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## Hydrogen diffusion in C15-type $\text{HfMo}_2\text{H}_{0.4}$ : nuclear magnetic resonance evidence of two frequency scales of H hopping

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**Abstract.** Nuclear magnetic resonance measurements of the proton spin–lattice relaxation rate in C15-type  $\text{HfMo}_2\text{H}_{0.4}$  have been performed over the temperature range 20–420 K and the resonance frequency range 13–90 MHz. The temperature dependence of the relaxation rate is found to exhibit two peaks. This is consistent with a coexistence of two types of H hopping with different frequency scales. The experimental results are analysed to evaluate the parameters of hydrogen motion and the electronic (Korringa) contribution to the relaxation rate. Our results support the idea that the ratio of the characteristic frequencies of the two types of H motion in C15 compounds  $\text{AB}_2$  is related to the ratio of the metallic radii of elements A and B.

### 1. Introduction

Hydrogen diffusion in Laves-phase intermetallic compounds shows a number of interesting features including high hydrogen mobility down to low temperatures [1–5] and a coexistence of two frequency scales of H hopping [2, 3, 6–9]. The most impressive manifestation of the two frequency scales is the double-peak temperature dependence of the proton spin–lattice relaxation rate  $T_1^{-1}$  found in the cubic (C15-type) Laves-phase compounds  $\text{TaV}_2\text{H}_x$  [2, 3]. Proton spin–lattice relaxation data for some other Laves-phase hydrides ( $\text{TiCr}_2\text{H}_x$  [1],  $\text{HfV}_2\text{H}_x$  and  $\text{ZrV}_2\text{H}_x$  [10],  $\text{ZrCr}_2\text{H}_x$  [5],  $\text{ZrMo}_2\text{H}_x$  [9]) have also been interpreted in terms of two frequency scales of H hopping; however, the second peak in the temperature dependence of  $T_1^{-1}$  is not observed for these systems. The origin of the two frequency scales in those C15 Laves phases  $\text{AB}_2$  where H atoms occupy only tetrahedral sites of g type ( $\text{A}_2\text{B}_2$ ) has been clarified by recent quasielastic neutron scattering (QENS) experiments [7, 8]. It has been found that the faster jump process implies the localized H motion within hexagons formed by g sites, and the slower process corresponds to H jumps from one g-site hexagon to the other. The difference between the characteristic frequencies of these jump processes is believed to result from the difference between the g–g distances  $r_1$  (within the hexagons) and  $r_2$  (between the nearest hexagons). The value of the ratio  $r_2/r_1$  depends on the positional parameters ( $X$ ,  $X$ ,  $Z$ ) of H atoms at g sites; this value may differ strongly for different compounds with the same C15-type host lattice. For example, the value of  $r_2/r_1$  is 1.45 for  $\text{TaV}_2\text{H}_x$  [7] and 1.07 for  $\text{ZrCr}_2\text{H}_x$  [8].

It has also been suggested [7] that the ratio  $r_2/r_1$  is related to the ratio of the metallic radii  $R_A/R_B$  of the elements A and B forming the  $\text{AB}_2$  intermetallic. The ‘ideal’  $R_A/R_B$  value for Laves phases (derived from the condition of the closest packing of hard spheres) is 1.225. However, Laves phases can be formed by pairs of elements with considerable deviations of

$R_A/R_B$  from this ideal value. In particular, for TaV<sub>2</sub> the ratio  $R_A/R_B$  is equal to 1.09, which is one of the lowest among all Laves-phase compounds [11]. Nuclear magnetic resonance (NMR) [2, 3] and QENS [7] studies of hydrogen motion in TaV<sub>2</sub> have revealed a very strong difference between the two frequency scales of H hopping. On the other hand, for hydrogen in C15-type ZrCr<sub>2</sub> with  $R_A/R_B = 1.25$ , similar NMR [5] and QENS [8] experiments have found only a modest difference between these two frequency scales. Therefore, the absence of the resolved second  $T_1^{-1}$ -peak in such systems as TiCr<sub>2</sub>H<sub>x</sub>, HfV<sub>2</sub>H<sub>x</sub>, ZrV<sub>2</sub>H<sub>x</sub>, ZrCr<sub>2</sub>H<sub>x</sub> and ZrMo<sub>2</sub>H<sub>x</sub> may be ascribed to insufficient difference between the two frequency scales of H motion. This difference is expected to increase with decreasing value of  $R_A/R_B$ . In order to verify the relation between the H hopping rates and  $R_A/R_B$ , it is interesting to study the parameters of H motion in a C15-type Laves phase for which the value of  $R_A/R_B$  is as low as possible. One of the possible choices is HfMo<sub>2</sub> for which the value of  $R_A/R_B (=1.129)$  is close to that for TaV<sub>2</sub>.

