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# Quasielastic neutron scattering study of hydrogen motion in $C15$-type $HfMo_2H_{0.26}$

A. V. Skripov,[1] J. C. Cook,[2] T. J. Udovic,[2] and V. N. Kozhanov[1]
[1]*Institute of Metal Physics, Urals Branch of the Academy of Sciences, Ekaterinburg 620219, Russia*
[2]*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8562*

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In order to evaluate the parameters of H motion in the cubic ($C15$-type) Laves phase $HfMo_2$, we have performed quasielastic neutron scattering measurements on $HfMo_2H_{0.26}$ in the temperature range 15–390 K. The results are consistent with the fast localized H motion within the hexagons formed by interstitial $g(Hf_2Mo_2)$ sites. The slower jump process corresponding to H hopping from one hexagon to another has been probed by recent proton NMR measurements [A. V. Skripov *et al.*, J. Phys.: Condens. Matter **11**, 10 393 (1999)]. Comparison of the NMR and the quasielastic neutron scattering results shows that the ratio of the characteristic hopping rates for the two jump processes, $\tau_d/\tau_l$, is $2.4\times10^3$ at 300 K; this ratio increases with decreasing temperature. For the series of $C15$-type $AB_2$ compounds $TaV_2$–$HfMo_2$–$ZrMo_2$–$ZrCr_2$, it is found that the increase in the ratio of the metallic radii of the elements $A$ and $B$, $R_A/R_B$, leads to the decrease in $\tau_d/\tau_l$.

## I. INTRODUCTION

One of the most intriguing features of hydrogen diffusion in Laves-phase intermetallic compounds is the coexistence of two frequency scales of H hopping.[1–6] It has been found[6,7] that in those cubic ($C15$-type) Laves phases $AB_2$ where hydrogen atoms occupy only tetrahedral sites of $g$ type ($A_2B_2$), the faster jump process corresponds to the localized H motion within the hexagons formed by $g$ sites, and the slower process is associated with H jumps from one $g$-site hexagon to another. 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 ($X_g$ and $Z_g$) of H atoms in $g$ 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 $C15$-type $TaV_2H_x$,[6] and 1.07 for $C15$-type $ZrCr_2H_x$.[7] In agreement with the changes in $r_2/r_1$, nuclear magnetic resonance (NMR) and quasielastic neutron scattering (QENS) studies of hydrogen motion in these two systems have revealed a very large difference between the two frequency scales of H hopping for $TaV_2H_x$,[4–6] whereas for $ZrCr_2H_x$ only a modest difference between the two frequency scales has been found.[7,8]

The positional parameters of hydrogen in interstitial sites formed by different metal atoms ($A_2B_2$ in the case of $g$ sites) are expected to depend on the metallic radii $R_A$ and $R_B$ of the elements $A$ and $B$. In fact, it is known that for many intermetallic hydrides, the metal-hydrogen distances remain approximately the same as in the corresponding metal hydrides.[9,10] Therefore it has been suggested[6] that for Laves-phase hydrides, the ratio $r_2/r_1$ is related to the ratio of the metallic radii $R_A/R_B$. 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 may be formed by elements with considerable deviations of $R_A/R_B$ from this ideal value. In particular, for $TaV_2$, the ratio $R_A/R_B$ is equal to 1.09, being one of the lowest among all Laves-phase compounds.[11] On the other hand, for $ZrCr_2$, this ratio is equal to 1.25, being higher than the ideal one. Thus the systematics of two frequency scales of H hopping in cubic Laves phases $AB_2$ may be rationalized in terms of $R_A/R_B$. One may expect that the difference between the two characteristic hopping rates of H atoms increases with decreasing $R_A/R_B$. In order to verify this idea, it is necessary to probe the hydrogen hopping rates for both jump processes in a number of cubic Laves phases with different values of $R_A/R_B$. The combined QENS and NMR study of H motion in $C15$-type $ZrMo_2H_x$ (Ref. 12) has become the first step in such a program; the parameters of H motion for this system with $R_A/R_B=1.144$ appear to bridge those for $TaV_2H_x$ and $ZrCr_2H_x$. It is of special interest to study hydrogen mobility in cubic Laves phases for which the value of $R_A/R_B$ is as low as possible. Among the hydrogen-absorbing $C15$-type compounds, this condition is met for $HfMo_2$, for which the value of $R_A/R_B$ ($=1.129$) is close to that for $TaV_2$.

