent. Therefore, it is natural to attribute the elastic component of the QENS spectra to the contribution of immobile nuclei. In principle, the elastic component can contain the *coherent* diffuse scattering contribution due to a random distribution of carbon vacancies. However, since the coherent scattering lengths of both C and H are much smaller than the incoherent scattering length of H, this contribution is expected to be negligible. The incoherent scattering cross sections of both Nb and C are very small; their contribution to the total incoherent scattering intensity for $\text{NbC}_{0.71}\text{H}_{0.28}$ does not exceed 0.02%. Thus, the value of A_0 can be ascribed to the fraction of protons that remain static on the timescale corresponding to the spectrometer resolution. It should be stressed that both Γ and A_0 show the same qualitative behaviour for the spectra measured on IN10 and DCS.

Since A_0 appears to be nearly Q -independent, at the next stage of the analysis it has been fixed (being equal to its average value at a given temperature). The average values of A_0 at different temperatures are found to vary in the range 0.69–0.75. This means that about 30% of all H atoms participate in the fast motion. Note that such a considerable fraction of mobile protons cannot be attributed to hydrogen in the minor Nb_2C phase. When the value of A_0 is fixed, Γ is the only fitting parameter and the fitting procedure becomes quite stable. The Q dependences of the half-width Γ resulting from the fits of the QENS spectra measured on IN10 and DCS are shown in figures 3 and 4, respectively. For parametrization of these dependences, we have used the orientationally averaged

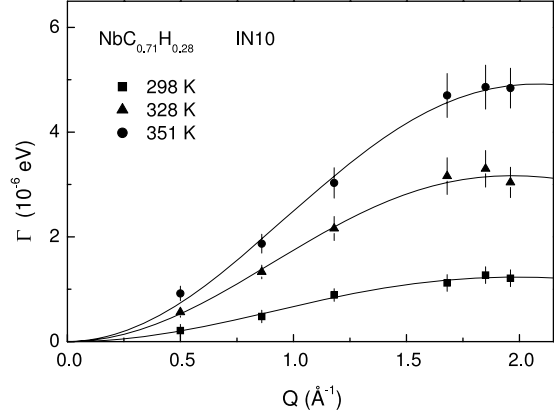


Figure 3. The half-width (HWHM) of the Lorentzian quasielastic component as a function of Q derived from the IN10 data at $T = 298, 328$ and 351 K. Vertical error bars represent one standard deviation. The full curves show the fits of the Chudley–Elliott model (equation (2)) to the data.

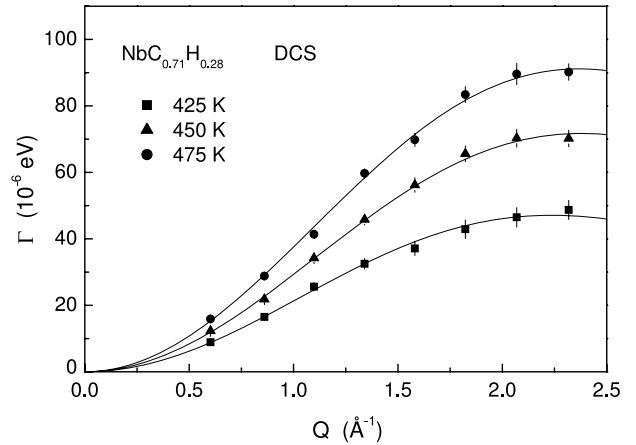


Figure 4. The half-width (HWHM) of the Lorentzian quasielastic component as a function of Q derived from the DCS data at $T = 425, 450$ and 475 K. Vertical error bars represent one standard deviation. The full curves show the fits of the Chudley–Elliott model (equation (2)) to the data.

