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LETTER TO THE EDITOR

Hydrogen in the A15-type compound Ti_3Sb : NMR evidence for low-frequency localized motion of H atoms

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Abstract. Nuclear magnetic resonance measurements of the proton spin-lattice relaxation times in A15-type Ti_3SbH_x ($0.6 \leq x \leq 2.4$) have revealed the existence of a low-frequency localized motion of H atoms. The experimental results are consistent with the hopping of H atoms between closely spaced tetrahedral interstitial sites on the space diagonals of the unit cell.

A number of A_3B intermetallic compounds with the cubic A15 structure are known to absorb considerable amounts of hydrogen [1-6]. The host lattice usually retains the A15 structure after hydrogen absorption. Previous studies of the effects of hydrogen in A15 compounds were devoted mainly to its impact on the superconducting transition temperature T_c [1-3, 7, 8]. However, little is known about the properties of the hydrogen sublattice in these compounds including the positions and mobility of H atoms. The aim of the present work is to study the microscopic features of the diffusive hydrogen motion in the A15-type compound Ti_3Sb . We have measured the proton spin-lattice relaxation times in Ti_3SbH_x over wide ranges of temperature (11-470 K) and resonance frequency (19-90 MHz). The experimental results are consistent with the existence of the localized motion of H atoms between closely spaced tetrahedral interstitial sites on the space diagonals of the unit cell.

The sample of Ti_3Sb was prepared by arc melting the appropriate amounts of high-purity Ti and Sb under helium pressure of 0.5 bar. X-ray diffraction analysis had shown that the sample was a single-phase compound with the cubic A15 structure and the lattice parameter $a_0 = 5.216 \text{ \AA}$. Small pieces of the Ti_3Sb ingot were charged with H_2 gas at a pressure of about 1 bar using a Sieverts-type vacuum system. The hydrogen content was determined from the pressure change in the calibrated volume of the system. Measurements were made on the powder samples of Ti_3SbH_x ($x = 0.6, 1.8$ and 2.4). According to the x-ray diffraction analysis, all the samples studied are single-phase solid solutions with the A15 host-lattice structure; their lattice parameters are listed in table 1. Our structural data are consistent with those of Rama Rao *et al* [4] for Ti_3SbH_x ($0.11 \leq x \leq 1.74$).

Nuclear magnetic resonance (NMR) measurements were performed on a Bruker SXP pulse spectrometer at the frequencies $\omega/2\pi = 19, 35$ and 90 MHz . Proton spin-lattice relaxation times T_1 were measured using the inversion-recovery method. In all cases the relaxation was single-exponential.

Table 1. Lattice parameters, electronic contributions to the proton spin-lattice relaxation rates, temperatures of the relaxation rate maxima and the maximum values of T_{1d}^{-1} for Ti_3SbH_x .

Sample	a_0 (Å)	$(T_{1e}T)^{-1}$ ($s^{-1} K^{-1}$)	$T_{max}†$ (K)	$(T_{1d}^{-1})_{max}†$ (s^{-1})
$Ti_3SbH_{0.6}$	5.250	1.6×10^{-2}	278	5.65
$Ti_3SbH_{1.8}$	5.332	8.8×10^{-3}	340	4.31
$Ti_3SbH_{2.4}$	5.368	6.1×10^{-3}	≈ 460	5.07

† At $\omega/2\pi = 19$ MHz.

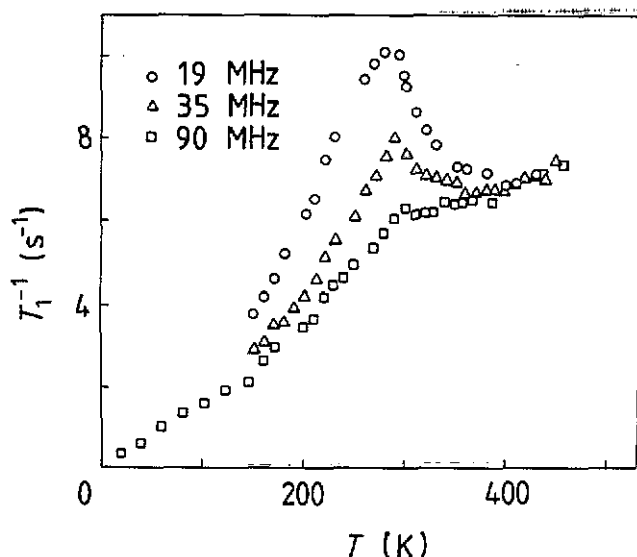


Figure 1. Temperature dependence of the proton spin-lattice relaxation rate in $Ti_3SbH_{0.6}$ measured at 19, 35 and 90 MHz.