We have found that $C15$-type $HfMo_2$ absorbs hydrogen forming solid solutions $HfMo_2H_x$ with $x\leqslant0.4$ (at a hydrogen pressure of about 1 bar). Note that the maximum hydrogen content in $HfMo_2$ is lower than in the related $C15$-type compound $ZrMo_2$ for which $x\leqslant1.05$.[13] According to recent neutron diffraction measurements,[14] D atoms in $HfMo_2D_{0.2}$ occupy only tetrahedral $g$ sites. The aim of the present work is to evaluate the parameters of the faster (localized) H hopping in $HfMo_2H_x$ using incoherent quasielastic neutron scattering. We have performed QENS measurements for $HfMo_2H_{0.26}$ over the temperature range 15–390 K. The results are analyzed to determine the hopping rate and the jump length of hydrogen atoms participating in the fast localized motion. These results are compared to those derived from the recent NMR measurements on $HfMo_2H_{0.4}$ (Ref. 15) which have probed H motion on a slower frequency scale.

## II. EXPERIMENTAL DETAILS

The $HfMo_2$ compound was prepared by arc melting of high-purity Hf and Mo in a helium atmosphere followed by

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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 $\mathrm{HfMo_2}$ were charged with $\mathrm{H_2}$ 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 $\mathrm{HfMo_2H_{0.26}}$. According to x-ray-diffraction analysis, this sample is a single-phase solid solution having $C15$-type host-metal structure with $a_0 = 7.565$ Å.

QENS measurements were performed on the Fermi-chopper time-of-flight spectrometer at the NIST Center for Neutron Research (National Institute of Standards and Technology, Gaithersburg, Maryland). The sample was placed into a flat Al container with a depth of 0.5 mm. The incident neutron wavelength was 6.0 Å. QENS spectra were recorded at the temperatures $T = 15$, 230, 260, 300, 350, and 390 K. The instrumental resolution functions $R(Q,\omega)$ (where $\hbar\omega$ is the energy transfer and $\hbar Q$ is the momentum transfer) were determined from the QENS spectra of $\mathrm{HfMo_2H_{0.26}}$ at 15 K, the energy resolution being about 65 $\mu$eV (full width at half maximum). For data treatment, the detectors were divided into eight groups with the weighted average elastic $Q$ values ranging from 0.36 to 1.93 $\text{Å}^{-1}$.

## III. RESULTS AND DISCUSSION

The experimental QENS spectra for $\mathrm{HfMo_2H_{0.26}}$ in the temperature range 230–390 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. Similar shapes of QENS spectra have been found for the related systems $\mathrm{TaV_2H}_x$ (Ref. 6) and $\mathrm{ZrMo_2H}_x$ (Ref. 12) in the same temperature range. As the first step of the analysis, we have fitted the experimental scattering function $S_{\mathrm{exp}}(Q,\omega)$ with the model incoherent scattering function

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

convoluted with $R(Q,\omega)$. Here $\delta(\omega)$ is the elastic $\delta$ function, $L(\omega,\Gamma)$ is the quasielastic Lorentzian with the half-width $\Gamma$ and $A_0(Q)$ is the elastic incoherent structure factor (EISF). The relative intensity of the quasielastic component is found to increase with increasing $Q$, its half-width $\Gamma$ being nearly $Q$ independent. These features are typical of the case of spatially confined (localized) motion.[16] The value of $\Gamma$ is proportional to the hydrogen hopping rate $\tau_l^{-1}$, and $A_0(Q)$ contains information on the geometry of the localized motion.[16] Thus the results of our measurements are consistent with the existence of a localized H motion in $\mathrm{HfMo_2H_{0.26}}$ with the characteristic hopping rates lying within the frequency ''window'' of the time-of-flight spectrometer for the temperature range $230 \leqslant T \leqslant 390$ K.

