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## Hydrogen mobility in the C15-type compounds $ZrCr_2H_x$ : proton spin relaxation study

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**Abstract.** Nuclear magnetic resonance (NMR) measurements of the proton spin–lattice relaxation times in the C15-type compounds  $ZrCr_2H_x$  ( $x = 0.2$  and  $0.5$ ) have been performed over the temperature range 11–440 K. The experimental results are analysed to obtain the electronic (Korringa) contributions to the relaxation rates and the parameters of hydrogen motion. For both samples hydrogen is found to retain high mobility on the NMR frequency scale down to 78 K. The average activation energies for hydrogen diffusion in  $ZrCr_2H_x$  (81 and 84 meV for  $x = 0.2$  and  $0.5$ , respectively) are lower than in the other studied hydrides of intermetallic compounds.

### 1. Introduction

Hydrogen diffusion in the Laves-phase intermetallic compounds shows a number of unusual features [1–4]. Recent nuclear magnetic resonance (NMR) experiments on C14- and C15-type  $ZrCr_2H_x$  [5] have revealed that, in C15  $ZrCr_2H_{0.3}$ , hydrogen retains a very high mobility down to low temperatures. In fact, for this system the complete motional narrowing of the proton NMR line is observed down to liquid-nitrogen temperature. However, hydrogen diffusion parameters for C15  $ZrCr_2H_{0.3}$  have not been determined from the data [5], the analysis being mainly qualitative.

The aim of the present work is to evaluate the hydrogen diffusion parameters in the C15-type  $ZrCr_2H_x$  at low  $x$ . We have measured the proton spin–lattice relaxation times in  $ZrCr_2H_{0.2}$  and  $ZrCr_2H_{0.5}$  over wide ranges of temperature and resonance frequency. The experimental results are analysed to obtain the hopping rates of H atoms and the electronic (Korringa) contributions to the proton relaxation rates.

### 2. Experimental details

The  $ZrCr_2$  alloy was prepared by arc melting the appropriate amounts of pure Zr and Cr in a helium atmosphere. The melting resulted in the formation of the hexagonal C14-type compound with the lattice parameters  $a = 5.09$  Å and  $c = 8.20$  Å. Afterwards this sample was annealed in argon at 1300°C for 3 h. The annealing resulted in the formation of the single-phase cubic C15-type compound with  $a = 7.19$  Å. Small pieces of the host compound were charged with  $H_2$  gas at a pressure of about 0.3 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 powdered

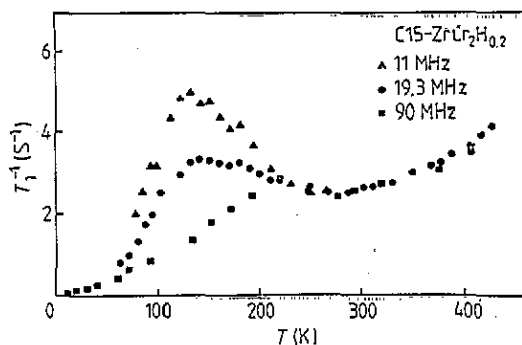


Figure 1. Temperature dependence of the proton spin-lattice relaxation rate in  $\text{ZrCr}_2\text{H}_{0.2}$  measured at 11, 19.3 and 90 MHz.

samples of  $\text{ZrCr}_2\text{H}_x$  ( $x = 0.2$  and  $0.5$ ). According to the x-ray diffraction analysis, these samples are single-phase solid solutions having the cubic C15-type host-metal structure with  $a = 7.219 \text{ \AA}$  ( $x = 0.2$ ) and  $7.265 \text{ \AA}$  ( $x = 0.5$ ).

Proton NMR measurements were performed on a Bruker SXP pulse spectrometer. Spin-lattice relaxation times  $T_1$  were measured at the frequencies  $\omega/2\pi = 11$ , 19.3 and 90 MHz using the conventional inversion-recovery method. In all cases the recovery could be fitted by an exponential function.