We have found that the C15-type intermetallic compound HfMo<sub>2</sub> absorbs hydrogen, forming solid solutions HfMo<sub>2</sub>H<sub>x</sub> with  $x \leq 0.4$  (at hydrogen pressure of about 1 bar). Note that the maximum hydrogen content in HfMo<sub>2</sub> is lower than in the related C15-type compound ZrMo<sub>2</sub> for which  $x \leq 1.05$  [12]. On the basis of the general trends of site occupancy in hydrides of intermetallics [13, 14] and the neutron diffraction data for ZrMo<sub>2</sub>D<sub>0.9</sub> [15], we may expect H atoms to occupy g sites in HfMo<sub>2</sub>H<sub>x</sub>. The aim of the present work is to evaluate the parameters of hydrogen motion in HfMo<sub>2</sub>H<sub>0.4</sub>. We have measured the proton spin–lattice relaxation times  $T_1$  in HfMo<sub>2</sub>H<sub>0.4</sub> over wide ranges of temperature (20–420 K) and resonance frequency (13–90 MHz). The temperature dependence of  $T_1^{-1}$  is found to exhibit two peaks, which is consistent with a strong difference between two frequency scales of H hopping.

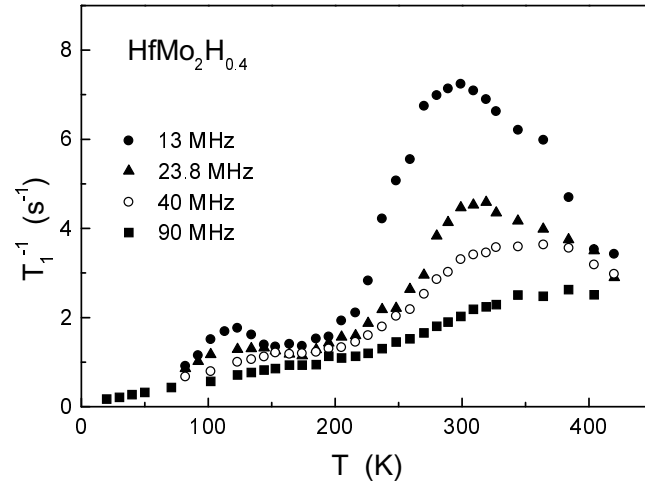
## 2. Experimental details

The HfMo<sub>2</sub> compound was prepared by arc melting of high-purity Hf and Mo in a helium atmosphere followed by an annealing in vacuum at 1600 °C for 1 h, at 1500 °C for 5 h and at 1200 °C for 45 h. This procedure resulted in the formation of a single-phase intermetallic having the cubic C15-type structure with the lattice parameter  $a_0 = 7.546$  Å. Small pieces of HfMo<sub>2</sub> were charged with H<sub>2</sub> gas at a pressure of about 1 bar using a Sieverts-type vacuum system, and the hydrogen content was determined from the pressure change in the calibrated volume of the system. Measurements were made on the powdered sample of HfMo<sub>2</sub>H<sub>0.4</sub>. According to x-ray diffraction analysis, this sample is a single-phase solid solution having C15-type host-metal structure with  $a_0 = 7.568$  Å.

Measurements of the proton spin–lattice relaxation times were performed on a modernized Bruker SXP pulse NMR spectrometer at the frequencies  $\omega/2\pi = 13, 23.8, 40$  and 90 MHz using the saturation–recovery method. In all cases the recovery of nuclear magnetization could be fitted with a single exponential function.

