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Electrical resistivity of zirconium hydrides and deuterides at high temperatures

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Abstract. Electrical resistivity ρ of zirconium hydrides ZrH_x and deuterides ZrD_x has been measured over the range of hydrogen concentration $0 \leq x < 0.9$ (x : H/Zr or D/Zr) and temperature $700 \text{ K} \leq T \leq 1100 \text{ K}$. It has been found that ρ increases linearly with x in the α phase and exhibits a parabolic change in the β phase, shows almost no difference for H and D in the range $0 \leq x < 0.9$ and deviates from Matthiessen's rule in the α phase. To help discuss the findings, we have made energy band calculations of ZrH_x and computed quantities that are closely related to ρ . The observed change in ρ with x can be explained by assuming that H atoms form independent electron scatterers in the α phase and H atom vacancies additionally form electron scatterers in the β phase. The lack of difference observed in ρ for H and D can be explained by the fact that electron–optical phonon coupling constant obtained from the energy band calculations is much smaller than the electron–acoustic phonon coupling constant. It is difficult to give a reasonable explanation of the deviation from Matthiessen's rule only by the energy band calculation result.

1. Introduction

Metallic zirconium (Zr) can absorb hydrogen (H) up to a concentration x of about two in atomic ratio H/Zr to form Zr hydrides [1]. In this rather wide range of $0 \leq x < 2$ the electrical resistivity ρ of the Zr hydrides may change differently with x depending on the origins of ρ in the Zr–H system. It has been reported that for $1.5 < x < 1.9$ the optical phonon, as well as the acoustic phonon, plays an important role in ρ [2]. However, almost no precise knowledge is available for ρ at small x although there are some reports on ρ in the Zr–H system [3–5] and in the Ti–H system [6], which has similar physical properties to the Zr–H system. In the Pd–H system, the optical phonon has been found to be important for $x < 0.01$ [7] and $x > 0.7$ [8, 9]. In the V–, Nb– and Ta–H systems, on the other hand, measured ρ has been found to show no difference for H and its isotope D up to $x = 0.1$ [10], suggesting a slight contribution of the optical phonon. The purpose of this paper is to estimate the main origin of ρ in the Zr–H system particularly for $0 \leq x < 1$ at high temperatures.

In the present study we first obtain experimentally the temperature–H concentration–resistivity (T – x – ρ) relationship for Zr hydrides (ZrH_x) and deuterides (ZrD_x). We next

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discuss possible origins of ρ in ZrH_x by considering the interaction of electrons with H atoms and with vibrations of H and Zr atoms and by comparing ρ obtained experimentally with ρ resulting from the interaction. The difference in ρ for H and D is made use of to identify the main possible origins. In addition, quantities that are closely related to ρ are computed with the aid of energy band calculations of ZrH_x and are used to help with identifying the main possible origins. In the present study we do not attempt to discuss ρ due to the hopping conduction arising from localization of electrons [11–13] although the band picture is found to give only an incomplete explanation of measured ρ of ZrH_x and the hopping conduction may be a clue to a better explanation.

2. Experiment

Figure 1 shows a schematic illustration of the apparatus used to make *in situ* measurements of ρ of ZrH_x and ZrD_x . The value of ρ was obtained from the voltage drop across and the current through a sample. To measure accurately the current, we applied a sinusoidal current (1 kHz, 1 mA) to a circuit that includes the sample and a resistor (120 Ω , temperature coefficient $5 \times 10^{-5} \text{ K}^{-1}$), and measured the voltage on the resistor. Two lock-in amplifiers were used to pick out two voltages, on the sample and on the resistor, that had the same phase as the applied current. This resulted in eliminating successfully the effect of thermopower generated at contacts between the sample and current leads on it when the sample was heated. We found almost no frequency dependence of the measured voltages between 100 Hz and 100 kHz. The current of 1 mA was small enough not to give any effect on the temperature of the sample.

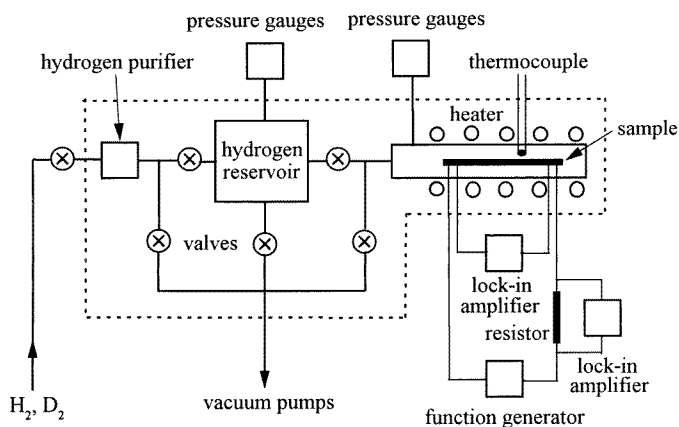


Figure 1. Schematic illustration of the apparatus used to make *in situ* measurements of ρ . The dotted line indicates the part of the apparatus that can be baked out.

