A pulsed-field-gradient NMR study of hydrogen diffusion in the Laves-phase compounds $ZrCr_2H_x$

W Renz, G Majer, A V Skripov† and A Seeger

Max-Planck-Institut für Metallforschung, Institut für Physik, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

Abstract. Hydrogen diffusivities D in C14-$ZrCr_2H_{0.4}$ and C15-$ZrCr_2H_x$ ($0.2 \leqslant x \leqslant 0.5$) have been measured by means of pulsed-field-gradient nuclear magnetic resonance over the temperature range 130–430 K. In all the samples studied the temperature dependence of D follows an Arrhenius law above 200 K but shows marked deviations from Arrhenius behaviour below about 180 K. This suggests that different diffusion mechanisms dominate at high and low temperatures. The jump length of H atoms estimated by comparing $D(T)$ and the proton spin–lattice relaxation rates appears to be greater than the closest distance between tetrahedral [Zr_2Cr_2] sites occupied by hydrogen in these compounds. A diffusion model that considers jumps between next-nearest-neighbour [Zr_2Cr_2] sites via metastable [$ZrCr_3$] sites is discussed.

1. Introduction

The Laves-phase intermetallic compound $ZrCr_2$, which may exist in two modifications with related but different crystal structures (hexagonal C14 or cubic C15), absorbs large amounts of hydrogen. Recent nuclear-magnetic-resonance (NMR) measurements of the proton spin–lattice relaxation rates Γ_1 have revealed high hydrogen mobility down to low temperatures in both C14- and C15-$ZrCr_2H_x$ with $x \leqslant 0.5$ [1, 2]. The microscopic picture of hydrogen motion in these compounds is not clear yet, however. While the hopping rates of H atoms can in principle be obtained from Γ_1 data using an appropriate relaxation theory [3, 4], it is not possible to deduce the diffusivity and the jump lengths of the hydrogen atoms from spin–lattice relaxation measurements alone. The pulsed-field-gradient (PFG) spin-echo NMR technique [5], on the other hand, permits direct measurement of the diffusivities D. The combination of the two NMR techniques is very suitable to distinguish between long-range diffusion and localized motions of the protons. Coexistence of two types of hydrogen motion with different characteristic frequencies has been found in the related C15 system $TaV_2H_x(D_x)$ [6, 7].

In order to clarify the mechanism of hydrogen motion in $ZrCr_2H_x$ we measured the hydrogen diffusivities of C14-$ZrCr_2H_{0.4}$ and C15-$ZrCr_2H_x$ ($x = 0.2, 0.3$ and 0.5) over the temperature range 130–430 K using the PFG NMR technique on the samples previously studied by NMR spin–lattice relaxation measurements [1, 2]. The comparison of Γ_1 and D provides information on the mean jump length d of the hydrogen atoms. The dependence of D on the hydrogen concentration and on the host-metal structure may clarify the role of site occupation in the process of hydrogen diffusion.

† Alexander von Humboldt research fellow. Permanent address: Institute of Metal Physics, Urals Branch of the Academy of Sciences, Ekaterinburg 620219, Russia.

2. Experimental details

The preparation and characterization of the samples are described in earlier papers [1, 2].
For NMR measurements the powdered samples were sealed in quartz tubes under a pressure
of about 0.1 bar of He. According to the x-ray diffraction analysis, all the samples were
single phased and had retained the host-metal structure (C14 or C15) of the corresponding
hydrogen-free materials. The spin–lattice relaxation measurements [1, 2] gave no indications
of a phase separation in $ZrCr_2H_x$ with $x \leqslant 0.5$ down to 11 K. This is consistent with the
phase diagram of the $ZrCr_2$–H(D) system proposed by Somenkov and Irodova [8].