Figures 1 and 2 show the temperature dependences of proton spin-lattice relaxation rates T_1^{-1} in $Ti_3SbH_{0.6}$ and $Ti_3SbH_{1.8}$ measured at three resonance frequencies. The proton relaxation rate in metal-hydrogen systems usually results from the sum of contributions due to the hyperfine interactions with conduction electrons (T_{1e}^{-1}) and the nuclear dipole interactions modulated by hydrogen motion (T_{1d}^{-1}). The electronic contribution is typically proportional to temperature, $T_{1e}^{-1} = CT$. At low temperatures the T_{1d}^{-1} term is negligible, and T_{1e}^{-1} can be obtained directly from T_1 measurements. For all the samples studied at $T < 130$ K the $T_1^{-1}(T)$ dependences measured at 90 MHz are linear, as expected. The corresponding values of $(T_{1e}T)^{-1}$ are presented in table 1. It can be seen that $(T_{1e}T)^{-1}$ decreases with increasing H content. Since in transition-metal-hydrogen systems $(T_{1e}T)^{-1}$ is approximately proportional to a square of the density of d-electron states at the Fermi level $N_d^2(E_F)$ [9], our results suggest that the value of $N_d(E_F)$ decreases with increasing x . This trend is consistent with the observed depression of T_c in Ti_3SbH_x with increasing hydrogen concentration [8].

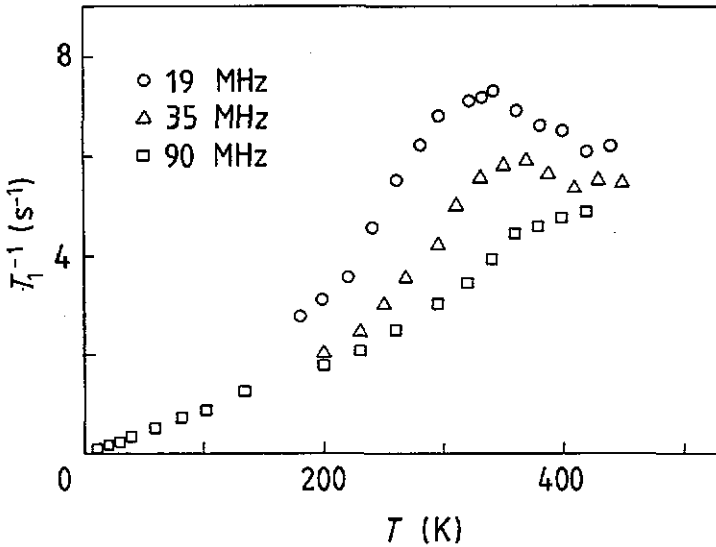


Figure 2. Temperature dependence of the proton spin-lattice relaxation rate in $\text{Ti}_3\text{SbH}_{1.8}$ measured at 19, 35 and 90 MHz.