## 3. Results and discussion

The results of the proton spin–lattice relaxation rate measurements on HfMo<sub>2</sub>H<sub>0.4</sub> at four resonance frequencies are presented in figure 1. It can be seen that the temperature dependence of  $T_1^{-1}$  shows two frequency-dependent peaks. As the resonance frequency increases, the amplitude of each of the peaks decreases and the position of each of the peaks is shifted to higher temperatures. Such a behaviour is typical of the relaxation rate maxima due to thermally activated atomic motion [16]. These maxima are observed at temperatures at which



**Figure 1.** The temperature dependence of the proton spin–lattice relaxation rate in  $\text{HfMo}_2\text{H}_{0.4}$  measured at 13, 23.8, 40 and 90 MHz.

the hopping rate of atoms becomes nearly equal to the resonance frequency. The occurrence of two  $T_1^{-1}(T)$  peaks is a clear indication of the coexistence of two characteristic hopping rates  $\tau_d^{-1}$  and  $\tau_l^{-1}$ . The high-temperature and the low-temperature relaxation rate peaks correspond to the conditions  $\omega\tau_d \approx 1$  and  $\omega\tau_l \approx 1$ , respectively,  $\tau_l^{-1}$  being much higher than  $\tau_d^{-1}$  at the same temperature.

In order to evaluate the parameters of hydrogen motion, we have to separate contributions of different nature to  $T_1^{-1}$ . The measured proton spin–lattice relaxation rate in metal–hydrogen systems usually results from the sum of contributions due to conduction electrons ( $T_{1e}^{-1}$ ), paramagnetic impurities ( $T_{1p}^{-1}$ ) and the internuclear dipole–dipole interaction modulated by H motion ( $T_{1d}^{-1}$ ):

$$T_1^{-1} = T_{1e}^{-1} + T_{1p}^{-1} + T_{1d}^{-1}. \quad (1)$$

At low temperatures the  $T_{1d}^{-1}$ -term is negligible, and the sum of  $T_{1e}^{-1}$  and  $T_{1p}^{-1}$  can be determined directly from  $T_1^{-1}$ -measurements. The low-temperature part of the temperature dependence of  $T_1^{-1}$  measured at 90 MHz is shown in figure 2. At  $T \leq 102$  K this temperature dependence is well described by the linear function,

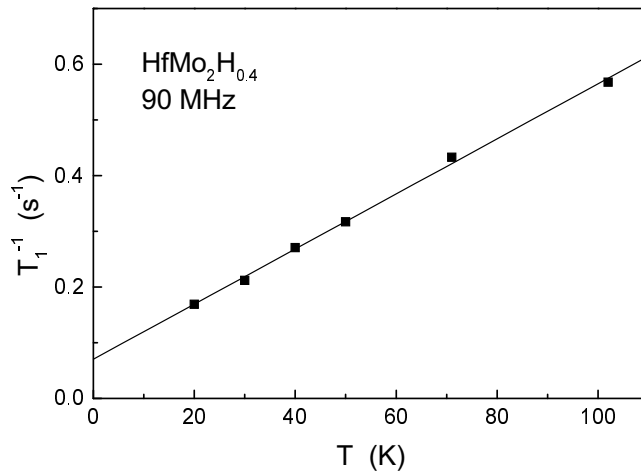
$$(T_1^{-1})_{\text{LT}} = R_e T + B \quad (2)$$

with  $R_e = 4.95 \times 10^{-3} \text{ s}^{-1} \text{ K}^{-1}$  and  $B = 0.07 \text{ s}^{-1}$ . Such a behaviour is typical of  $T_{1e}^{-1} + T_{1p}^{-1}$  in systems with low impurity concentrations [17]. The value of  $R_e = (T_{1e}T)^{-1}$  characterizing the electronic (Korringa) contribution for  $\text{HfMo}_2\text{H}_{0.4}$  is close to that for the isostructural and isoelectronic system  $\text{ZrMo}_2\text{H}_x$  ( $R_e = 5.0 \times 10^{-3} \text{ s}^{-1} \text{ K}^{-1}$  for  $\text{ZrMo}_2\text{H}_{0.5}$  [9]). The dipole–dipole contribution to the relaxation rate can be obtained by subtracting  $T_{1e}^{-1} + T_{1p}^{-1}$  from the measured  $T_1^{-1}$ .