Figure 1 shows the $Q$ dependence of EISF obtained from the fits of $S_{\mathrm{inc}}(Q,\omega)$ [Eq. (1)] to the data at 230, 300, and 390 K. The values of EISF have been corrected for a contribution of the host-metal lattice to the observed intensity of the elastic line ($\sim 13\%$, as estimated from the corresponding scattering cross sections). As in the other Laves-phase hydrides,[6,7,12] the measured EISF appears to be temperature-dependent, decreasing with increasing $T$. Similar temperature dependence of EISF has also been observed for the localized H motion in $\alpha$-$\mathrm{ScH}_x$.[17,18] In order to account for this feature, we have to assume that only a fraction $p(T)$ of H atoms participates in the fast localized motion, and this fraction increases with temperature. The fraction $1 - p(T)$ of ''static'' protons (on the frequency scale determined by the spectrometer resolution) contributes only to the elastic line and makes the observed values of EISF higher than those expected in the case of $p = 1$. The existence of ''static'' protons may result from H–H interactions leading to the formation of some ordered atomic configurations at low temperatures. As the temperature increases, such ordered configurations are expected to be progressively destroyed by thermal fluctuations; this leads to the observed growth of the fraction $p(T)$.

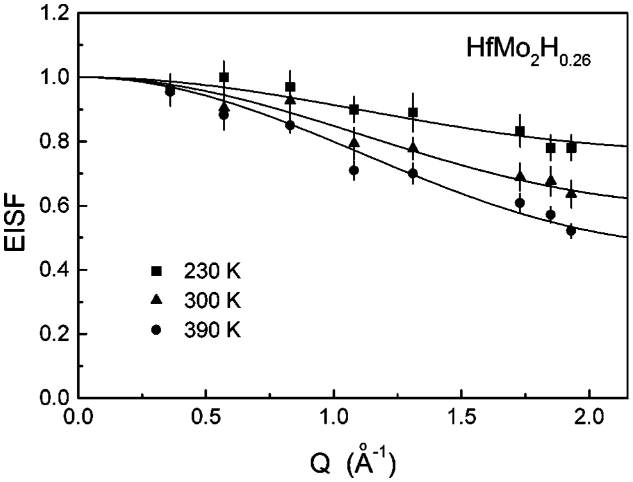

FIG. 1. The elastic incoherent structure factor for $\mathrm{HfMo_2H_{0.26}}$ as a function of $Q$ at $T = 230$, 300, and 350 K. The solid lines represent the fits of the six-site model [Eq. (2)] with the fixed $r = 1.10$ Å to the data.

In order to obtain the parameters of the localized hydrogen motion, we have first to verify whether the observed $Q$ dependence of EISF is consistent with the geometrical model of H hopping. The structure of the network of interstitial $g$ sites in the $C15$ lattice has been discussed in detail in our previous papers (see, e.g., Figs. 5 and 6 of Ref. 6). The sublattice of $g$ sites consists of hexagons, the distance $r_1$ between the nearest sites within the hexagon being shorter than the distance $r_2$ between the nearest sites on different hexagons. A hydrogen atom moving on such a sublattice is expected to perform many jumps within a hexagon before jumping to another hexagon. Since $\mathrm{HfMo_2}$ absorbs only small amounts of hydrogen, it is difficult to determine the positional parameters of hydrogen at $g$ sites reliably from diffraction measurements. Therefore, in order to evaluate $r_1$ and $r_2$ in our sample, we have used the experimental value of the lattice parameter for $\mathrm{HfMo_2H_{0.26}}$ and the experimental values of the positional parameters of D atoms at $g$ sites in the closely related system $\mathrm{ZrMo_2D_{0.9}}$ ($X_g = 0.060$, $Z_g = 0.882$).[19] We obtain $r_1 = 1.10$ Å and $r_2 = 1.39$ Å. In the case of $p<1$ the elastic incoherent structure factor for the model of hopping between six sites on a circle of radius $r$ (Ref. 16) is given by