The motional contribution to the relaxation rate, $T_{1d}^{-1} = T_1^{-1} - T_{1e}^{-1}$, is expected to have a maximum when $\omega\tau_d \simeq 1$, τ_d being the mean dwell time of the H atom in an interstitial site. The maximum value of T_{1d}^{-1} is expected to be proportional to ω^{-1} . For each of the Ti_3SbH_x samples studied the measured proton relaxation rate shows the characteristic frequency-dependent maximum which can be attributed to hydrogen motion. The temperatures of the relaxation rate maxima, T_{max} , and the maximum values of T_{1d}^{-1} at 19 MHz are presented in table 1. The maximum of T_{1d}^{-1} in metal-hydrogen systems usually results from the thermally activated long-range diffusion of hydrogen. However, for Ti_3SbH_x the values of $(T_{1d}^{-1})_{\text{max}}$ appear to be much lower than those expected in the case of long-range diffusion. For example, the estimates based on calculations of the rigid-lattice second moment M_2 of the proton NMR line in $\text{Ti}_3\text{SbH}_{1.8}$ give the values $(T_{1d}^{-1})_{\text{max}}^{\text{long-r}} = 23 \text{ s}^{-1}$ and 39 s^{-1} at 19 MHz for H atoms occupying the tetrahedral interstitial sites of d-type (4 Ti) and i-type (3 Ti + 1 Sb), respectively. Thus, only a small part of the rigid-lattice dipole-dipole interaction is modulated by the hydrogen motion in $\text{Ti}_3\text{SbH}_{1.8}$. This is supported by the behaviour of the proton NMR linewidth $\Delta\omega$: for $\text{Ti}_3\text{SbH}_{1.8}$ $\Delta\omega$ shows only 15% decrease between 160 and 380 K. Similar results have been obtained for the other Ti_3SbH_x samples. These results indicate that the observed hydrogen motion in Ti_3SbH_x is localized, while the onset of the long-range diffusion on the NMR frequency scale is expected to occur above 470 K.

Localized hydrogen motion has recently been found in the Laves-phase hydrides TaV_2H_x (D_x) [10, 11] and in HCP $\alpha\text{-ScH}_x$ [12]. In these systems the low-amplitude T_1^{-1} maximum due to hopping of H (D) atoms between closely spaced sites is observed at $T \sim 100 \text{ K}$. For Ti_3SbH_x the onset of the localized motion on the NMR frequency scale is shifted to higher temperatures. The temperature of the T_1^{-1} maximum in Ti_3SbH_x increases with increasing x . This means that the localized

motion becomes slower with increasing hydrogen content. As in the case of α -ScH_x [12], the behaviour of T_{1d}^{-1} in Ti₃SbH_x shows features that are typical for a motion characterized by a distribution of τ_d values (or activation energies E_a [13]: the shape of the log T_{1d}^{-1} versus T^{-1} dependence is asymmetric and the frequency dependence of $(T_{1d}^{-1})_{\max}$ is weaker than ω^{-1} . If a certain distribution of activation energies exists in the system, the most probable E_a value nearly coincides with the one estimated from the high-temperature slope of the T_{1d}^{-1} peak [13]. Since in our experiments the high-temperature slope of the T_{1d}^{-1} peak is well pronounced only for Ti₃SbH_{0.6}, we can reliably estimate the probable activation energy and the attempt frequency τ_{d0}^{-1} for this sample only: $E_a = 0.19$ eV, $\tau_{d0}^{-1} = 3 \times 10^{11}$ s⁻¹.

The mobilities of hydrogen in A15 compounds have been earlier investigated for Nb₃SnH_x by means of internal friction [14] and for Ti₃IrH_x ($x < 0.02$) by hydrogen absorption measurements [15]. The activation energy for H diffusion in Nb₃SnH_x is found to be in the range between 0.6 and 1.4 eV, depending on interpretation of the internal friction data [14]. For the long-range diffusion of H in Ti₃IrH_x $E_a = 0.25$ eV [15]. Thus, the value of the activation energy for Ti₃SbH_{0.6} is considerably lower than for Nb₃SnH_x and Ti₃IrH_x with the same host-lattice structure. This is also consistent with the localized character for H motion in Ti₃SbH_x, since potential barriers for localized motion are expected to be lower than for the long-range diffusion.