In the case of two types of H motion with strongly differing characteristic hopping rates, the dipole–dipole term can be written as [18]

$$T_{1d}^{-1} = (T_{1d}^{-1})_L + (T_{1d}^{-1})_D \quad (3)$$

where  $(T_{1d}^{-1})_L$  and  $(T_{1d}^{-1})_D$  are the contributions due to the motion with the hopping rates  $\tau_l^{-1}$  and  $\tau_d^{-1}$ , respectively. The slower process with the hopping rate  $\tau_d^{-1}$  gives rise to the



**Figure 2.** The low-temperature part of the temperature dependence of the proton spin-lattice relaxation rate in  $\text{HfMo}_2\text{H}_{0.4}$  at 90 MHz. The solid line represents the fit of equation (2) to the data.

high-temperature relaxation rate peak; this process is expected to be responsible for the long-range H diffusion. The simplest Bloembergen–Purcell–Pound (BPP) model [19] gives

$$(T_{1d}^{-1})_D = \frac{4M_2}{3\omega}(1 - C) \left[ \frac{y_d}{4 + y_d^2} + \frac{y_d}{1 + y_d^2} \right] \quad (4)$$

where  $y_d = \omega\tau_d$ ,  $M_2$  is the ‘rigid-lattice’ second moment of the proton NMR line due to H–H dipole interactions and  $C$  is the fraction of  $M_2$  that is averaged out by the faster jump process. For  $\text{HfMo}_2\text{H}_{0.4}$  we can neglect the dipole–dipole interactions between protons and host-metal nuclei because of the small magnetic moments and low natural abundances of  $^{177}\text{Hf}$ ,  $^{179}\text{Hf}$ ,  $^{95}\text{Mo}$  and  $^{97}\text{Mo}$ . Note that for H–H dipole interactions  $\tau_d$  is twice the correlation time in the proton pair. The faster process with the hopping rate  $\tau_l^{-1}$  gives rise to the low-temperature relaxation rate peak; this process is expected to imply the localized H motion. The exact form of expression for the corresponding contribution to the relaxation rate depends on the model of localized motion. For the simplest model of H hopping between two wells of equal depth,  $(T_{1d}^{-1})_L$  is given by

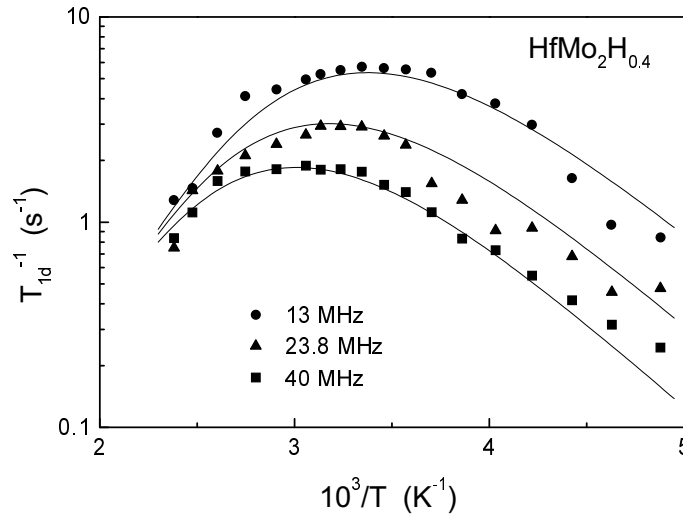
$$(T_{1d}^{-1})_L = \frac{4M_2}{3\omega}C \left[ \frac{y_l}{4 + y_l^2} + \frac{y_l}{1 + y_l^2} \right] \quad (5)$$

where  $y_l = \omega\tau_l$ .

