Hydrogen jump motion in Laves-phase hydrides: Two frequency scales

A.V. Skripov*

Institute of Metal Physics, Urals Branch of the Academy of Sciences, Ekaterinburg 620219, Russian Federation

Abstract

Two types of hydrogen jump motion with different characteristic jump rates have been found to coexist in a number of Laves-phase hydrides. While the slower jump process is responsible for the long-range diffusion, the faster process corresponds to localized hydrogen motion over small groups of interstitial sites. In some of the Laves-phase compounds, the localized hydrogen motion is not 'frozen out' on the frequency scale of 10^7 to $10^8\,s^{-1}$ down to 20 K. This paper reviews recent progress in investigations of the microscopic picture and systematics of H jump motion in Laves-phase hydrides. The relation between the hydrogen jump rates and the structure of hydrogen sublattice is emphasized.
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1. Introduction

One of the most intriguing features of hydrogen diffusion in Laves-phase intermetallic compounds is a coexistence of two types of H jump motion with different characteristic frequencies [1]. The primary aim of the present paper is to discuss the progress in investigations of the microscopic picture and systematics of hydrogen jump motion in this class of materials. Laves phases AB_2 can have either the cubic (C15-type) structure or the hexagonal (C14-type or C36-type) structures. All interstitial sites in Laves phases are tetrahedral; they can be coordinated by the $[A_2B_2]$, $[AB_3]$ or $[B_4]$ tetrahedra. In most of the Laves-phase hydrides AB_2H_x, H atoms occupy only the $[A_2B_2]$ sites at low and intermediate hydrogen concentrations (up to $x \approx 2.5$) [2,3]. For the cubic C15-type intermetallics (space group $Fd\bar{3}m$) which will be in a focus of our discussion, the $[A_2B_2]$ sites are represented by crystallographic g sites (12 sites per formula unit AB_2).

Early nuclear magnetic resonance (NMR) experiments on the Laves-phase hydrides $TiCr_{1.8}H_x$ (C15) and $TiCr_{1.9}H_x$ (C14) [4] and on the C15-type ZrV_2H_x and HfV_2H_x [5] have revealed significant deviations of the measured nuclear spin relaxation rates from the behavior expected for a single frequency scale of H motion. In [5] the experimental results have been interpreted in terms of a broad distribution of H jump rates. On the other hand, Bowman et al. [4] have suggested the possibility of a coexistence of two hydrogen jump processes with different rates. The unambiguous evidence for a coexistence of two types of hydrogen jump motion with different characteristic frequencies has been found in the series of NMR experiments on the C15-type TaV_2–H(D) system [6–9]. These experiments have revealed the temperature dependence of the nuclear spin-lattice relaxation rate R_1 with two well-separated peaks. The origin of the two frequency scales of hydrogen motion will be discussed below.

2. Systematics of two frequency scales of H jump motion in cubic Laves-phase hydrides

According to the neutron diffraction data [2,10], hydrogen atoms in $TaV_2H_x(D_x)$ occupy only g sites coordinated by two Ta and two V atoms. The sublattice of g sites consists of hexagons lying in the planes perpendicular to $\langle 1\,1\,1 \rangle$ directions [3]. Each g site has three nearest neighbors: two

* Tel.: +7 3432 783781; fax: +7 3432 745244.
  E-mail address: skripov@imp.uran.ru (A.V. Skripov).

g sites (on the same hexagon) at a distance r_1 and one g site (on the adjacent hexagon) at a distance r_2. The ratio r_2/r_1 is determined by the positional parameters (X_g and Z_g) of hydrogen atoms at g sites. Using the values $X_g = 0.055$ and $Z_g = 0.888$ derived from the neutron diffraction measurements for TaV$_2$D$_x$ [10] we obtain $r_2/r_1 = 1.45$. This means that the g-site hexagons in TaV$_2$H$_x$(D$_x$) are *well separated from each other*. Therefore, a hydrogen atom is expected to perform many jumps within a hexagon before jumping to another hexagon. In this case the faster jump rate τ_1^{-1} can be attributed to the localized hydrogen motion within g-site hexagons, and the slower jump rate τ_d^{-1} can be associated with hydrogen jumps from one g-site hexagon to another.