We now consider a crystallographic model of the localized motion in Ti₃SbH_x. The only A15-type hydride for which the sites occupied by hydrogen have been determined from neutron diffraction measurements is Nb₃SnH_{1.0} [7]. In this case H atoms have been found to occupy the sixfold d positions of the space group $Pm\bar{3}n$, i.e. the tetrahedral interstitial sites (formed by four A atoms) on the faces of the unit cell. It is generally assumed that hydrogen occupies the d sites also in the other A15 compounds. Complete occupancy of these sites corresponds to the maximum hydrogen content $x = 3$. However, a number of A15-type hydrides with $x > 3$ have been prepared recently, including Ti₃IrH_{3.8} [5], Nb₃AuH_{4.3}, Nb₃IrH_{4.7}, Nb₃PtH_{5.1} and Nb₃OsH_{4.0} [3]. These results indicate that other interstitial sites may be occupied by H in A15 compounds (either exclusively or in addition to the d sites). Possible alternative sites are the 16-fold i sites (formed by one B and three A atoms) on the space diagonals of the unit cell. The volume of these tetrahedral sites is larger than that of the d sites. The i sites form closely spaced pairs between each pair of B atoms in the $\langle 111 \rangle$ direction, as shown in figure 3. The distance between the nearest i sites is only $0.144a_0$, i.e. 0.77 \AA for Ti₃SbH_{1.8}. Because of the 'blocking' effect, only one i site in this pair can be occupied at a given time; hence the complete occupancy of the i sites corresponds to $x = 4$. It should be noted that such a configuration of the i sites is favourable for the occurrence of the localized motion of hydrogen. In fact, in HCP α -ScH_x hydrogen is known to hop between similar closely spaced tetrahedral interstitial sites forming pairs along the c axis [12].

The maximum contribution of the localized motion to the proton relaxation rate can be estimated as $(T_{1d}^{-1})_{\max}^{\text{loc}} = F(T_{1d}^{-1})_{\max}^{\text{long-r}}$, where F is the fraction of M_2 that is averaged out by this motion. For a hydrogen atom hopping between sites 1 and 2 the value of F is given by [11]

$$1 - F = \frac{1}{4} \sum_j x_j r_{1j}^{-6} / \sum_j r_{1j}^{-6} \quad (1)$$

$$X_j = (r_{1j}/r_{2j})^6 + (r_{1j}/r_{2j})^3 (3 \cos^2 \beta_j - 1) + 1 \quad (2)$$

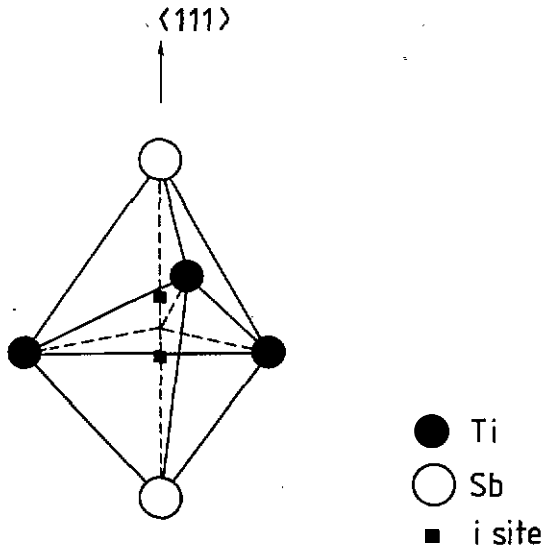


Figure 3. The pair of closely spaced tetrahedral i sites on a space diagonal of the unit cell of Ti_3Sb .

where β_j is the angle between the vectors r_{1j} and r_{2j} connecting the j th nuclear spin with sites 1 and 2. For a hopping between closely spaced i sites in $\text{Ti}_3\text{SbH}_{1.8}$ the estimate based on (1) and (2) gives $F = 0.18$. Hence, $(T_{1d}^{-1})_{\text{max}}^{\text{loc}} = 7.0 \text{ s}^{-1}$ at 19 MHz. This value is of the same order of magnitude as the experimental $(T_{1d}^{-1})_{\text{max}}$ (see table 1). The numerical difference between the calculated and the experimental $(T_{1d}^{-1})_{\text{max}}$ values may be related to a distribution of τ_d which is known to reduce the maximum relaxation rate [13].

In conclusion, we have found localized motion of hydrogen in Ti_3SbH_x on the NMR frequency scale. This is the first time that such hydrogen motion has been observed in a compound with the A15 structure. Our analysis suggests that the A15 lattice is favourable for the occurrence of localized hydrogen motion since it contains pairs of closely spaced tetrahedral interstitial sites.

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