Chudley–Elliott model [12]. The corresponding form of $\Gamma(Q)$ is

$$\Gamma(Q) = \frac{\hbar}{\tau_d} \left(1 - \frac{\sin QL}{QL} \right), \quad (2)$$

where τ_d is the mean time between two successive H jumps and L is the jump length. The fits of equation (2) to the data are shown by the solid curves in figures 3 and 4. It can be seen that the experimental data are well described by equation (2); this fact suggests that multiple scattering effects for our sample are negligible. The value of L resulting from the Chudley–Elliott fits shows only a slight variation with temperature, changing from $2.2 \pm 0.2 \text{ \AA}$ at 298 K to $1.90 \pm 0.03 \text{ \AA}$ at 475 K. The temperature dependence of the jump rate τ_d^{-1} resulting from the Chudley–Elliott fits is presented in figure 5. As can be seen from this figure, the values of τ_d^{-1} derived from the measurements on IN10 and DCS are likely to originate from

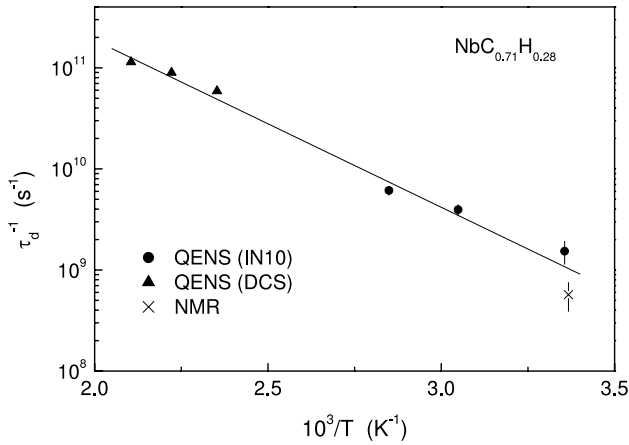


Figure 5. The hydrogen jump rate τ_d^{-1} in $\text{NbC}_{0.71}\text{H}_{0.28}$ as a function of the inverse temperature. The values of τ_d^{-1} are obtained from the QENS spectra measured on IN10 (solid circles) and DCS (solid triangles). The full line shows the global Arrhenius fit to the QENS data. The cross represents the H jump rate derived from the maximum of the proton spin-lattice relaxation rate [8].

the same motional process described by an Arrhenius law:

$$\tau_d^{-1} = \tau_{d0}^{-1} \exp(-E_a/k_B T), \quad (3)$$

where E_a is the activation energy of the H jump process. The solid line in figure 5 shows the global Arrhenius fit to the τ_d^{-1} data (including both the IN10 and DCS results); the corresponding fitting parameters are $E_a = 328 \pm 9$ meV and $\tau_{d0}^{-1} = (3.8 \pm 0.9) \times 10^{14} \text{ s}^{-1}$. Also included in figure 5 is the τ_d^{-1} value estimated at the maximum of the proton spin-lattice relaxation rate for $\text{NbC}_{0.71}\text{H}_{0.28}$ [8]. It can be seen that this point is close to the Arrhenius plot of $\tau_d^{-1}(T)$ obtained from the QENS data. Thus, our QENS results are consistent with the position of the $R_1(T)$ peak found in the NMR experiments [8]. However, the value of E_a derived from our QENS data is considerably higher than that evaluated from the slopes of the $R_1(T)$ peak (180 meV) [8]. Since the NMR data [8] were analysed in a rather narrow range of R_1 variation, it is likely that such an analysis could lead to an underestimated value of E_a .