The results of quasielastic neutron scattering (QENS) measurements for TaV$_2$H$_x$ [11] are consistent with this microscopic picture of H motion. First, on the frequency scale of τ_1^{-1} the measured QENS spectra $S(Q, \omega)$, where $\hbar Q$ is the momentum transfer and $\hbar\omega$ is the energy transfer, are well described by a sum of a narrow elastic line and a broader quasielastic line having Q-dependent intensity, but Q-independent width. These features are typical of the case of spatially confined (localized) motion [12]. Second, the Q-dependence of the measured elastic incoherent structure factor (EISF) appears to be in excellent agreement with the predictions of the model [12] of localized atomic motion over a hexagon with the distance between the nearest-neighbor sites equal to the experimental r_1 value.

It can be expected that for the other cubic Laves-phase hydrides, where H atoms occupy only g sites, the microscopic picture of hydrogen motion is qualitatively the same as for TaV$_2$H$_x$. This has been confirmed by recent QENS experiments for ZrCr$_2$H$_x$ [13], ZrMo$_2$H$_x$ [14], HfMo$_2$H$_x$ [15] and ZrV$_2$H$_x$ [16,17]. However, in these systems the difference between the two frequency scales of H motion appears to be smaller than in TaV$_2$H$_x$. Besides TaV$_2$H$_x$, two well-resolved $R_1(T)$ peaks have been observed only for HfMo$_2$H$_x$ [18] and Nb(V$_{1-y}$Cr$_y$)$_2$H$_x$(D$_x$) [19]. NMR data for other cubic Laves-phase hydrides including TiCr$_{1.8}$H$_x$ [4], ZrCr$_2$H$_x$ [20], HfV$_2$H$_x$ and ZrV$_2$H$_x$ [5,21] and ZrMo$_2$H$_x$ [14] do not show any additional low-temperature R_1 peak; the localized H motion in these systems contributes only to the low-temperature slope of the single-peak $R_1(T)$ dependence. In order to find out why the difference between the two frequency scales of H motion is most pronounced for TaV$_2$H$_x$, we may compare the ratios r_2/r_1 in different Laves-phase hydrides. Examination of the available neutron diffraction data for cubic Laves-phase deuterides reveals strong changes in the ratio r_2/r_1 from one compound to another. For example, the value of r_2/r_1 is 1.45 for TaV$_2$D$_x$ [10], 1.07 for ZrCr$_2$D$_x$ [22] and 0.78 for YMn$_2$D$_x$ [23]. This means that although the structure of the host-metal lattice is the same for all cubic Laves-phase hydrides, *the structure of the g-site sublattice (partially occupied by hydrogen) shows significant variations from one compound to another*. These variations caused by changes in the positional parameters of hydrogen atoms at g sites can be rationalized in terms of the metallic radii R_A and R_B of ele-

ments A and B forming the AB$_2$ intermetallic. In fact, since g sites are coordinated by two A and two B atoms, one may expect that the positional parameters X_g and Z_g (and hence, r_2/r_1) are related to R_A/R_B. In order to verify this, we have analyzed the available neutron diffraction data for paramagnetic C15-type deuterides AB$_2$D$_x$ where both A and B are transition metals. The results are presented in Fig. 1 showing r_2/r_1 as a function of R_A/R_B for different cubic Laves-phase deuterides. In the cases where the neutron diffraction data are available for different deuterium concentrations x, we have used the positional parameters corresponding to lower x. It should be noted that the changes in X_g and Z_g with x are much smaller than the range of variation of these parameters for different Laves-phase compounds. As can be seen from Fig. 1, there is a clear correlation between r_2/r_1 and R_A/R_B for C15-type systems. The highest r_2/r_1 ratios are observed for compounds with the lowest values of R_A/R_B. In particular, the value of R_A/R_B for TaV$_2$ (=1.090) appears to be the lowest one among all hydrogen-absorbing Laves phases. Therefore, the most pronounced separation of the g-site hexagons from each other in TaV$_2$H$_x$(D$_x$) can be related to the anomalously low R_A/R_B ratio.