The hydrogen diffusivity was measured with a home-built PFG NMR spectrometer [9, 10]
at the resonance frequency of 37.2 MHz using the stimulated-echo sequence [11]. Typical
operating parameters were gradient pulse lengths of 1.3 ms and diffusion times Δ of
10 ms. In addition to pulsed magnetic field gradients G, which reached up to 25 T m^{-1}
(corresponding to a current of 60 A through the anti-Helmholtz gradient coil), a small time-
independent field gradient was applied for echo stabilization [12]. The diffusivities D were
determined from the dependence of the echo amplitude

$$M(G) = M_0 \exp \left[-D\gamma^2 \left(\int\limits_0^{T_e} \left(\int\limits_0^{t'} G(t'') \, dt'' \right)^2 \, dt' \right) \right] \tag{1}$$

on the field gradient G, where $\gamma = 2.6752 \times 10^8$ rad s^{-1} T^{-1} denotes the gyromagnetic ratio
of the proton and T_e the time between the first RF pulse and the spin echo. The deviations
from the rectangular shape of the gradient pulses were taken into account by measuring the
time dependence of the current through the gradient coil and evaluating the integrals in (1)
numerically.

3. Results and discussion

The results of the hydrogen diffusivity measurements in $ZrCr_2H_x$ are summarized in figures
1 and 2. In the entire temperature range covered in the present work (430 K $\geqslant T \geqslant$ 130 K)
D lies well above 10^{-13} m^2 s^{-1} in all samples. This indicates that hydrogen in $ZrCr_2H_x$
retains high *long-range* diffusivity down to low temperatures. In no other metal–hydrogen
system with comparable hydrogen concentration has such a high diffusivity at 130 K been
previously observed.

As may be seen from figures 1 and 2, below about 200 K the temperature dependence of
D deviates markedly from the Arrhenius behaviour. These deviations are more pronounced
in the C15 samples than in the C14 sample. The effective activation enthalpies H_a and
the pre-exponential factors D_0 obtained by fitting Arrhenius laws to the diffusivities above
200 K are presented in table 1. Below 180 K the effective activation enthalpy deduced from
the slope of an Arrhenius plot of $D(T)$ is of the order of 60 meV for the C15 compounds
and about 80 meV for the C14 sample. Similar changes in the slope of Arrhenius plots of
$D(T)$ were earlier found for α-NbH$_x$ and α-TaH$_x$ [13–16].

Figure 3 shows the diffusion data for C15-$ZrCr_2H_x$ ($x = 0.2, 0.3$, and 0.5) and C14-
$ZrCr_2H_{0.4}$ in the low-temperature range (200 K $\geqslant T \geqslant$ 130 K). It is evident that in the
C15 compounds the hydrogen diffusivity decreases with increasing x at low temperatures.
Below 180 K the D-values in C15-$ZrCr_2H_x$ are considerably higher than those in C14-
$ZrCr_2H_{0.4}$. We conclude from this that the C15 structure favours the occurrence of high
hydrogen diffusivities at low temperatures. Similar trends were found in proton spin-
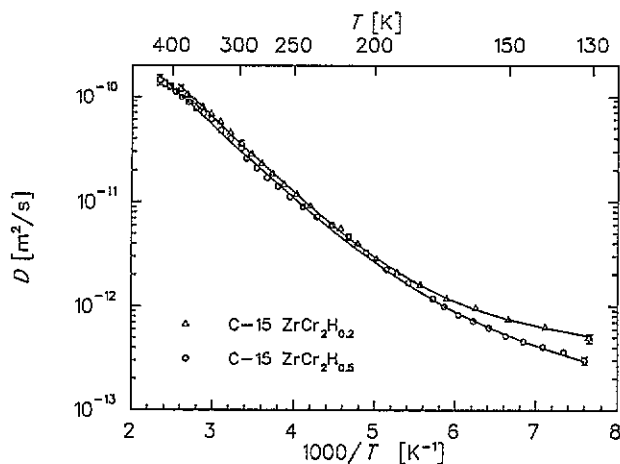
Figure 1. Temperature dependence of hydrogen diffusivity in C15-ZrCr₂H$_{0.2}$ (△) and C15-ZrCr₂H$_{0.5}$ (○) measured by PFG NMR. The solid lines represent the fits of equation (2) to the data with parameters given in table 1.
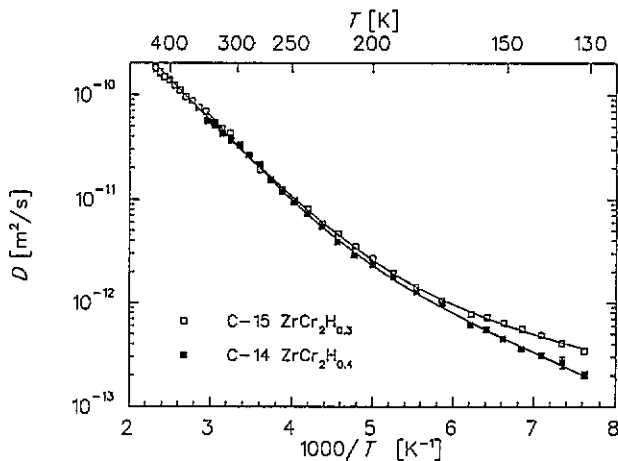
Figure 2. Temperature dependence of hydrogen diffusivity in C15-ZrCr₂H$_{0.3}$ (□) and C14-ZrCr₂H$_{0.4}$ (■) measured by PFG NMR. The solid lines represent the fits of equation (2) to the data with parameters given in table 1.