We first consider the data in the high-temperature region. Figure 3 shows the dipole–dipole contributions to the proton relaxation rate at 13, 23.8 and 40 MHz as functions of reciprocal temperature for  $T > 200$  K. According to equation (4), in the limit of fast diffusion ( $y_d \ll 1$ ) the value of  $(T_{1d}^{-1})_D$  is proportional to  $\tau_d$ , and in the limit of slow diffusion ( $y_d \gg 1$ ) the value of  $(T_{1d}^{-1})_D$  is proportional to  $\omega^{-2}\tau_d^{-1}$ . It should be noted that more accurate lattice-specific Monte Carlo calculations of  $(T_{1d}^{-1})_D$  (see, e.g., [20]) lead to results that are close to the BPP predictions. In particular, the asymptotic behaviour of  $(T_{1d}^{-1})_D$  in the limits of fast and slow diffusion appears to be the same as in the BPP model. If  $\tau_d$  follows the Arrhenius relation,

$$\tau_d = \tau_{d0} \exp(E_a/k_B T) \quad (6)$$

where  $E_a$  is the activation energy for hydrogen diffusion, then a plot of  $\log(T_{1d}^{-1})_D$  versus  $T^{-1}$  is expected to be linear both in the fast-diffusion and slow-diffusion limits with the slopes



**Figure 3.** Dipolar contributions to the proton spin–lattice relaxation rate in  $\text{HfMo}_2\text{H}_{0.4}$  at 13, 23.8 and 40 MHz as functions of reciprocal temperature. The solid curves represent the fit of the BPP model with the distribution of activation energies to the data (see the text for details).

$E_a/k_B$  and  $-E_a/k_B$ , respectively. However, for  $\text{HfMo}_2\text{H}_{0.4}$  the observed low-temperature slope of the plot of  $\log T_{1d}^{-1}$  versus  $T^{-1}$  is less steep than the high-temperature slope (figure 3), and the frequency dependence of  $T_{1d}^{-1}$  in the low-temperature slope is considerably weaker than  $\omega^{-2}$ . These features can be accounted for in the model employing a distribution of values of  $\tau_d$  (or  $E_a$ ) [21, 22]. In this case the dipole–dipole contribution to the relaxation rate is calculated as

$$T_{1d}^{-1} = \int T_{1d}^{-1}(E_a)G(E_a) dE_a \quad (7)$$

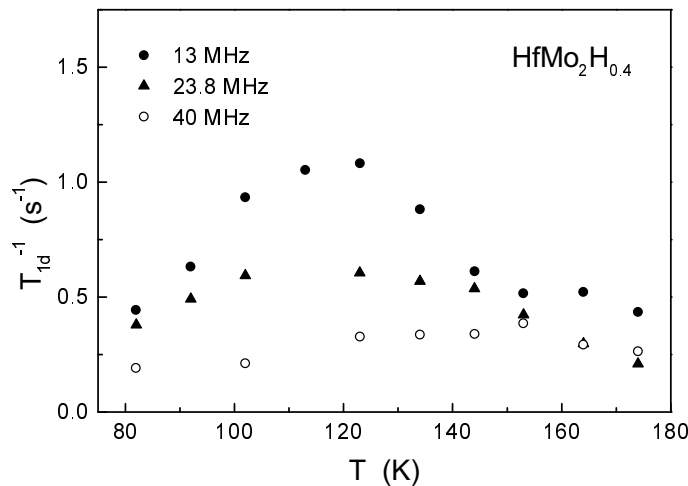
where  $G(E_a)$  is the normalized distribution of  $E_a$ -values, and  $T_{1d}^{-1}(E_a)$  is defined by equations (4) and (6).