$$A_0(Q,T)=1-p(T)+\frac{1}{6}p(T)[1+2j_0(Qr)+2j_0(Qr\sqrt{3})+j_0(2Qr)], \tag{2}$$

where $j_0(x)$ is the spherical Bessel function of zeroth order. The fit of Eq. (2) to the $A_0(Q)$ data at 300 K yields $p=0.39\pm0.02$ and $r=1.19\pm0.16$ Å. Thus the fitted $r$ value is close to the value $r=r_1=1.10$ Å obtained from the structure. By fixing the value of $r$ to 1.10 Å, we have found reasonable fits of the six-site model [Eq. (2)] to the data at all temperatures in the studied range with $p(T)$ as the only fit parameter. The results of these fits are shown by solid lines in Fig. 1.

As the next step of the data analysis, we may use a more rigorous approach entailing a simultaneous fit of the six-site model with the fixed $r$ to the spectra at all $Q$. Taking into account that only a fraction $p(T)$ of protons participates in the fast localized motion, $S_{\mathrm{inc}}(Q,\omega)$ for the six-site model[16] can be written in the form

$$S_{\mathrm{inc}}(Q,\omega)=A_0(Q)\delta(\omega)+p(T)\sum_{i=1}^{3}A_i(Q)L(\omega,\Gamma_i), \tag{3}$$

where $A_0(Q)$ is given by Eq. (2),

$$A_1(Q)=\frac{1}{6}[2+2j_0(Qr)-2j_0(Qr\sqrt{3})-2j_0(2Qr)], \tag{4}$$

$$A_2(Q)=\frac{1}{6}[2-2j_0(Qr)-2j_0(Qr\sqrt{3})+2j_0(2Qr)], \tag{5}$$

$$A_3(Q)=\frac{1}{6}[1-2j_0(Qr)+2j_0(Qr\sqrt{3})-j_0(2Qr)]. \tag{6}$$

$L(\omega,\Gamma_i)$ is the Lorentzian function with the half-width $\Gamma_i$, $\Gamma_1=0.5\tau_l^{-1}$, $\Gamma_2=1.5\tau_l^{-1}$, $\Gamma_3=2\tau_l^{-1}$, and $\tau_l$ is the mean time between two successive jumps of a proton within a hexagon. Thus, for the six-site model, the quasielastic line consists of three Lorentzian components with different half-widths $\Gamma_i$ and $Q$-dependent amplitudes $A_i(Q)$. By fixing the value of $r$ to 1.1 Å, for each of the studied temperatures, we have found good simultaneous fits of the six-site model [Eqs. (3)–(6) and (2)] to the QENS spectra at all $Q$ with $\tau_l^{-1}$ and $p$ as the fit parameters. The temperature dependences of $\tau_l^{-1}$ and $p$ resulting from these simultaneous fits are shown in Figs. 2 and 3.

The solid line in Fig. 2 shows the Arrhenius fit to $\tau_l^{-1}(T)$ with the activation energy of 33 meV and the pre-exponential factor $\tau_{l0}^{-1}=5.2\times10^{11}$ s$^{-1}$. Note that this value of the activation energy appears to be considerably lower than the activation energies for the localized H motion estimated from the empirical potentials for interstitial hydrogen in a number of $C15$-type compounds (0.13–0.20 eV).[20] As we shall discuss below, comparison of the present QENS results with the NMR data for $\mathrm{HfMo_2H_{0.4}}$ (Ref. 15) leads to the activation energy value being in general agreement with the estimates of Ref. 20.