For C15-type compounds with $R_A/R_B > 1.35$, the r_2/r_1 ratio becomes less than 1. In this case, each g site has only one nearest neighbor lying at the adjacent hexagon. Such a transformation of the g-site sublattice may lead to a qualitative change in the microscopic picture of H jump motion: the faster jump process is expected to be transformed into the back-and-forth jumps within *pairs* of g sites belonging to adjacent hexagons. The results of recent QENS experiments
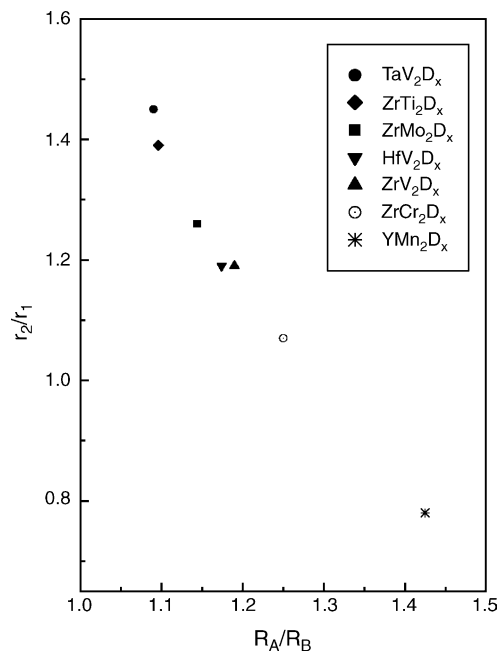

Fig. 1. The ratio of the g–g distances as a function of R_A/R_B for a number of C15-type deuterides AB$_2$D$_x$. The values of r_2/r_1 are derived from the neutron diffraction data for TaV$_2$D$_x$ [10], ZrTi$_2$D$_x$ [24], ZrMo$_2$D$_x$ [25], HfV$_2$D$_x$ [26], ZrV$_2$D$_x$ [27], ZrCr$_2$D$_x$ [22] and YMn$_2$D$_x$ [23].

[28] on YMn_2H_x ($R_A/R_B = 1.425$, $x = 0.4$, 0.65 and 1.26) are consistent with these expectations.