For parametrization of the data we have used a Gaussian distribution function  $G(E_a)$ . The parameters of the model are  $M_2(1 - C)$ ,  $\tau_{d0}$ , the average activation energy  $\bar{E}_a$  and the distribution width  $\Delta E_a$  (full width at half-maximum). These parameters are varied to find the best fit to the  $T_{1d}^{-1}(T)$  data at three frequencies simultaneously. The results of the fit are shown as solid curves in figure 3, the corresponding fit parameters being  $M_2(1 - C) = 7.2 \times 10^8 \text{ s}^{-2}$ ,  $\bar{E}_a = 0.26 \text{ eV}$ ,  $\Delta E_a = 0.04 \text{ eV}$  and  $\tau_{d0} = 5.0 \times 10^{-13} \text{ s}$ . Taking into account the small amplitude of the relaxation rate peak in our sample (resulting from low hydrogen concentration), we can conclude that the model gives a reasonable description of the data at three frequencies with the *same* set of parameters. The value of  $\bar{E}_a$  for  $\text{HfMo}_2\text{H}_{0.4}$  is close to that for the related system  $\text{ZrMo}_2\text{H}_x$  ( $\bar{E}_a = 0.23 \text{ eV}$  for  $\text{ZrMo}_2\text{H}_{0.5}$  [9]). The value of the pre-exponential factor  $\tau_{d0}^{-1} = 2 \times 10^{12} \text{ s}^{-1}$  for  $\text{HfMo}_2\text{H}_{0.4}$  is considerably lower than the characteristic hydrogen vibration frequency  $\nu_H \approx 4 \times 10^{13} \text{ s}^{-1}$  [23] in Laves-phase hydrides. This is also typical of the other C15-type hydrides [3, 5, 9, 10]. The second moment  $M_2$  calculated for protons in  $\text{HfMo}_2\text{H}_{0.4}$  (using the model of random g-site occupation restricted by blocking effects) is  $1.1 \times 10^9 \text{ s}^{-1}$ . Comparing this value of  $M_2$  with the value of  $M_2(1 - C)$  from the  $T_{1d}^{-1}$ -fit, we obtain  $C \approx 0.35$ . This means that at the temperature of the high- $T$  relaxation rate peak a considerable fraction of  $M_2$  is already averaged out by the faster jump process.

Figure 4 shows the behaviour of  $T_{1d}^{-1}$  at 13, 23.8 and 40 MHz in the region of the low- $T$  relaxation rate peak. The maximum value of  $T_{1d}^{-1}$  changes with frequency approximately as  $\omega^{-1}$ , in agreement with equation (5). The ratio of the amplitudes of the low-temperature and high-temperature  $T_{1d}^{-1}$ -peaks at 13 MHz is 0.19. Note that the values of this ratio for protons in TaV<sub>2</sub>H<sub>x</sub> [2, 3] are also close to 0.2. Small values of this ratio result from two factors.

- (1) The localized hydrogen motion modulates only a part of the dipole–dipole interaction in the ‘rigid’ lattice, whereas the long-range diffusion leads to the full modulation of the dipole–dipole interaction.
- (2) Only a fraction  $p$  of H atoms participates in the localized motion in Laves phases [7, 8]; in this case a single value of the observed proton relaxation rate is expected to result from the rapid equalization of spin polarization (spin diffusion) [18], so  $(T_{1d}^{-1})_L$  is proportional to  $p$ .

Since the value of  $p$  is known to increase with increasing temperature [7, 8], the value of  $C$  in equations (4) and (5) should also show similar temperature dependence. This means, in particular, that the values of  $C$  in the regions of the low- $T$  and high- $T$  relaxation rate peaks are not the same. The temperature dependence of  $C$  is consistent with the results of recent NMR measurements [24] of the rotating-frame spin relaxation rate  $T_{1\rho}^{-1}$  in C15-type ZrCr<sub>2</sub>H<sub>x</sub>. Both  $T_{1\rho}^{-1}(T)$  and  $T_{1d}^{-1}(T)$  show a single peak in this system, the temperature of the  $T_{1\rho}^{-1}$ -maximum being much lower than the temperature of the  $T_{1d}^{-1}$ -maximum. It has been found [24] that the maximum values of  $T_{1\rho}^{-1}$  are considerably higher than those expected on the basis of the  $T_1^{-1}$ -data for the same samples. This can be qualitatively explained in terms of the decrease of  $1 - C$  with increasing temperature, so the localized H motion leads to a slight reduction of the  $T_{1\rho}^{-1}$ -maximum and to a stronger reduction of the  $T_{1d}^{-1}$ -maximum.