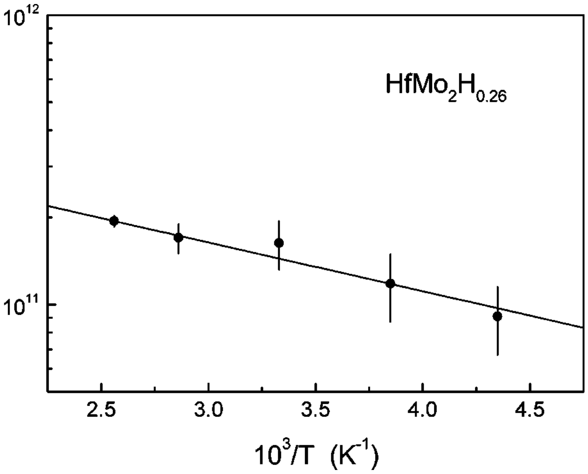

FIG. 2. Temperature dependence of the hydrogen hopping rate $\tau_l^{-1}$ derived from the fits of the six-site model [Eqs. (2)–(6)] to the data. The solid line shows the Arrhenius fit to $\tau_l^{-1}(T)$.

The usual approach to the description of $p(T)$ is based on the assumption of a certain energy gap $\Delta E$ between static and mobile H states (see, e.g., Ref. 18). In this case,

$$p(T)=\frac{b(T)}{1+b(T)}, \tag{7}$$

$$b(T)=b_m\exp(-\Delta E/k_BT), \tag{8}$$

where $b_m$ is the relative degeneracy factor of mobile states. The dashed line in Fig. 3 shows the fit of this model to $p(T)$; the resulting values of the fit parameters: $\Delta E=68\pm7$ meV, $b_m=11\pm3$. It should be noted, however, that in the studied range 230–390 K, the temperature dependence of $p$ can also be described by the linear function, $p(T)=cT$. Similar linear dependence of $p(T)$ has been observed for $\mathrm{TaV_2H}_x$ in the range 75–300 K.[6] This feature resembles the well-

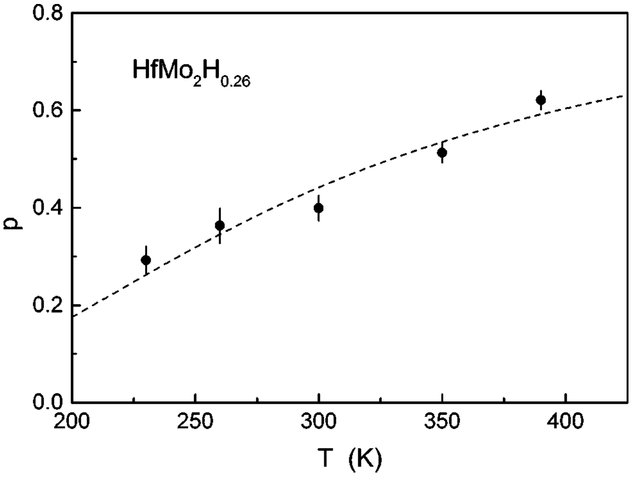

FIG. 3. Temperature dependence of the fraction of protons participating in the fast localized motion, as determined from the fits of the six-site model [Eqs. (2)–(6)] to the data. The dashed line shows the fit of the model described by Eqs. (7) and (8) to $p(T)$.

known behavior of glasses originating from two-level systems with a nearly uniform $\Delta E$ distribution at low $\Delta E$.[21] The existence of such a distribution may be ascribed to a spread in local H configurations, as is typical of nonstoichiometric hydrides.

It is interesting to compare the QENS data of the present work with the results of the proton spin-lattice relaxation measurements for $HfMo_2H_{0.4}$.[15] In metal-hydrogen systems, the proton spin-lattice relaxation rate $T_1^{-1}$ is known to have a maximum at the temperature at which the condition