In order to consider the relation between the intersite distances and hydrogen jump rates, we have to choose a certain temperature for comparison of the data for different compounds. In fact, both τ_l^{-1} and τ_d^{-1} depend on temperature; however, the temperature dependence of τ_d^{-1} is found to be stronger than that of τ_l^{-1}. Thus, the ratio τ_d/τ_l increases with decreasing T. At $T < 200$ K the value of τ_d^{-1} in Laves-phase hydrides (except for $ZrCr_2H_x$ and $HfCr_2H_x$) becomes too low to be determined from R_1 or QENS measurements. On the other hand, at room temperature both τ_l^{-1} and τ_d^{-1} can be measured (the former from the time-of-flight QENS and the latter from R_1 or the backscattering QENS). At present, the measured values of both τ_l^{-1} and τ_d^{-1} are available for five cubic Laves-phase systems with the exclusive g-site occupation and $r_2/r_1 > 1$: TaV_2H_x [7,11], $ZrCr_2H_x$ [13,29], $ZrMo_2H_x$ [14], $HfMo_2H_x$ [15,18] and ZrV_2H_x [16,17,21]. In Fig. 2 the values of τ_l^{-1}(300 K) for different compounds are plotted versus r_1, and the values of τ_d^{-1}(300 K) are plotted versus r_2. It can be seen that there is a certain correlation between the hydrogen jump rate and the corresponding g–g distance: the value of τ_l^{-1}(300 K) tends to decrease with increasing r_1, and the value of τ_d^{-1}(300 K) tends to decrease with increasing r_2. Note that the range of the measured jump rates exceeds three orders of magnitude. Fig. 2 should be considered only as an illustration of the general trend; a quantitative relation between the jump length and the jump rate of H atoms is expected to include some other factors of electronic origin.
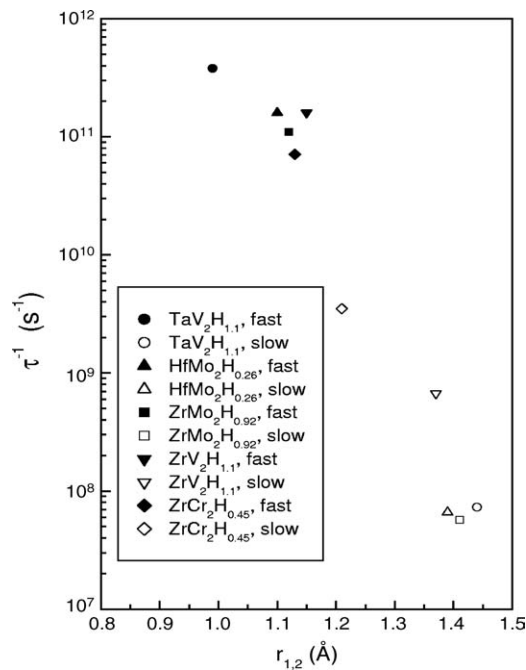
For cubic Laves-phase hydrides with mixed occupation of g and e ([AB_3]) sites, the microscopic picture of H motion is less tractable. However, for the hydrogen-stabilized C15-type phases $ZrTi_2H_x$ and $HfTi_2H_x$ ($x \approx 4$) with the nearly completely filled e-site sublattice, the coexistence of two frequency scales of H motion has been convincingly demonstrated [30,31]. In these systems the long-range diffusion occurs by jumps from one e site to another via intermediate g sites; while being located at the nearly empty g-site sublattice H atoms participate in the fast localized motion over g-site hexagons.

3. Hexagonal Laves-phase hydrides

The coexistence of at least two frequency scales of hydrogen jump motion has also been found in a number of hexagonal (C14-type) Laves-phase hydrides [13,32,33]. As an example of the data, Fig. 3 shows the temperature dependences of τ_l^{-1} and τ_d^{-1} for H motion in C14-type $HfCr_2H_{0.74}$. These results are obtained from QENS measurements using the time-of-flight spectrometer FCS (NIST) and the backscattering spectrometer IN10 (ILL). It can be seen that in the studied temperature range the behavior of both $\tau_l^{-1}(T)$ and $\tau_d^{-1}(T)$ is satisfactorily described by the Arrhenius relation; the values of the activation energies derived from the Arrhenius fits are 122 meV for τ_l^{-1} and 148 meV for τ_d^{-1}.
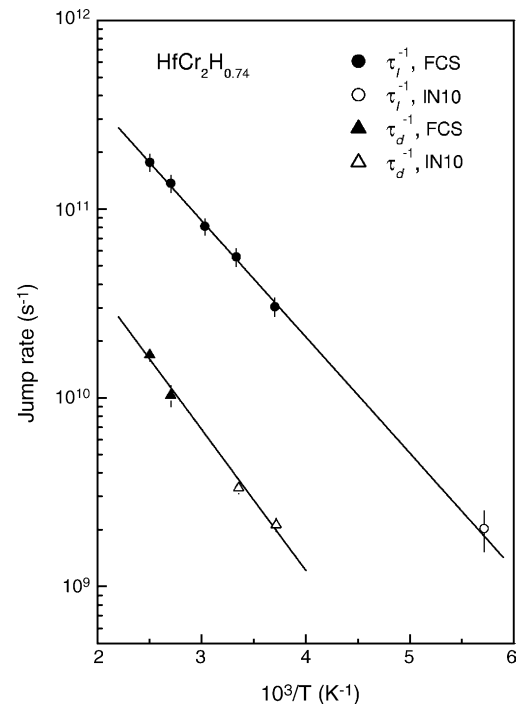

Fig. 2. The hydrogen jump rates τ_l^{-1} (solid symbols) and τ_d^{-1} (open symbols) at $T = 300$ K as functions of the corresponding g–g distances r_1 and r_2.