relaxation measurements [17] on the related system TiCr$_{1.8}$H$_x$, which exists in C14 and C15 modifications, too.

The statistical errors in the present PFG NMR experiments are well below 5%. The accuracy of the experiments is known to be affected by the presence of background magnetic field gradients arising from the distribution of demagnetizing fields over the volume of powdered metallic samples [18]. We have estimated the mean square value of these background gradients from the decay of the spin-echo signal in the absence of any applied field gradient. For different samples this value varies between 1.3 and 1.8 T m⁻¹. This results in an upper limit for a systematic error in D of about 4% at 200 K. At higher temperatures (and therefore higher D-values) the random background gradients may affect the accuracy of the D-values more severely.

In the entire temperature range studied the behaviour of $D(T)$ for ZrCr₂H$_x$ can be

Table 1. Parameters of hydrogen diffusion in C14-ZrCr$_2$H$_{0.4}$ and C15-ZrCr$_2$H$_x$ ($x = 0.2, 0.3$ and 0.5) as deduced from PFG NMR measurements. D_0 and H_a were obtained by fitting a single Arrhenius term to the PFG results above 200 K. The sum of two Arrhenius terms with the parameters D_{01}, H_{a1}, D_{02} and H_{a2} (cf. (2)) satisfactorily describes the diffusivity over the entire temperature range. Estimated uncertainties are ±5% in activation enthalpies H_{aj}, and ±20% in pre-exponential factors D_{0j}.

Sample	D_0 (10^{-8} m^2 s^{-1})	H_a (meV)	D_{01} (10^{-8} m^2 s^{-1})	H_{a1} (meV)	D_{02} (10^{-12} m^2 s^{-1})	H_{a2} (meV)
C15-ZrCr$_2$H$_{0.2}$	0.64	133	1.1	148	3.1	21
C15-ZrCr$_2$H$_{0.3}$	0.78	141	1.3	157	11.2	39
C15-ZrCr$_2$H$_{0.5}$	0.62	137	0.8	146	8.5	39
C14-ZrCr$_2$H$_{0.4}$	0.82	144	3.6	186	77.2	68
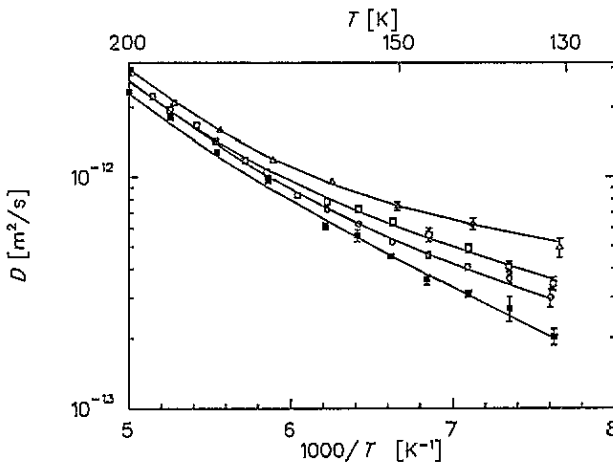
Figure 3. Comparison of temperature dependence of hydrogen diffusivity below 200 K in C15-ZrCr$_2$H$_x$ ($x = 0.2$ (△), $x = 0.3$ (□), $x = 0.5$ (○)) and C14-ZrCr$_2$H$_x$ ($x = 0.4$ (■)). The solid lines represent the fits of equation (2) to the data with parameters given in table 1.