### 3. Results and discussion

The results of the proton spin-lattice relaxation rate measurements in  $\text{ZrCr}_2\text{H}_{0.2}$  and  $\text{ZrCr}_2\text{H}_{0.5}$  at three different frequencies are presented in figures 1 and 2. For both compounds the relaxation rate  $T_1^{-1}$  shows the characteristic frequency-dependent maximum associated with hydrogen motion. This maximum is observed when  $\omega\tau_d \simeq 1$ ,  $\tau_d$  being the mean dwell time of the H atom in an interstitial site. It can be seen that the temperature  $T_{\text{max}}$  of the  $T_1^{-1}$  maximum increases with increasing hydrogen content. The value of  $T_{\text{max}}$  for  $\text{ZrCr}_2\text{H}_{0.2}$  (about 130 K at  $\omega/2\pi = 11$  MHz) appears to be lower than for the other studied metal-hydrogen systems with non-vanishing H content. This means that hydrogen in  $\text{ZrCr}_2\text{H}_{0.2}$  retains a high mobility down to lower temperatures than in the other systems.

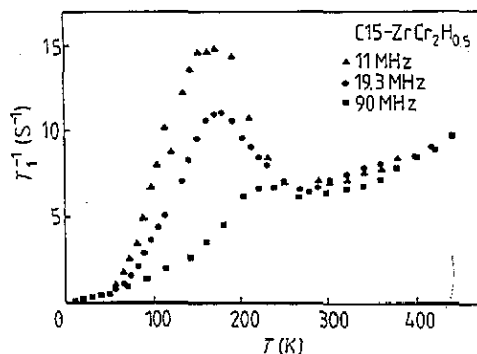


Figure 2. Temperature dependence of the proton spin-lattice relaxation rate in  $\text{ZrCr}_2\text{H}_{0.5}$  measured at 11, 19.3 and 90 MHz.

In order to evaluate the parameters of hydrogen diffusion we have to separate the different contributions to  $T_1^{-1}$ . The measured proton spin-lattice relaxation rate in metal-hydrogen systems usually results from the sum of the contribution  $T_{1e}^{-1}$  due to the hyperfine interactions with conduction electrons and the contribution  $T_{1d}^{-1}$  due to the dipole-dipole interactions modulated by hydrogen motion:

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

The electronic contribution is typically proportional to temperature, i.e.  $T_{1e}^{-1} = CT$ , and does not depend on the resonance frequency. The motional contribution can be expressed in terms of the spectral density functions for fluctuating dipolar fields. For the simplest model [6], known as the Bloembergen-Purcell-Pound (BPP) approximation, the spectral density functions are Lorentzian, and  $T_{1d}^{-1}$  is given by

$$T_{1d}^{-1} = (4M_2/3\omega)[y/(4+y^2) + y/(1+y^2)] \quad (2)$$

where  $y = \omega\tau_d$  and  $M_2$  is the 'rigid-lattice' second moment of the proton NMR line due to H-H dipole interactions:

$$M_2 = \frac{3}{5}\gamma^4\hbar^2 I(I+1) \sum_i r_i^{-6}. \quad (3)$$

Here  $I$  is the spin and  $\gamma$  is the gyromagnetic ratio for protons,  $r_i$  is the distance from the  $i$ th proton to a proton at the origin, and the sum is over all occupied interstitial sites. According to the neutron diffraction data [7], hydrogen atoms in C15  $ZrCr_2$  occupy tetrahedral interstitial sites of the  $g$  type formed by two Zr and two Cr atoms. For  $ZrCr_2H_x$  we can neglect the dipole-dipole interactions between protons and host-metal nuclei because of small magnetic moments and low natural abundances of  $^{91}Zr$  and  $^{53}Cr$ . The asymptotic behaviours of  $T_{1d}^{-1}$  in the limits of fast ( $y \ll 1$ ) and slow ( $y \gg 1$ ) diffusion are given by

$$T_{1d}^{-1} \propto \tau_d \quad y \ll 1 \quad (4)$$

$$T_{1d}^{-1} \propto \omega^{-2}\tau_d^{-1} \quad y \gg 1. \quad (5)$$

It should be noted that more accurate lattice-specific calculations of the spectral density functions (see, e.g., [8]) lead to results that are close to the BPP predictions. In particular, the asymptotic behaviour of  $T_{1d}^{-1}$  in the framework of lattice-specific calculations can also be written in the form of equations (4) and (5).