Fig. 3. The hydrogen jump rates τ_l^{-1} and τ_d^{-1} in C14-type $HfCr_2H_{0.74}$ as functions of the inverse temperature. The jump rates are obtained from the QENS spectra measured on the time-of-flight spectrometer FCS (solid symbols) and on the backscattering spectrometer IN10 (open symbols). The solid lines are the Arrhenius fits to the data.

The microscopic picture of H motion in C14-type compounds has been addressed in the QENS study of $ZrCr_2H_x$ [13] (note that $ZrCr_2$ may exist in the form of either the hexagonal C14 or the cubic C15 modification). At low hydrogen concentrations H atoms are known to occupy the tetrahedral sites with $[A_2B_2]$ coordination. In contrast to the C15 structure where all $[A_2B_2]$ sites are equivalent (g sites), in the C14 structure there are four inequivalent types of $[A_2B_2]$ site (h_1, h_2, k and l). The sublattice of $[A_2B_2]$ sites in the C14 structure [34] also consists of hexagons; however, these hexagons are formed by inequivalent sites. Type I hexagons are in the basal plane; they are formed by alternating h_1 and h_2 sites. Type II hexagons are formed by two k and four l sites in the sequence k–l–l–k–l–l. While all the distances between the nearest-neighbor sites in type I hexagons are equal, in type II hexagons there is a small difference between the l–l and k–l distances. All the distances between the nearest sites within the hexagons appear to be shorter than the distances between the nearest sites on different hexagons [13]. Therefore, general features of the microscopic picture of H motion in C14-$ZrCr_2H_x$ are expected to be similar to those of H motion in C15-type compounds with g-site occupation. The experimental QENS results for C14-$ZrCr_2H_{0.5}$ [13] have been interpreted in terms of a model neglecting the small difference between type I and type II hexagons and the difference between the l–l and k–l distances in type II hexagons. The observed Q-dependence of the EISF for C14-$ZrCr_2H_{0.5}$ is well described by the model of localized H motion over hexagons with the intersite distance $\langle r \rangle = 1.16$ Å, where $\langle r \rangle$ is the weighted average of the intersite distances for type I and type II hexagons.

Since the sublattice of $[A_2B_2]$ sites in C14-type compounds is more complex than that in C15-type compounds, the detailed microscopic picture of H motion in hexagonal Laves phases may imply more than two frequency scales. In order to clarify the systematics of H jump processes in hexagonal Laves-phase hydrides, further QENS experiments (combined with neutron diffraction studies of hydrogen positions) are required.

4. Quantum aspects of the low-temperature localized H(D) motion

The localized motion of hydrogen has been most extensively investigated for the TaV_2–H(D) system (where this motion is the fastest among the studied Laves-phase hydrides). Therefore, the discussion in this section will be based on the experimental results obtained for $TaV_2H_x(D_x)$. Three interesting features of the localized hydrogen motion will be emphasized: (i) the strong dependence of the jump rate τ_1^{-1} on hydrogen concentration, (ii) the unusual isotope effects on the parameters of the localized motion, and (iii) non-Arrhenius temperature dependence of the jump rate τ_1^{-1} at low T.

The hydrogen jump rate τ_1^{-1} in $TaV_2H_x(D_x)$ has been found to increase strongly with decreasing H(D) content [7–

9]. In NMR measurements, this is reflected in the marked shift of the position of the low-T maximum of R_1 to lower temperatures. For example, at the frequency of 90 MHz the low-T maximum of R_1 is observed at 187 K for $TaV_2H_{1.33}$ [7], at 125 K for $TaV_2H_{0.87}$ [7] and at 45 K for $TaV_2H_{0.06}$ [9]. The strong dependence of τ_1^{-1} on x has also been found in the QENS measurements on TaV_2H_x [11] and in the ultrasonic experiments on TaV_2D_x [35]. Qualitatively, such a dependence is consistent with the fact that the g–g distance r_1 becomes shorter with decreasing x due to the decrease of the lattice parameter. In this case, the hydrogen jump rate τ_1^{-1} should be extremely sensitive to changes in r_1, which suggests that the localized H motion may be governed by tunneling transitions.