satisfactorily described by the sum of two Arrhenius terms,

$$D = D_{01} \exp(-H_{a1}/k_B T) + D_{02} \exp(-H_{a2}/k_B T). \qquad (2)$$

The fits of (2) to the present measurements are shown as solid lines in figures 1 and 2; the fit parameters are listed in table 1. The temperature dependence (2) is expected if the long-range diffusion proceeds by two mechanisms operating in parallel, and their relative contributions depend markedly on temperature.

In the original analysis of the proton spin–lattice relaxation data on ZrCr$_2$H$_x$ [2] the possibility of changes in the effective activation enthalpy with temperature was not considered. Rather, the Γ_1 results were analysed in terms of Gaussian distributions of activation enthalpies. These distributions came out much wider than could be justified for crystalline compounds. This led to the conclusion [2] that an adequate description of hydrogen motion in ZrCr$_2$H$_x$ requires a more complex model than a Gaussian distribution of activation enthalpies. The present results suggest that part of the observed asymmetry of the log Γ_1 against T^{-1} plots is due to the deviations from the Arrhenius behaviour of $D(T)$. A certain distribution of hydrogen hopping rates, though much narrower than the original one, is nevertheless necessary in order to account for the weak frequency dependence of Γ_1

observed at low temperatures.

Comparison of the measured D-values with the results of the proton Γ_1 measurements on the same sample allows us to estimate the jump length d of the hydrogen atoms. Such an analysis has been previously applied to dihydrides of Ti [18] and Zr [19] and to α-phases of NbH$_x$ and TaH$_x$ [15, 16, 20]. The relationship between D as measured by PFG NMR, d and the mean dwell time τ_d of hydrogen at an interstitial site is given by

$$D = \frac{f^{\mathrm{T}}d^2}{6\tau_d} \tag{3}$$

where f^{T} denotes the tracer correlation factor [21]. For interstitial diffusion in ZrCr$_2$H$_x$ with $x \leqslant 0.5$ we may assume $f^{\mathrm{T}} = 1$, since less than 5% of all tetrahedral sites are occupied by hydrogen. The value of τ_d at the temperature of the relaxation rate maximum, T_{max}, can be estimated from $\tau_d = C/\omega$, where $\omega/2\pi$ is the resonance frequency for protons and C is a constant of the order of unity whose exact value depends on the model used for the calculation of pair correlation functions determining the proton relaxation rate. The simplest approximation, the so-called Bloembergen–Purcell–Pound (BPP) model [22], gives $C = 1.23$ if only hydrogen–hydrogen interactions are taken into account. Lattice-specific Monte Carlo calculations of the relaxation rate are available only for jumps between nearest-neighbour sites on simple cubic, BCC and FCC hydrogen sublattices [23] and for jumps between third-nearest-neighbour sites on a simple cubic hydrogen sublattice [18]. The hydrogen sublattice in the Laves-phase compounds is much more complex [24], however. In order to compare the predictions of the liquid-like BPP model with lattice-specific calculations we have used the Monte Carlo result $C \simeq 0.93$ [23] for the FCC lattice which reflects the general symmetry of the C15 structure. The results of the estimates of d at T_{max} based on (3) are summarized in table 2.

Table 2. Hydrogen jump lengths d estimated from measurements of the H diffusivity, D, and the proton spin–lattice relaxation rate [1, 2] on the same samples. T_{max} is the temperature of the relaxation rate maximum at $\omega/2\pi = 19.3$ MHz. d-values were obtained from the BPP model [22] and from the Monte Carlo (MC) calculations [23] for the FCC lattice.

