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Journal of Alloys and Compounds 253–254 (1997) 432–434

Journal of ALLOYS AND COMPOUNDS

Localized motion of hydrogen in C15-type TaV_2: nuclear magnetic resonance and neutron scattering study

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Abstract

The localized motion of hydrogen in TaV_2 revealed by nuclear magnetic resonance experiments has been studied by quasielastic neutron scattering measurements on $TaV_2H_{0.6}$ and $TaV_2H_{1.1}$ in the temperature range 10–300 K. The behaviour of the elastic incoherent structure factor in the Q range 0.09–3.69 $Å^{-1}$ is consistent with the model of H jumps between six [Ta_2V_2] sites on a ring with radius $r \approx 1.0$ Å. This model is also supported by neutron diffraction measurements. The hopping rate of hydrogen is found to depend strongly on H concentration, decreasing with increasing H content.

Keywords: Quasielastic neutron scattering; Metal hydrides; Diffusion

1. Introduction

Nuclear magnetic resonance (NMR) measurements of ^1H, ^2D and ^{51}V spin-lattice relaxation rates in C15-type $TaV_2H_x(D_x)$ ($0.22 \leq x \leq 1.54$) [1,2] have revealed the unusual localized H(D) motion which is not frozen out on the frequency scale 10^7–10^9 s^{-1} down to 30 K. This localized motion appears to be intrinsic (i.e., not related to hydrogen trapped by impurities or defects) and shows a number of interesting features including non-Arrhenius temperature dependence of the hopping rate and pronounced isotope effects [2]. However, the geometry of this motion has not been elucidated. According to the neutron diffraction data [3–5], D atoms in TaV_2D_x occupy only tetrahedral interstitial sites of g type (Ta_2V_2), the other two types of tetrahedral sites, e (TaV_3) and b (V_4), being empty. The results of our recent quasielastic neutron scattering (QENS) measurements on $TaV_2H_{0.6}$ are consistent with each of the following two models of localized H motion: (i) hopping between three g sites (being the nearest neighbours of one e site) on a circle with radius $r \approx 1.1$ Å, and (ii) hopping over six g sites lying on a circle with nearly the same radius. In the present work we report the results of high-resolution QENS measurements on TaV_2H_x ($x = 0.6$ and 1.1) including the extended range of momentum transfer $\hbar Q$. The emphasis is made on the discussion of geometry of the localized H motion and the effects of H concentration.

2. Experimental

The preparation of TaV_2H_x samples was analogous to that described in Ref. [1]. QENS measurements on $TaV_2H_{0.6}$ were performed on the high-resolution backscattering spectrometer IN10 (in the range 10–140 K) and the cold neutron time-of-flight spectrometer IN5 (10 K and 220–300 K) at the Institute Laue-Langevin. The measurements on $TaV_2H_{1.1}$ were performed using IN10 with Si(111) analysers (10–160 K) and Si(311) analysers (10 K and 140–160 K). The energy resolution FWHM and the Q range were 1 μeV and 0.41–1.94 $Å^{-1}$ (IN10 with Si(111)), 3.5 μeV and 1.77–3.69 $Å^{-1}$ (IN10 with Si(311)), and 109 μeV and 0.09–2.18 $Å^{-1}$ (IN5). In all cases the instrumental resolution function was determined from the measurements at 10 K. The scattering function $S(Q,\omega)$ of the hydrogen sublattice was determined by subtracting the QENS spectra of the identical outgassed TaV_2 sample from those of TaV_2H_x.