$$\omega_H \tau_c \approx 1 \tag{9}$$

is fulfilled, where $\omega_H$ is the Larmor frequency for $^1$H and $\tau_c$ is the appropriate correlation time. For $HfMo_2H_x$, the correlation time $\tau_c$ should be equal to one-half of the mean time between two successive jumps of a hydrogen atom. Since typical $\omega_H$ values are of the order of $10^8\ s^{-1}$, the $T_1^{-1}$ measurements probe H motion on a slower frequency scale as compared to the time-of-flight QENS measurements. The temperature dependence of the measured proton spin-lattice relaxation rate in $HfMo_2H_{0.4}$ shows two peaks;[15] this is consistent with the coexistence of two types of H motion. In the region of the low-temperature peak (110–130 K), the role of $\tau_c$ in Eq. (9) is played by $\tau_l/2$, i.e., this peak results from the localized H motion. In the region of the high-temperature peak (290–320 K) the hopping rate of the localized H motion, $\tau_l^{-1}$, is too high to contribute significantly to $T_1^{-1}$, and the role of $\tau_c$ in Eq. (9) is played by $\tau_d/2$, where $\tau_d$ is the mean residence time of a hydrogen atom at a $g$-site hexagon,[6] $\tau_d \gg \tau_l$. Thus the high-temperature $T_1^{-1}$ peak is determined by the slower jump process leading to the long-range H diffusion. The difference between hydrogen concentrations in the samples studied by QENS ($x=0.26$) and NMR ($x=0.4$) is small, and their lattice parameters are close to each other (7.565 and 7.568 Å, respectively). Therefore we may neglect the effect of H content on the hopping rates in these samples and compare the results obtained by QENS and NMR directly.

Figure 4 shows the values of $\tau_l^{-1}$ found from the present QENS experiments together with the values of $\tau_l^{-1}$ and $\tau_d^{-1}$ derived from the proton $T_1^{-1}$ measurements.[15] The value of $\tau_d^{-1}$ shown by the solid triangle is obtained at the high-temperature peak for $\omega_H/2\pi = 13$ MHz from the Bloembergen-Purcell-Pound (BPP) (Ref. 22) condition $\omega_H \tau_d = 1.23$. The value of $\tau_l^{-1}$ shown by the solid square is obtained from the analogous condition at the low-temperature $T_1^{-1}$ peak. The dashed line represents the Arrhenius temperature dependence of $\tau_d^{-1}$ with the activation energy $E_a^d = 0.26$ eV and the pre-exponential factor $\tau_{d0}^{-1} = 2 \times 10^{12}\ s^{-1}$, as found from the $T_1^{-1}$ measurements.[15] In order to estimate the effective activation energy for $\tau_l^{-1}$ over a wide temperature range, we may use the point derived from the low-temperature $T_1^{-1}$ peak and the point from QENS at 390 K (having the smallest error). The resulting dotted line in Fig. 4 corresponds to $E_a^l = 0.12$ eV and $\tau_{l0}^{-1} = 8 \times 10^{12}\ s^{-1}$. The value of $E_a^l$ estimated in this way appears to be considerably higher than the value of 0.033 eV derived above from the QENS data in the range 230–390 K. Neutron diffraction measurements on $HfMo_2D_{0.2}$ (Ref. 14) have not revealed any changes in the structure between 18 and 300 K. Therefore the discrepancy between the two estimates of $E_a^l$ cannot be ascribed to structural changes. Such a discrepancy may result from the existence of a certain distribution of the hopping rates $\tau_l^{-1}$. As has been shown in Ref. 23, in this case, the apparent quasielastic linewidth at the low-$T$ end of the experimental temperature range (limited by the instrumental energy resolution) may be higher than the linewidth determined by the most probable value of $\tau_l^{-1}$. This is expected to lead to the underestimation of the activation energy for the localized H motion in QENS experiments using a single instrument. The value of $E_a^l$ can also be roughly estimated from the temperature dependence of $T_1^{-1}$ in the region of the low-$T$ peak. The complicating factors here are the small amplitude of the low-$T$ relaxation-rate peak[15] and the temperature dependence of $p$ that affects the measured $T_1^{-1}(T)$ (see the discussion in Ref. 6). Using the experimental $T_1^{-1}$ data[15] in the range 110–160 K and assuming that $p$ is temperature independent, we obtain $E_a^l \approx 0.07$ eV. This value is expected to increase, if the actual temperature dependence of $p$ (increasing with temperature) is taken into account. Thus the value of 0.1 eV seems to be a reasonable estimate of $E_a^l$ in $HfMo_2H_{0.26}$ over a wide temperature range. It should be noted that the value of $E_a^l$ is still considerably lower than the activation energy $E_a^d$ for the long-range H diffusion. Therefore the ratio of the hopping rates $\tau_d/\tau_l$ increases with decreasing temperature.