**Figure 4.** The temperature dependence of the dipolar contributions to the proton spin–lattice relaxation rate at 13, 23.8 and 40 MHz in the region of the low- $T$  relaxation rate peak.

Since the amplitude of the low- $T$  relaxation rate peak for HfMo<sub>2</sub>H<sub>0.4</sub> is small and it is difficult to evaluate the temperature dependence of  $C$  from our data, we have not tried to fit  $T_{1d}^{-1}(T)$  in the region of the low- $T$  peak. However, we can roughly estimate the ratio of the hopping rates  $\tau_l^{-1}$  and  $\tau_d^{-1}$  at the temperature of the low- $T$  peak (123 K for  $\omega/2\pi = 13$  MHz). The BPP condition  $\omega\tau_l = 1.23$  at the low- $T$  peak yields  $\tau_l^{-1}(123 \text{ K}) = 6.6 \times 10^7 \text{ s}^{-1}$ . Using

the values of  $\tau_{d0}$  and  $\bar{E}_a$  derived from the fit to the data in the region of the high- $T$  peak, we obtain  $\bar{\tau}_d^{-1}(123\text{ K}) \approx 50\text{ s}^{-1}$  for the most probable  $\tau_d^{-1}$ -value at 123 K. Hence the ratio of the hopping rates is  $\tau_l^{-1}(123\text{ K})/\bar{\tau}_d^{-1}(123\text{ K}) \approx 1.3 \times 10^6$ . Thus, we can conclude that the two frequency scales of H hopping in HfMo<sub>2</sub>H<sub>0.4</sub> are well separated from each other. As discussed in the introduction, this is consistent with the idea that the ratio of the hydrogen hopping rates in Laves-phase compounds AB<sub>2</sub> is related to the ratio  $R_A/R_B$ . It should be noted, however, that this estimate of the ratio of H hopping rates is based on extrapolation of the high-temperature data to the region of the low- $T$  peak, i.e. it does not allow for possible changes in the effective activation energy of the slower jump process at low temperatures (as observed for C15-type ZrCr<sub>2</sub>H<sub>x</sub> [25]). More accurate estimates of  $\tau_d/\tau_l$  can be found by combining the results obtained by two techniques (for example, NMR and QENS, or QENS data collected on two instruments with different energy resolution) *at the same temperature*. Such estimates of  $\tau_d/\tau_l$  at 300 K have been reported recently for TaV<sub>2</sub>H<sub>1.1</sub> and ZrMo<sub>2</sub>H<sub>0.92</sub> [9].

#### 4. Conclusions

Measurements of the proton spin–lattice relaxation rate in C15-type HfMo<sub>2</sub>H<sub>0.4</sub> have revealed two frequency-dependent  $T_1^{-1}(T)$  peaks. As in the case of TaV<sub>2</sub>H<sub>x</sub> [2, 3], this indicates a coexistence of two well-separated frequency scales of H hopping. The low-temperature relaxation rate peak (observed in the region 120–140 K) can be attributed to the fast localized H motion within the hexagons formed by g sites. The high-temperature relaxation rate peak (observed in the region 300–320 K) is related to H jumps from one hexagon to another that are responsible for the long-range diffusion. The behaviour of the relaxation rate in the region of the high- $T$  peak can be reasonably described in terms of the BPP model with a Gaussian distribution of activation energies. It should be noted that the localized H motion may also contribute to the low-temperature slope of the high- $T$  peak, since the fraction of H atoms participating in the fast localized motion is expected to increase with increasing temperature.

Our proton spin–lattice relaxation data for HfMo<sub>2</sub>H<sub>0.4</sub> support the idea [7] that the highest ratios  $\tau_d/\tau_l$  of the characteristic frequencies of two types of H motion are expected to occur in C15 compounds with the lowest ratios of the metallic radii  $R_A/R_B$ . In fact, the temperature dependence of  $T_1^{-1}$  with two peaks is found only for those C15-type systems (TaV<sub>2</sub>–H and HfMo<sub>2</sub>–H) that have the lowest  $R_A/R_B$  values among the cubic Laves phases where H diffusion has been studied.

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