Sample	T_{max} (K)	$D(T_{max})$ (10^{-13} m^2 s^{-1})	d (10^{-10} m) BPP	MC
C15-ZrCr$_2$H$_{0.2}$	140	6.3	1.95	1.70
C15-ZrCr$_2$H$_{0.3}$	167	9.3	2.38	2.07
C15-ZrCr$_2$H$_{0.5}$	170	10.0	2.46	2.14
C14-ZrCr$_2$H$_{0.4}$	175	11.2	2.61	2.27

In C15-ZrCr$_2$H$_x$ hydrogen is known to occupy the so-called g sites, i.e. tetrahedral interstitial sites surrounded by two Zr and two Cr atoms [8]. Each g site has three nearest-neighbour (two of them at a distance of $0.152a$ and one at $0.181a$) and eight next-nearest-neighbour g sites at a distance of $0.265a$, where a is the cubic lattice parameter. For C15-ZrCr$_2$H$_{0.5}$ these distances are equal to 1.10, 1.31 and 1.93×10^{-10} m, respectively. As can be seen from table 2, for all the C15 samples the estimated values of d are considerably longer than the distance between the nearest-neighbour tetrahedral sites available for hydrogen atoms. In order to actually test whether longer-range hops are involved in the process of hydrogen diffusion, the correlation functions have to be calculated on the basis of such longer hops on the hydrogen sublattice in ZrCr$_2$H$_x$. However, the difference between the

C-values of the BPP model, that disregards the discrete lattice structure, and the lattice-specific calculations is rather small for the hydrogen concentrations studied in the present work [23]. The d-values obtained by either one of the two models are close to those found from the quasielastic neutron-scattering experiments in the related C15 compounds $ZrV_2H_{2.9}$ ($d = (2.36 \pm 0.07) \times 10^{-10}$ m) [25] and $HfV_2H_{3.3}$ ($d = (2.0\text{--}2.5) \times 10^{-10}$ m) [26]. This meets the expectation that a common mechanism of hydrogen diffusion occurs in the C15 compounds. A jump length of $d \simeq 2 \times 10^{-10}$ m allows us to conclude that the most frequent diffusion paths lead to jumps between next-nearest-neighbour g sites at the distance of $0.265a$. This suggests that the tetrahedral e interstices, formed by one Zr and three Cr atoms, play an important role in the diffusion process. Each g site has one nearest-neighbour e site at a distance of $0.152a$ that forms a link to its three next-nearest-neighbour g sites (cf. figure 4). Although in $ZrCr_2H_x$ no evidence for hydrogen location on e sites has been found, the transitions between next-nearest-neighbour g sites are likely to occur via this metastable site. Results deduced from Γ_1 studies of hydrogen in HfV_2H_x and ZrV_2H_x [27, 28] suggest that a path which includes the e sites provides a lower barrier height for hydrogen diffusion. In these systems hydrogen atoms start to occupy e sites at high hydrogen concentrations ($x \geqslant 3$), resulting in an increased hydrogen diffusivity and a reduced effective activation enthalpy H_a.
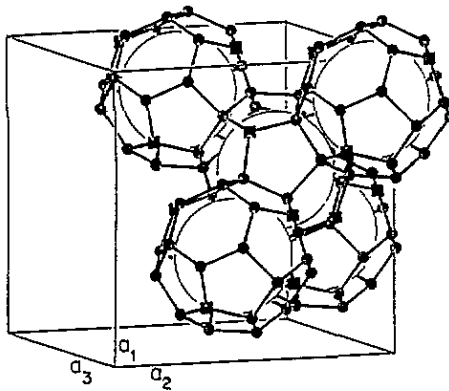

Figure 4. Different interstitial sites in C15-$ZrCr_2H_x$: g sites (○) and e sites (■). The large open circles represent Zr atoms (from [24]).