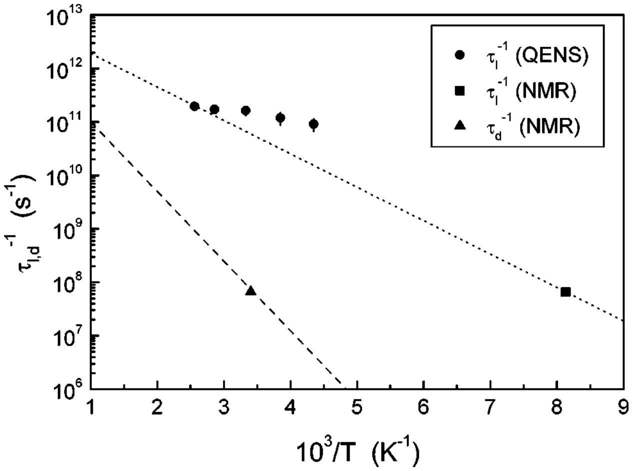

FIG. 4. The hydrogen hopping rates $\tau_l^{-1}$ and $\tau_d^{-1}$ derived from the present QENS measurements and from the proton NMR measurements (Ref. 15) for $HfMo_2H_x$. The dashed line shows the Arrhenius temperature dependence of $\tau_d^{-1}$, as determined from the proton spin-lattice relaxation measurements (Ref. 15). The dotted line connects the $\tau_l^{-1}$ points derived from the low-temperature peak of the proton spin-lattice relaxation rate and from QENS at 390 K.

In order to discuss the relation between $\tau_d/\tau_l$, $r_2/r_1$ and $R_A/R_B$, it is useful to compare the QENS and NMR results for $HfMo_2H_x$ with those for $TaV_2H_x$,[5,6] $ZrCr_2H_x$,[7,8] and $ZrMo_2H_x$.[12] The microscopic picture of hydrogen diffusion in all of these compounds appears to be qualitatively the same. Since the value of $\tau_d/\tau_l$ depends on temperature, we have to choose a certain temperature for comparison of the

TABLE I. The ratios of metallic radii of the elements $A$ and $B$ forming the $AB_2$ intermetallics, the intersite distances, and the hydrogen hopping rates at 300 K in $C15$-type $TaV_2H_{1.1}$, $HfMo_2H_{0.26}$, $ZrMo_2H_{0.92}$, and $ZrCr_2H_{0.45}$.

| Parameter | $TaV_2H_{1.1}$ | $HfMo_2H_{0.26}$ | $ZrMo_2H_{0.92}$ | $ZrCr_2H_{0.45}$ |
|---|---|---|---|---|
| $R_A/R_B$ | 1.090 | 1.129 | 1.144 | 1.250 |
| $r_1$, Å | 0.99 | 1.10 | 1.12 | 1.13 |
| $r_2$, Å | 1.44 | 1.39 | 1.41 | 1.21 |
| $r_2/r_1$ | 1.45 | 1.26 | 1.26 | 1.07 |
| $\tau_l^{-1}$ (300 K), $s^{-1}$ | $3.8\times10^{11}$ | $1.6\times10^{11}$ | $1.1\times10^{11}$ | $7.1\times10^{10}$ |
| $\tau_d^{-1}$ (300 K), $s^{-1}$ | $7.3\times10^{7}$ | $6.6\times10^{7}$ | $5.7\times10^{7}$ | $3.5\times10^{9}$ |
| $\tau_d/\tau_l$(300 K) | $5.2\times10^{3}$ | $2.4\times10^{3}$ | $1.9\times10^{3}$ | 20 |