3. Results and discussion

The experimental QENS spectra can be satisfactorily described by a sum of two components: a narrow elastic

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PII S0925-8388(96)02888-5

line represented by the spectrometer resolution function and a resolution-broadened Lorentzian quasielastic line. The quasielastic component has not been detected below 75 K for $TaV_2H_{0.6}$ and below 105 K for $TaV_2H_{1.1}$. Fig. 1 shows the Q dependence of the elastic incoherent structure factor (EISF), defined as the ratio of the elastic line intensity to the total incoherent scattering intensity, for $TaV_2H_{1.1}$ at 160 K. It should be noted that the measured EISF for TaV_2H_x depends on temperature, decreasing with increasing T. In order to describe the temperature dependence of EISF, we have to assume that only a fraction p of H atoms participates in the localized motion, and this fraction increases with temperature [6]. The solid line in Fig. 1 shows the fit of the 6-site model (ii) to the data. The radius of the 6-site ring is fixed to 1.0 Å, as results from the neutron diffraction measurements on TaV_2D_x [5]. Therefore the only fit parameter is p, the fitted p value being 0.25 ± 0.02. The dashed line shows the behaviour of EISF for the 3-site model (i) with the same r and p as for model (ii). Note that for the 3-site model EISF is expected to increase with increasing Q above 2.4 $Å^{-1}$.

As can be seen from Fig. 1, the 6-site model appears to be preferable. This is also consistent with the neutron diffraction measurements on TaV_2D_x [5] which have revealed considerable displacements of D atoms from the geometrical centres of g sites. The pattern of these displacements is such that the sublattice of g sites appears to be split into 6-site rings well separated from each other. In fact, the distance between the nearest-neighbour g sites within the ring is 1.0 Å, whereas the minimum distance between g sites at different rings is 1.5 Å.

In order to obtain parameters of the localized H motion at each temperature, we have used a simultaneous fit of $S(Q,\omega)$ for the 6-site model to the data at all Q. The quasielastic line for the 6-site model consists of three Lorentzian components with the half-widths $0.5\tau^{-1}$, $1.5\tau^{-1}$ and $2\tau^{-1}$ (where τ is the mean residence time between two successive jumps) and Q-dependent amplitudes [7]. The fit parameters are τ^{-1} and p. Fig. 2 shows the temperature dependence of the fitted hopping rate τ^{-1} for $TaV_2H_{0.6}$ and $TaV_2H_{1.1}$. It can be seen that, in agreement with the NMR results [1,2], the hopping rate strongly depends on H concentration, decreasing with increasing x.

The temperature dependence of the fitted p value is shown in Fig. 3. The usual approach to the description of $p(T)$ is based on the assumption of a certain energy gap ΔE between ''static'' and ''mobile'' H states (see, e.g., Ref. [8]). We have found, however, that such a model can only describe the observed $p(T)$ if there is a broad ΔE distribution. In fact, the observed $p(T)$ may be reasonably described by a linear dependence (Fig. 3). This feature resembles the well-known behaviour of glasses originating

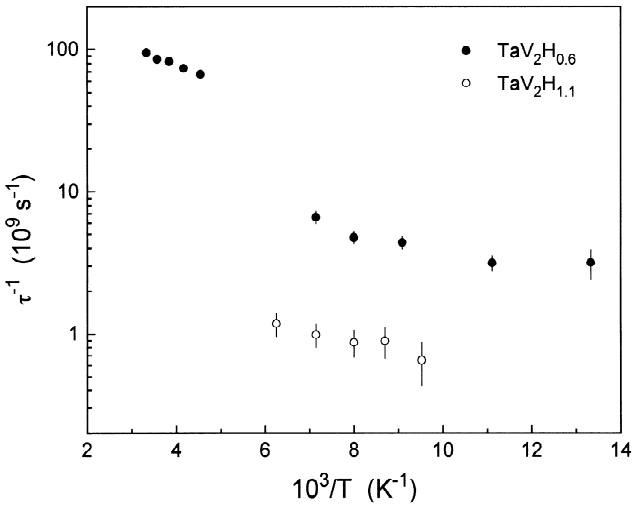

Fig. 2. Hydrogen hopping rate in $TaV_2H_{0.6}$ and $TaV_2H_{1.1}$ as a function of reciprocal temperature.