There is no direct information on the positions occupied by hydrogen atoms in C14-$ZrCr_2H_x$. It is expected that only tetrahedral interstices formed by two Zr and two Cr atoms are occupied. This is consistent with neutron diffraction experiments on the related C14 compound $ZrMn_2D_3$ [29]. However, in contrast to the C15 structure, where all $[Zr_2Cr_2]$ interstices are equivalent, in the C14 structure there are four inequivalent types of $[Zr_2Cr_2]$ site (named h_1, h_2, k and l) [30]. The distance between the nearest-neighbour $[Zr_2Cr_2]$ sites in the C14 structure is nearly the same as in the C15 structure. Thus the estimated d-value for C14-$ZrCr_2H_{0.4}$ is also considerably higher than this distance.

From the pre-exponential factors D_{0j} of the contributions to the diffusivity we may calculate an attempt frequency

$$\nu_j^a = \frac{6 \times D_{0j}}{d^2 z} \tag{4}$$

of the underlying diffusion mechanism. In view of the small hydrogen concentrations

we assumed $f^T = 1$ and neglected blocking of occupied sites. z denotes the number of possible jump paths for the hopping hydrogen. For jumps between next-nearest g sites via e sites this number is one. With these assumptions and $d \simeq 2 \times 10^{-10}$m we find for the mechanisms dominating at high temperatures attempt frequencies $\nu_j^a = 1$–2×10^{12} s^{-1}. This is significantly lower than the typical hydrogen vibration frequency $\nu_H \simeq 4 \times 10^{13}$ s^{-1} [31] in Laves-phase hydrides and therefore incompatible with the picture of classical (over-barrier) diffusion jumps. On the other hand, in the so-called adiabatic model of quantum diffusion [32] ν_j^a is expected to be slightly smaller than the Debye frequency of the host metal, $\nu_D \simeq 9 \times 10^{12}$ s^{-1} [31], and not related to the hydrogen vibration frequency. We propose therefore that the hydrogen diffusion in the ZrCr₂Hₓ Laves phase should be discussed in the framework of quantum diffusion [33]. The change in the effective activation enthalpy of $D(T)$ below 200 K can then be understood quite naturally as due to a change in the dominant mechanism from tunnelling between excited states [32] to the phonon-assisted tunnelling between the ground states [34]. Such a change-over has been observed previously for hydrogen diffusion in α-NbHₓ and α-TaHₓ [4, 14–16].

4. Conclusions and outlook

The present pulsed-field-gradient NMR study of hydrogen diffusion in C14- and C15-ZrCr₂Hₓ ($x \leqslant 0.5$) shows that in these compounds hydrogen retains high *long-range* diffusivity down to low temperatures. In the cubic structure C15 the low-temperature diffusivities decrease with increasing x. Below about 180 K the hydrogen diffusivities observed in the C15 structure are significantly higher than those in the hexagonal C14 structure. In all samples studied, below about 200 K the temperature dependence of D shows marked deviations from the Arrhenius behaviour, suggesting a change in the dominant diffusion mechanism. The diffusion data can be interpreted consistently in terms of quantum mechanical mechanisms of diffusion. The change in the effective activation enthalpy below 200 K may be ascribed to the increasing contribution of tunnelling transitions between the ground states, whereas above 200 K the tunnelling occurs between excited states in neighbouring interstices. In all compounds investigated the jump length of H atoms obtained from a combined analysis of the diffusivity and the proton spin–lattice relaxation rate exceeds the distance between the nearest-neighbour tetrahedral interstitial sites considerably. The data are consistent with hydrogen jumps between next-nearest-neighbour tetrahedral sites. Additional information on the mechanisms of hydrogen diffusion in the ZrCr₂Hₓ compounds may be obtained from studies of isotope effects on hydrogen motion. We plan to perform such experiments in the near future.