We now turn to a discussion of the hydrogen jump length derived from the Chudley–Elliott fits. The basic NaCl-type structure of NbC_{1-y} is shown in figure 6. For $\text{NbC}_{0.71}\text{H}_{0.28}$, the distance between the centres of the nearest-neighbour carbon vacancies (open squares in figure 6) is 3.14 Å. It is clear that the values of L resulting from the Chudley–Elliott fits are not consistent with this distance. A recent neutron diffraction study [9] has revealed that the structure of $\text{NbC}_{0.71}\text{H}_{0.28}$ is tetragonally distorted (space group $I4/mmm$), and at least a fraction of H atoms occupy the off-centre 4e sites (crosses in figure 6), which form pairs along the c direction. The distance between two paired 4e sites (points A_1 and A_2 in figure 6) is 1.64 Å and the distance between the nearest-neighbour 4e sites belonging to different pairs (points A_2 and B_1 in figure 6) is 2.29 Å. Thus, the appearance of the off-centre H sites leads to shorter intersite distances and opens ‘easy’ paths for H diffusion (such as A_1 – A_2 – B_1 in figure 6). The values of L derived from the Chudley–Elliott fits

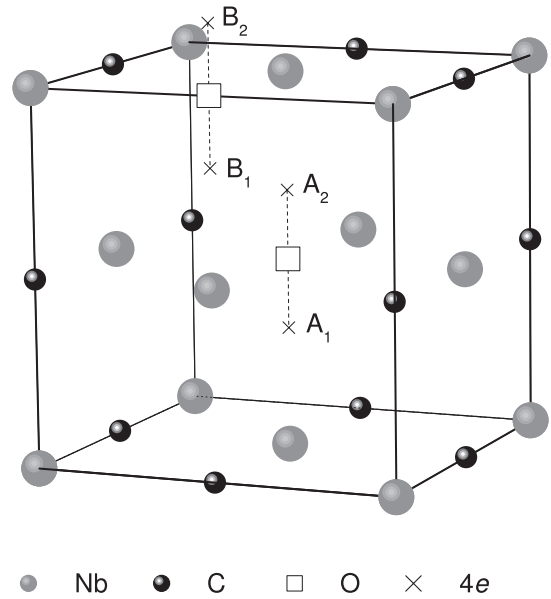


Figure 6. The NaCl-type structure of NbC_{1-y} with the carbon vacancies (octahedral sites) and the displaced 4e sites.

(1.9–2.2 Å) appear to be close to the average of A_1 – A_2 and A_2 – B_1 distances. The ‘immobile’ hydrogen fraction can be attributed to H atoms occupying isolated carbon vacancies, i.e. vacancies having no other nearest-neighbour vacancies in the carbon sublattice. We can conclude that our QENS data are consistent with the jump motion of a fraction of H atoms over off-centre 4e sites in the nearest-neighbour carbon vacancies, although no definitive path can be discerned. It should be noted that chains of the nearest-neighbour carbon vacancies are required to make the long-range H diffusion possible. While such chains are likely to exist in $\text{NbC}_{0.71}\text{H}_{0.28}$, their probability strongly drops for the carbides with higher carbon concentrations. In particular, the ordering of carbon vacancies found for the $\text{NbC}_{0.76}$ –H(D) system [9] prevents the formation of nearest-neighbour vacancy–vacancy pairs. In contrast to the case of H motion in Laves-phase hydrides [13–15], for $\text{NbC}_{0.71}\text{H}_{0.28}$ we have not found any signs of a coexistence of H jump processes with different rates, such as a fast localized motion and a slower jump process leading to long-range diffusion. This suggests that the correlation between the H jump rate and the corresponding intersite distance [16] for hydrogen in Nb carbides is not as strong as in Laves phases.

4. Conclusions

The results of our quasielastic neutron scattering studies of the hydrogenated Nb carbide $\text{NbC}_{0.71}\text{H}_{0.28}$ indicate that a certain fraction (~30%) of H atoms in this compound participate in the fast jump motion. In the temperature range 298–475 K, the jump rate of this motion can be satisfactorily described by the Arrhenius law with an activation energy of 328 ± 9 meV. The Q dependence of the QENS data suggests that the observed jump motion corresponds to long-range diffusion of H atoms over chains of displaced sites in carbon vacancies. The ‘immobile’ hydrogen fraction can be associated with H atoms occupying isolated carbon vacancies, i.e. vacancies having no nearest-neighbour vacancies in the carbon sublattice.

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