The electronic contribution to  $T_1^{-1}$  can be obtained directly from relaxation measurements at temperatures much lower or much higher than  $T_{max}$ , since in these regions the motional contribution  $T_{1d}^{-1}$  is negligible. Figure 3 shows the low-temperature part of the temperature dependences of  $T_1^{-1}$  for  $ZrCr_2H_{0.2}$  and  $ZrCr_2H_{0.5}$  at 90 MHz. At  $T \leq 40$  K the observed  $T_1^{-1}(T)$  dependences are well approximated by the linear functions  $CT$ , as expected. The corresponding values of  $C$  are presented in table 1. Included in table 1 are also the values of  $C$  for the C15-type  $ZrCr_2H_{0.3}$  and  $ZrCr_2H_{3.3}$  from [5]. It can be seen that  $C$  strongly increases with increasing H content. In transition-metal-hydrogen systems,  $C$  is usually dominated by the spin contribution of d electrons [9] proportional to the square  $N_d^2(E_F)$  of the density of d electrons at the Fermi level. Thus our experimental data suggest that in  $ZrCr_2H_x$  the value of  $N_d(E_F)$  increases significantly with increasing  $x$ . A similar behaviour of  $N_d(E_F)$  has been reported for the isoelectronic system  $TiCr_{1.8}H_x$  [1]. An

**Table 1.** Parameters of the electronic contribution to the proton spin-lattice relaxation rate (equation (6)).

Sample	$C = (T_{1e}T)^{-1}_{T \rightarrow 0}$ ( $s^{-1} K^{-1}$ )	$B$ ( $s^{-1} K^{-3}$ )	Reference
C15 ZrCr <sub>2</sub> H <sub>0.2</sub>	$5.8 \times 10^{-3}$	$2.1 \times 10^{-8}$	Present work
C15 ZrCr <sub>2</sub> H <sub>0.3</sub>	$7.0 \times 10^{-3}$		[5]
C15 ZrCr <sub>2</sub> H <sub>0.5</sub>	$9.7 \times 10^{-3}$	$7.0 \times 10^{-8}$	Present work
C15 ZrCr <sub>2</sub> H <sub>3.3</sub>	0.145		[5]

increase in  $N_d(E_F)$  with increasing H content may be expected if the Fermi level lies below a peak in the density of electron states.

The measured relaxation rates at  $T > 300$  K are also dominated by the electronic contribution, since  $T_1^{-1}$  increases with increasing temperature (figures 1 and 2), whereas  $T_{1d}^{-1}$  is expected to decrease in this region. However, for both compounds the values of  $T_1^{-1}$  at  $T > 300$  K are considerably higher than those obtained from the linear extrapolation of the low-temperature  $T_{1e}^{-1}(T)$  results. Moreover, the high-temperature  $T_1^{-1}(T)$  data show a slight upward curvature. The observed temperature dependence of  $(T_{1e}T)^{-1}$  may result from a rapid variation in  $N_d(E)$  near the Fermi level [10]. In this case the electronic contribution to the relaxation rate is given by [10]

$$(T_{1e}T)^{-1} = C + BT^2. \quad (6)$$

We show in table 1 the values of  $B$  resulting from the fit of equation (6) to the relaxation rate data in both the low-temperature and the high-temperature regions.

The motional contribution to the relaxation rate is then evaluated as  $T_{1d}^{-1} = T_1^{-1} - T_{1e}^{-1}$ , where  $T_{1e}^{-1}$  is given by equation (6). Figures 4 and 5 show the motional contributions to  $T_1^{-1}$  in ZrCr<sub>2</sub>H<sub>0.2</sub> and ZrCr<sub>2</sub>H<sub>0.5</sub> as functions of reciprocal temperature. The data at  $\omega/2\pi = 90$  MHz are not shown, since the motional contribution  $T_{1d}^{-1}$  at this frequency is too small to be analysed in detail. If  $\tau_d$  follows the Arrhenius relation

$$\tau_d = \tau_{d0} \exp(E_a/k_B T) \quad (7)$$

where  $E_a$  is the activation energy for hydrogen diffusion, then according to equations (4) and (5) a plot of  $\log T_{1d}^{-1}$  versus  $T^{-1}$  is expected to be linear in the fast-diffusion and slow-diffusion limits with the slopes  $E_a/k_B$  and  $-E_a/k_B$ , respectively. However, for both ZrCr<sub>2</sub>H<sub>x</sub> samples the low-temperature slope of the  $\log T_{1d}^{-1}$  versus  $T^{-1}$  plot appears to be less steep than the high-temperature slope (figures 4 and 5). Moreover, the frequency dependence of  $T_{1d}^{-1}$  at low temperatures is much weaker than  $\omega^{-2}$ . These features can be accounted for by the model employing a distribution of  $\tau_d$  (or  $E_a$ ) values [11–13]. In this case the motional contribution to  $T_1^{-1}$  may be written as

$$T_{1d}^{-1} = \int T_{1d}^{-1}(E_a)G(E_a)dE_a \quad (8)$$

where  $G(E_a)$  is the normalized distribution function of  $E_a$  values, and  $T_{1d}^{-1}(E_a)$  is defined by equations (2) and (7).