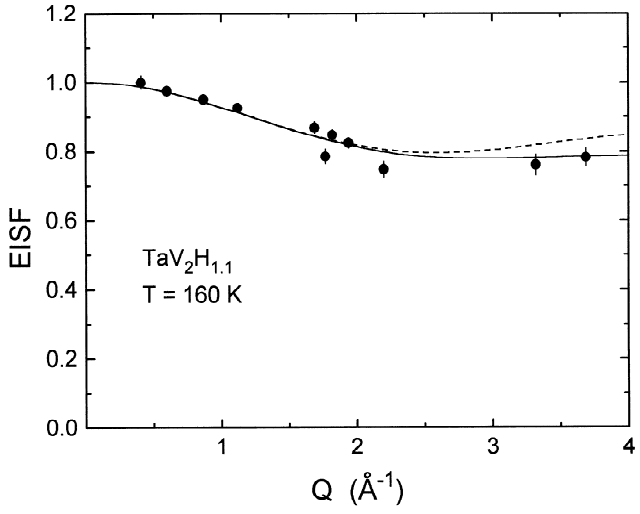

Fig. 1. Elastic incoherent structure factor for $TaV_2H_{1.1}$ at 160 K as a function of Q. The solid line shows the fit of the 6-site model to the data. The dashed line shows the expected behaviour for the 3-site model.

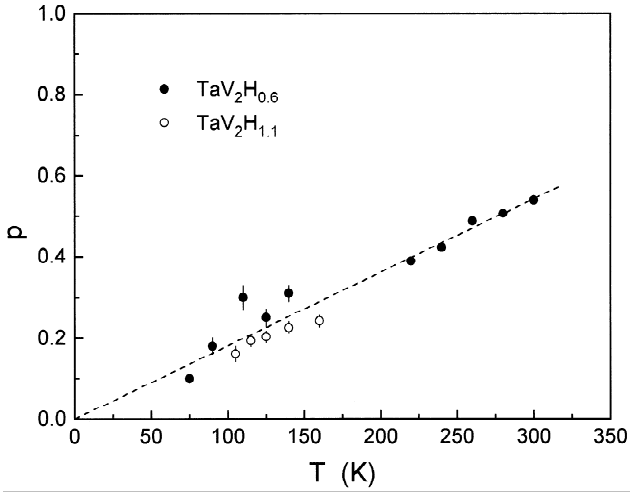

Fig. 3. Temperature dependence of the fraction of protons participating in the localized motion for $TaV_2H_{0.6}$ and $TaV_2H_{1.1}$. The dashed line shows a linear fit to the data for $TaV_2H_{0.6}$.

from two-level systems with a nearly uniform ΔE distribution at low ΔE [9]. As can be seen from Fig. 3, the values of $p(T)$ decrease with increasing H content. This may be related with H–H interactions, since the tendency to hydrogen ordering at higher x [5] is expected to suppress the fast localized H motion.

Acknowledgments

This work was partially supported by the Russian Foundation for Fundamental Research (grant 96-02-16517). AVS acknowledges financial support from the Alexander von Humboldt Foundation and Universität des Saarlandes.

References

[1] A.V. Skripov, M.Yu. Belyaev, S.V. Rychkova and A.P. Stepanov, *J. Phys.: Condens. Matter*, 1 (1989) 2121.
[2] A.V. Skripov, S.V. Rychkova, M.Yu. Belyaev and A.P. Stepanov, *J. Phys.: Condens. Matter*, 2 (1990) 7195.
[3] V.A. Somenkov and A.V. Irodova, *J. Less-Common Met.*, 101 (1984) 481.
[4] P.R. Stonadge, *Ph.D. Thesis*, University of Birmingham, 1992.
[5] P. Fischer, F. Fauth, A.V. Skripov, A.A. Podlesnyak, L.N. Padurets, A.L. Shilov and B. Ouladdiaf, these proceedings.
[6] A.V. Skripov, J.C. Cook, C. Karmonik and R. Hempelmann, *J. Phys.: Condens. Matter*, 6 (1996) L319.
[7] M. Bée, *Quasielastic Neutron Scattering*, Hilger, Bristol, 1988.
[8] N.F. Berk, J.J. Rush, T.J. Udovic and I.S. Anderson, *J. Less-Common Met.*, 172–174 (1991) 496.
[9] W.A. Phillips, *Rep. Progr. Phys.*, 50 (1987) 1657.