Studies of the effects of isotope (H $\leftrightarrow$ D) substitution on the parameters of hydrogen motion are expected to give additional information on the mechanisms of jump motion. Nuclear spin-lattice relaxation of host-metal nuclei with non-zero quadrupole moments appears to be a particularly efficient probe of isotope effects on hydrogen motion in metal hydrides [36]. For such nuclei the main motional contribution to R_1 originates from the electric quadrupole interaction modulated by motion of nearby H(D) atoms. Since for the quadrupole interaction only *charge* fluctuations are important, H and D atoms are expected to give the same contributions to the host-metal R_1 if their motional parameters are the same. The [51]V relaxation rate measurements for $TaV_2H_x(D_x)$ [7] have revealed that the amplitude of the low-temperature R_1 peak for TaV_2D_x is nearly three times higher than that for TaV_2H_x with the same x. These results have been attributed [11] to the difference in the fractions of H and D atoms participating in the localized motion. In fact, QENS measurements [11,13–17] indicate that only a certain fraction p of hydrogen atoms participate in the localized motion (on the appropriate experimental frequency scale) in Laves phases, and that this fraction decreases with decreasing T. The [51]V relaxation data for TaV_2H_x and TaV_2D_x with nearly the same x suggest that the value of p for D atoms is considerably higher than that for H atoms. The strong effect of H $\leftrightarrow$ D substitution on the amplitude of the low-T host-metal R_1 peak, with a larger peak appearing in the deuterides, has also been found for [51]V relaxation in the ternary Laves-phase $NbVCrH_x(D_x)$ [19] and for [45]Sc relaxation in α-$ScH_x(D_x)$ [37,38]. The nature of this isotope effect is not clear yet. One may assume that H(D) atoms become mobile when they are in the excited vibrational states. In this case, the higher value of p for D atoms would be quite natural, because of the lower excitation energy.

The ultrasonic attenuation is also well suited for probing isotope effects on hydrogen jump motion since the coupling between the ultrasound and the hydrogen motion is the same for both H and D. Measurements of the ultrasonic attenuation in $TaV_2H_x(D_x)$ in the frequency range of 1 MHz [35,39,40] have revealed even more dramatic isotope effects than those found in the [51]V NMR experiments. For example, for $TaV_2D_{0.17}$ the ultrasonic attenuation shows a distinct peak

near 20 K which can be attributed to localized D motion; however, for $TaV_2H_{0.18}$ the low-T attenuation peak is observed near 1 K, and its amplitude is about eight times lower than that for $TaV_2D_{0.17}$ [35]. These results demonstrate that at low temperatures the jump rate of H atoms is at least an order of magnitude faster than that of D atoms for similar concentrations. The ultrasonic data [35] are also consistent with the temperature-dependent fraction of 'mobile' atoms, the value of p decreasing with decreasing T.

The temperature dependence of the jump rate τ_1^{-1} for both H and D in $TaV_2H_x(D_x)$ is found to be strongly non-Arrhenius. The behavior of $\tau_1^{-1}(T)$ obtained from the proton R_1 measurements in TaV_2H_x [7] is reasonably described by the exponential function