We have described our proton relaxation data in terms of the model using a Gaussian distribution function  $G(E_a)$ . The values of  $M_2$ ,  $\tau_{d0}$ , the average activation energy  $\bar{E}_a$  and the distribution width  $\Delta E_a$  at half-maximum are varied until the best fit to the  $T_{1d}^{-1}(T)$  data

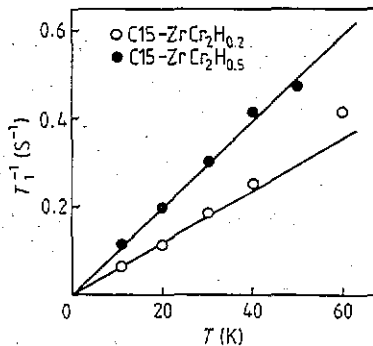


Figure 3. Low-temperature part of the temperature dependences of the proton spin-lattice relaxation rate in  $ZrCr_2H_{0.2}$  and  $ZrCr_2H_{0.5}$  at 90 MHz.

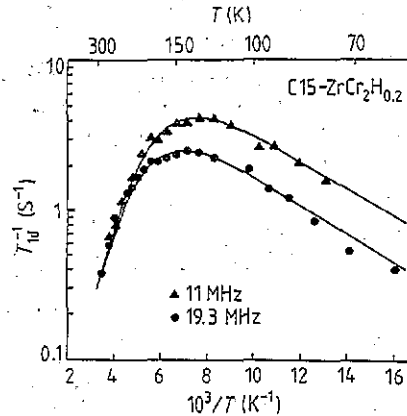


Figure 4. Motional contributions to the proton spin-lattice relaxation rate in  $ZrCr_2H_{0.2}$  at 11 and 19.3 MHz as functions of reciprocal temperature. The full curves represent the fit of the  $E_a$  distribution model to the data (see text for details).

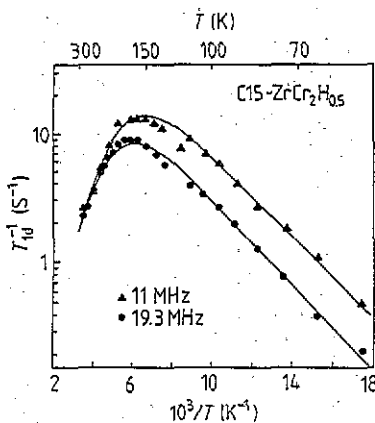


Figure 5. Motional contributions to the proton spin-lattice relaxation rate in  $ZrCr_2H_{0.5}$  at 11 and 19.3 MHz as functions of reciprocal temperature. The full curves represent the fit of the  $E_a$  distribution model to the data (see text for details).

Table 2. Parameters resulting from the fit of the model using a Gaussian distribution of activation energies to the proton spin-lattice relaxation data.

Sample	$M_2$ ( $s^{-2}$ )	$\bar{E}_a$ (meV)	$\Delta E_a$ (meV)	$\tau_{d0}$ (s)
C15 $ZrCr_2H_{0.2}$	$6.8 \times 10^8$	81	28	$7.0 \times 10^{-12}$
C15 $ZrCr_2H_{0.5}$	$1.7 \times 10^9$	84	21	$1.8 \times 10^{-11}$

at two frequencies is obtained. The results of this fitting procedure are shown as full curves in figures 4 and 5, and the fitting parameters are presented in table 2. As can be seen from figures 4 and 5, the model gives a satisfactory description of the  $T_{1d}^{-1}(T)$  data at two frequencies with the same set of parameters.