data. At $T<200$ K the value of $\tau_d^{-1}$ in the Laves phase hydrides (except for $ZrCr_2H_x$) becomes too low to be determined from QENS and $T_1^{-1}$ measurements. On the other hand, at room temperature both $\tau_l^{-1}$ and $\tau_d^{-1}$ can be measured (the former from the time-of-flight QENS and the latter from the backscattering QENS or NMR). Table I shows the ratios of metallic radii $R_A/R_B$, the $g$-$g$ distances $r_1$ and $r_2$, and the hydrogen hopping rates at 300 K for $C15$-type $TaV_2H_{1.1}$, $HfMo_2H_{0.26}$, $ZrMo_2H_{0.92}$, and $ZrCr_2H_{0.45}$. The positional parameters of hydrogen at $g$ sites, $X_g$ and $Z_g$, in these compounds have been determined from the neutron diffraction measurements on $TaV_2D_x$,[24] $ZrMo_2D_{0.9}$,[19] and $ZrCr_2D_{0.7}$;[19] the values of $X_g$ and $Z_g$ for $HfMo_2H_x$ are assumed to be the same as for $ZrMo_2H_x$. The $g$-$g$ distances $r_1$ and $r_2$ are calculated using the values of $X_g$ and $Z_g$ and the actual lattice parameters of the compounds. The values of $\tau_l^{-1}$ (300 K) are obtained[25] from the time-of-flight QENS data for $TaV_2H_{1.1}$,[6] $HfMo_2H_{0.26}$ (present work), $ZrMo_2H_{0.92}$,[12] and $ZrCr_2H_{0.5}$.[26] The values of $\tau_d^{-1}$ (300 K) are estimated from the proton spin-lattice relaxation measurements on $TaV_2H_{1.15}$,[5] $HfMo_2H_{0.4}$,[15] and $ZrMo_2H_{1.0}$.[12] For these compounds the $T_1^{-1}$ maximum is observed near room temperature. The value of $\tau_d^{-1}$ (300 K) for $ZrCr_2H_{0.45}$ is obtained from the backscattering QENS data.[7]

As can be seen from Table I, the increase in $R_A/R_B$ leads to the decrease in $r_2/r_1$. Furthermore, there is a clear correlation between the increase in $R_A/R_B$ and the decrease in $\tau_d/\tau_l$ (300 K). For the $HfMo_2$–H system, the values of both $R_A/R_B$ and $\tau_d/\tau_l$ (300 K) lie between the corresponding values for $TaV_2$–H and $ZrMo_2$–H. Thus the data on the parameters of hydrogen motion in $HfMo_2$ support the idea[6] concerning the relation between the H hopping rates, the intersite distances, and $R_A/R_B$ in cubic Laves phases.

## IV. CONCLUSIONS

The analysis of our quasielastic neutron scattering data for $C15$-type $HfMo_2H_{0.26}$ confirms that the fast localized hydrogen motion in this compound corresponds to H jumps within the hexagons formed by $g$ sites. It is found that only a fraction $p(T)$ of H atoms participates in the fast localized motion, and this fraction increases with temperature. The slower process corresponding to H jumps from one hexagon to another has been studied by NMR measurements of the proton spin-lattice relaxation rate in $HfMo_2H_x$.[15] Comparison of the NMR data[15] with the present quasielastic neutron scattering results shows that the ratio of the characteristic hopping rates for the two jump processes, $\tau_d/\tau_l$, at 300 K is $2.4\times10^3$.

In order to verify the relation between the hydrogen hopping rates, the $g$-$g$ distances and $R_A/R_B$,[6] we have compared our results for $HfMo_2H_x$ with those for $C15$-type $TaV_2H_x$, $ZrMo_2H_x$, and $ZrCr_2H_x$. In the series $TaV_2$–$HfMo_2$–$ZrMo_2$–$ZrCr_2$, there is a clear correlation between the increase in $R_A/R_B$ and the decrease in $\tau_d/\tau_l$. Such a correlation may give a key to understanding the systematics of H motion in cubic Laves phases. In particular, for $C15$-type compounds with $R_A/R_B>1.35$, the $g$-$g$ distance $r_2$ is expected to become shorter than $r_1$. This may lead to a qualitative change in the microscopic picture of H motion: the faster jump process is expected to be transformed into the back-and-forth jumps within *pairs* of $g$ sites separated by $r_2$. The search for this type of localized H motion in Laves phases is in progress now.

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