$$\tau_1^{-1} = \tau_0^{-1} \exp\left(\frac{T}{T_0}\right) \qquad (1)$$

over the temperature range 30–200 K. At low temperatures this dependence is much weaker than the Arrhenius one. Although the relation given by Eq. (1) should be considered as empirical, it is worth noting that a similar term in the jump rate has been found in the framework of the quantum diffusion theory taking into account the effects of barrier fluctuations [41]. While for protons the behavior of the measured spin-lattice relaxation rate at low T is affected by the temperature dependence of p [11], the ^{2}D spin-lattice relaxation rates can be measured separately for the 'mobile' and 'static' fractions [8]. Therefore, the temperature dependence of τ_1^{-1} derived from the ^{2}D relaxation data for the 'mobile' fraction of D atoms should be more reliable. Fig. 4 shows the behavior of $\tau_l^{-1}(T)$ obtained from the ^{2}D relaxation rate data for $TaV_2D_{0.5}$ and $TaV_2D_{1.3}$ [8]. It can be seen that $\tau_1^{-1}(T)$ for D atoms is satisfactorily described by Eq. (1). The corresponding fit parameters are $T_0 = 38$ and 33 K, $\tau_0^{-1} = 2.0 \times 10^7$ and $1.5 \times 10^6 \, s^{-1}$ for $TaV_2D_{0.5}$ and $TaV_2D_{1.3}$, respectively. For comparison, the low-temperature

behavior of τ_1^{-1} for H in $TaV_2H_{0.56}$ (dashed line in Fig. 4) is described by $T_0 = 50.3$ K, $\tau_0^{-1} = 1.1 \times 10^8 \, s^{-1}$ [7]. It is interesting to note that Eq. (1) with the values of T_0 and τ_0^{-1} derived from the ^{2}D NMR data for $TaV_2D_{0.5}$ also gives a reasonable description of the ultrasonic attenuation results for $TaV_2D_{0.5}$ [35]. The ultrasonic experiments on TaV_2H_x with low x [35] show that the hydrogen jump rate τ_1^{-1} remains finite down to the lowest temperature of the measurements (0.3 K) being well above the ultrasound frequency ($\sim$1 MHz). The strong difference between the motional parameters of H and D and the non-Arrhenius temperature dependence of the hydrogen jump rate resulting in high τ_1^{-1} values at low T indicate that the localized hydrogen motion is dominated by quantum effects.

5. Concluding remarks

This review emphasizes the relation between the parameters of hydrogen motion and the structure of hydrogen sublattice in Laves-phase compounds. It has been shown that the *actual* structures of hydrogen sublattice may differ considerably even for compounds with the same host-metal structure and the same type of sites occupied by hydrogen. Therefore the knowledge of the actual positional parameters of hydrogen is crucial for understanding of the H jump processes in Laves phases. For C15-type hydrides with g-site occupation and $r_2/r_1 > 1$ the microscopic picture of H jumps and the systematics of two frequency scales of H motion are well understood now. More work is required to clarify the details of H jump motion in C14-type hydrides and in C15-type hydrides with $r_2/r_1 < 1$ or with mixed g- and e-site occupation. Further studies are also necessary to elucidate the mechanism of the localized H motion at low temperatures.
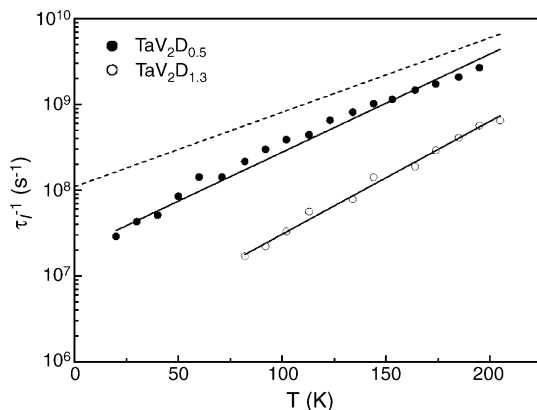
Fig. 4. The temperature dependence of the jump rates τ_1^{-1} for deuterium in $TaV_2D_{0.5}$ and $TaV_2D_{1.3}$, as determined from the ^{2}D spin-lattice relaxation data. The solid lines show the fits of Eq. (1) to the $\tau_1^{-1}(T)$ results. The dashed line represents the behavior of $\tau_1^{-1}(T)$ for H in $TaV_2H_{0.56}$, as derived from the fit of Eq. (1) to the proton spin-lattice relaxation data (Ref. [7]).

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