In table 3 we compare the values of  $\bar{E}_a$  derived from proton NMR measurements in several ternary and binary metal-hydrogen systems with low and intermediate hydrogen

concentrations. The values of  $\bar{E}_a$  for hydrogen in  $\text{ZrCr}_2\text{H}_x$  ( $x = 0.2$  and  $0.5$ ) are of the order of those for  $\alpha\text{-VH}_x$ , being lower than in the other intermetallic-based systems studied. The average activation energy in  $\text{ZrCr}_2\text{H}_x$  strongly increases with increasing  $x$ . This becomes evident if the  $\bar{E}_a$ -values for  $x = 0.2$  and  $0.5$  are compared with that for the concentrated hydride C15  $\text{ZrCr}_2\text{H}_{3.3}$  ( $E_a \simeq 270$  meV) [5]. The origin of such a strong concentration dependence of the activation energy in C15  $\text{ZrCr}_2\text{H}_x$  remains to be elucidated.

Table 3. Comparison of activation energies for hydrogen motion derived from proton NMR measurements in several metal-hydrogen systems.

Sample	Host structure (type)	$\bar{E}_a$ (meV)	Reference
$\text{ZrCr}_2\text{H}_{0.2}$	Cubic (C15)	81	Present work
$\text{ZrCr}_2\text{H}_{0.5}$	Cubic (C15)	84	Present work
$\text{TiCr}_{1.8}\text{H}_{0.55}$	Cubic (C15)	190	[1]
$\text{HfV}_2\text{H}_{0.5}$	Cubic (C15)	220	[14]
$\text{ZrV}_2\text{H}_{1.1}$	Cubic (C15)	160	[14]
$\text{TaV}_2\text{H}_{0.22}$	Cubic (C15)	230	[3]
$\text{TiCr}_{1.9}\text{H}_{0.63}$	Hexagonal (C14)	218	[1]
$\text{ZrBe}_2\text{H}_{1.4}$	Hexagonal (C32)	180	[15]
$\alpha\text{-PdH}_{0.70}$	Cubic (FCC)	228	[16]
$\beta\text{-TiH}_{0.57}$	Cubic (BCC)	155	[17]
$\alpha\text{-VH}_{0.17}$	Cubic (BCC)	87	[17]

Low  $E_a$ -values correspond to high H mobilities down to low  $T$ . For example, the average H hopping rate in  $\text{ZrCr}_2\text{H}_{0.2}$  at 130 K is estimated to be  $5.6 \times 10^7$  s<sup>-1</sup> (in the framework of the BPP model) and  $7.4 \times 10^7$  s<sup>-1</sup> (from calculations in [8] for the FCC lattice). Using the latter value of the hopping rate and assuming that the jump length is 1.2 Å (the distance between nearest-neighbour  $g$  sites) we obtain the following estimate of the hydrogen diffusion coefficient  $D$  for  $\text{ZrCr}_2\text{H}_{0.2}$ :  $D(130 \text{ K}) \simeq 2 \times 10^{-9}$  cm<sup>2</sup> s<sup>-1</sup>. This value is higher than for the other metal-hydrogen systems with comparable  $x$  at the same temperature. (Note that  $\alpha$ -phases of  $\text{VH}_x$ ,  $\text{NbH}_x$  and  $\text{TaH}_x$  having higher  $D$  values [18] can contain only extremely small amounts of hydrogen at 130 K;  $x < 10^{-3}$ .)

The above estimate of  $D$  in  $\text{ZrCr}_2\text{H}_x$  is based on the assumption that the observed relaxation rate maximum is due to the long-range diffusion. In a number of metal-hydrogen systems including the C15-type  $\text{TaV}_2\text{H}_x(\text{D}_x)$  [2, 3] and HCP  $\alpha\text{-ScH}_x$  [19], hydrogen shows fast localized motion at low temperatures coexisting with much slower long-range diffusion. This localized motion is responsible for the additional low-temperature peak of the relaxation rate. In all the cases studied, the localized motion averages out only a small part of the rigid-lattice dipolar interaction, and complete line narrowing occurs in the region of the high-temperature peak. For both  $\text{ZrCr}_2\text{H}_{0.2}$  and  $\text{ZrCr}_2\text{H}_{0.5}$  the complete proton NMR line narrowing is observed at temperatures as low as 78 K. This may be taken as evidence of the long-range nature of hydrogen motion responsible for the  $T_1^{-1}$  maximum in  $\text{ZrCr}_2\text{H}_x$ . In fact, such kinds of localized motion as hopping between a pair of nearest-neighbour interstitials or between displaced sites within an interstitial cannot average the dipole-dipole interaction effectively, since in  $\text{ZrCr}_2\text{H}_{0.2}$  and  $\text{ZrCr}_2\text{H}_{0.5}$  the rigid-lattice proton linewidth is determined by H-H interactions, and the hydrogen concentration is rather low. Thus the hydrogen motion in  $\text{ZrCr}_2\text{H}_x$  should be at least more extended in space than simple hopping between a pair of sites.