Acknowledgments

References

[1] Skripov A V, Belyaev M Yu and Stepanov A P 1991 *Solid State Commun.* **78** 909
[2] Skripov A V and Belyaev M Yu 1993 *J. Phys.: Condens. Matter* **5** 4767
[3] Cotts R M 1978 *Hydrogen in Metals I* ed G Alefeld and J Völkl (Berlin: Springer) p 227
[4] Messer R, Blessing A, Dais S, Höpfel D, Majer G, Schmidt C, Seeger A, Zag W and Lässer R 1986 *Z. Phys. Chem., NF* Suppl. H2 61

[5] Stejskal E O and Tanner J E 1965 *J. Chem. Phys.* **42** 288

[6] Skripov A V, Belyaev M Yu, Rychkova S V and Stepanov A P 1989 *J. Phys.: Condens. Matter* **1** 2121

[7] Skripov A V, Rychkova S V, Belyaev M Yu and Stepanov A P 1990 *J. Phys.: Condens. Matter* **2** 7195

[8] Somenkov V A and Irodova A V 1984 *J. Less-Common Met.* **101** 481

[9] Dippel T, Kreuer K D, Hampele M and Rabenau A 1990 *Proc. of the XXV Congress Ampere* ed M Mehring, J U von Schütz and H C Wolf (Stuttgart: Springer) p 424

[10] Dippel T 1992 *Dr. Rer. Nat. Thesis* University of Stuttgart

[11] Tanner J E 1970 *J. Chem. Phys.* **52** 2523

[12] Hrovat M I and Wade C G 1981 *J. Magn. Reson.* **44** 62

[13] Völkl J and Alefeld G 1978 *Hydrogen in Metals I* ed G Alefeld and J Völkl (Berlin: Springer) p 321

[14] Hampele M, Majer G, Messer R and Seeger A 1991 *J. Less-Common Met.* **172–174** 631

[15] Hampele M, Messer R and Seeger A 1989 *Z. Phys. Chem., NF* **164** 879

[16] Majer G, Messer R and Seeger A 1989 *Z. Phys. Chem., NF* **164** 873

[17] Bowman R C, Craft B D, Attalla A and Johnson J R 1983 *Int. J. Hydrogen Energy* **8** 801

[18] Bustard L D, Cotts R M and Seymour E F W 1980 *Phys. Rev.* B **22** 12

[19] Majer G, Renz W, Seeger A and Barnes R G 1993 *Z. Phys. Chem.* **181** 187

[20] Mauger P E, Williams W D and Cotts R M 1981 *J. Phys. Chem. Solids* **42** 821

[21] Bardeen J and Herring C 1952 *Imperfections in Nearly Perfect Crystals* ed W Shockley (New York: Wiley)

[22] Bloembergen N, Purcell E M and Pound R M 1948 *Phys. Rev.* **73** 679

[23] Faux D A, Ross D K and Sholl C A 1986 *J. Phys. C: Solid State Phys.* **19** 4115

[24] Yvon K 1984 *J. Less-Common Met.* **103** 53

Yvon K and Fischer P 1988 *Hydrogen in Intermetallic Compounds I* ed L Schlapbach (Berlin: Springer) p 87

[25] Schönfeld C, Schätzler R and Hempelmann R 1989 *Ber. Bunsenges. Phys. Chem.* **93** 1326

[26] Havill R L, Titman J M, Wright M S and Crouch M A 1989 *Z. Phys. Chem., NF* **164** 1083

[27] Shinar J, Davidov D and Shaltiel D 1984 *Phys. Rev.* B **30** 6331

[28] Skripov A V, Belyaev M Yu, Rychkova S V and Stepanov A P 1991 *J. Phys.: Condens. Matter* **3** 6277

[29] Didisheim J J, Yvon K, Shaltiel D and Fischer P 1979 *Solid State Commun.* **31** 47

[30] Magee C B, Liu J and Lundin C E 1981 *J. Less-Common Met.* **78** 119

[31] Hempelmann R, Richter D, Hartmann O, Karlsson E and Wäppling R 1989 *J. Chem. Phys.* **90** 1935

[32] Emin D, Baskes M I and Wilson W D 1979 *Z. Phys. Chem., NF* **114** 231

[33] Fukai Y 1992 *The Metal–Hydrogen System* (Berlin: Springer) ch 5

[34] Flynn C P and Stoneham A M 1970 *Phys. Rev.* B **1** 3966