The values of the relative distribution width  $\Delta E_a/\bar{E}_a$  for  $\text{ZrCr}_2\text{H}_x$  appear to be rather large:  $\Delta E_a/\bar{E}_a = 0.35$  and  $0.25$  for  $x = 0.2$  and  $0.5$ , respectively. These values are of

the same order of magnitude as those obtained for hydrogen motion in random BCC alloys [20, 21], being even higher than for the amorphous  $Zr_3RhH_{3.5}$  system [13]. However, in contrast with disordered alloys where hydrogen occupies a number of inequivalent sites, H atoms in  $C15 ZrCr_2H_x$  are known to occupy only the equivalent  $g$  sites. Thus, the origin of the broad distribution of  $E_a$  in  $ZrCr_2H_x$  is not quite clear. High values of  $\Delta E_a/\bar{E}_a$  derived from the fit may indicate that the picture of hydrogen motion is in fact more complex than that defined by the simple model with a Gaussian distribution. As in the other Laves-phase hydrides [2, 3, 14, 22], one may expect the coexistence of two types of H motion with different frequency scales. The presence of a second type of H motion (e.g. some kind of localized motion in addition to the long-range diffusion) is expected to result in

- (i) a reduction in the maximum  $T_{1d}^{-1}$ -value and
- (ii) a decrease in the low-temperature slope of the  $\log T_{1d}^{-1}$  versus  $T^{-1}$  plot.

Feature (i) is consistent with the fact that the  $M_2$ -values obtained from the fit (table 2) appear to be lower than those calculated for random  $g$ -site occupation restricted by blocking effects ( $1.11 \times 10^9 \text{ s}^{-2}$  and  $2.67 \times 10^9 \text{ s}^{-2}$  for  $x = 0.2$  and  $0.5$ , respectively). On the other hand, the values of  $\bar{E}_a$  for long-range diffusion are expected to be nearly unchanged, since they are determined mainly by the  $T_{1d}^{-1}(T)$  data above  $T_{\max}$  [22]. For  $C15 ZrCr_2H_x$ , however, there is no direct experimental evidence of the presence of a second type of H motion (such as an additional  $T_1^{-1}$  peak [2, 3] or a break in the low-temperature slope of the  $\log T_{1d}^{-1}$  versus  $T^{-1}$  plot [14, 22]). Therefore in our analysis we have used the simplest model which can give a reasonable description of the experimental data.

#### 4. Conclusions

Measurements of the proton spin-lattice relaxation rates in C15-type compounds  $ZrCr_2H_x$  ( $x = 0.2$  and  $0.5$ ) have revealed the extremely high mobility of hydrogen down to low temperatures. For these samples the temperatures of the  $T_1^{-1}$  maximum ( $T_{\max} \simeq 130$  and  $160 \text{ K}$  at  $\omega/2\pi = 11 \text{ MHz}$  for  $x = 0.2$  and  $0.5$ , respectively) are lower than for the other metal-hydrogen systems with comparable  $x$ , and complete motional narrowing of proton NMR lines is observed down to  $78 \text{ K}$ . The latter fact is consistent with a long-range type of hydrogen motion. The origin of such high hydrogen mobility in  $C15 ZrCr_2$  remains to be elucidated.

The experimental relaxation rate data can be reasonably described in terms of the BPP model with a Gaussian distribution of activation energies. Both the average activation energy  $\bar{E}_a$  and  $T_{\max}$  increase with increasing hydrogen content. The distribution width  $\Delta E_a$  for  $ZrCr_2H_x$  with low  $x$  is found to be rather large,  $\Delta E_a/\bar{E}_a$  being of the order of  $0.25$ – $0.35$ . This may indicate that for  $ZrCr_2H_x$  the picture of hydrogen motion is in fact more complex than that defined by the simple model with a Gaussian distribution.

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