H concentration x in the sample was calculated from the difference in H pressures in a chamber (H reservoir in figure 1) before and after admitting H gas to a chamber (sample chamber), which was made of a quartz tube and contained the sample in it. x was corrected for the corresponding H pressures in the sample chamber. Details of the procedure of admitting H and D gases have previously been described [14, 15]. To measure x accurately, we put near the sample a Zr piece (not shown in figure 1) of 120 g and of the same purity as the sample, and increased the difference in the H pressures in the H

reservoir. Temperature T of the sample was measured with a WRe5–WRe26 thermocouple placed near the sample and, by using it, controlled to within ± 0.2 K. The WRe5–WRe26 thermocouple was calibrated by comparing its emf with that of a Pt–PtRh13 thermocouple in a vacuum over the temperature range where the present study was made.

The measurements were made in the range $0 \leq x < 0.9$ and $700 \text{ K} \leq T \leq 1100 \text{ K}$. The dotted line in figure 2 shows the range over which the measurements were made. Phase boundaries in the T – x phase diagram were assumed to be the same for the Zr–H and Zr–D systems. We restricted the measurements to x somewhat less than those at the $\beta/\beta+\delta$ phase boundary because the presence of the δ phase, particularly at relatively low temperatures, caused cracks in the sample and large errors in the values of measured ρ .

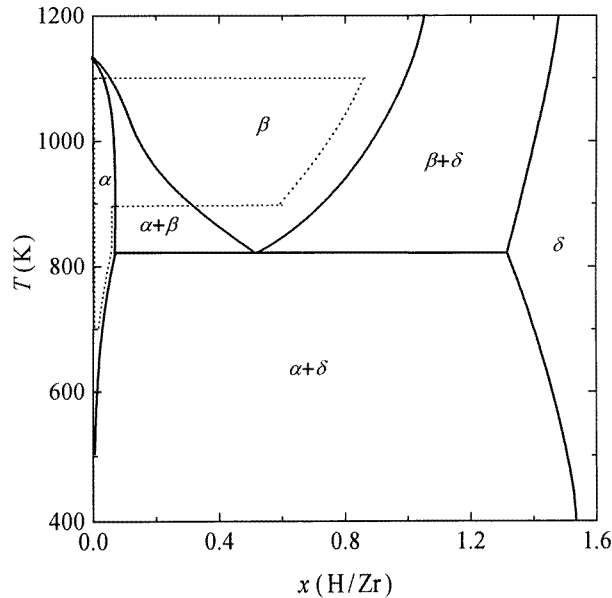


Figure 2. T – x phase diagram of the Zr–H system (adapted from Zurek *et al* [1]). The measurements of ρ were made in the T – x region encircled by the dotted line. The Greek letters indicate the phases.

The samples were polycrystalline Zr wires of 50 mm in length and 1 mm in diameter with a nominal purity of 99.97%. Each sample weighed 0.26 g and had a resistance of 0.1 Ω at room temperature. For the measurements of ρ in the α phase, which extends only to $x \approx 0.06$, we used a longer sample of 150 mm to increase the accuracy of the measurements and folded it into a piece of 50 mm in length to minimize the temperature distribution in the sample. Most experimental error came from measurements of the diameter of the sample. The diameter was not completely uniform along the sample and we made sixteen measurements along it. The resulting error in the area obtained for the cross section of the sample was typically $\pm 2.3\%$. The H and D gases were purified by permeating them through a heated Pd alloy membrane.

Contamination of the sample, particularly by oxidation, caused a serious effect on measured ρ . To minimize the oxidation during the measurements, we heated before the measurements the part of the apparatus indicated by the dashed line in figure 1 to 500 K for 10 h and kept the base pressure of the apparatus in the order of 10^{-8} Pa. After repeated

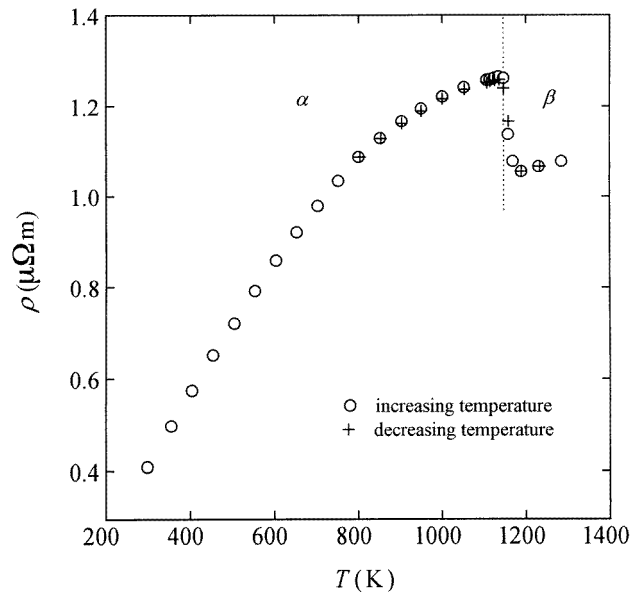


Figure 3. T - ρ relationship for Zr at the twentieth measurement on the same sample. The dotted line indicates the α/β phase transition temperature of Zr.

measurements, we could observe at the α/β transformation temperature 1135 K a sharp change in ρ , which readily becomes less sharp as the sample is contaminated by oxidation. Twenty measurements resulted in a practically identical T - ρ relationship and figure 3 shows the result of the twentieth measurement, which is in agreement with previously reported measurements [16].

3. Results and discussion

3.1. Summary of experimental results

Figure 4(a) shows the x - ρ relationship obtained for H and D at 1050 K. ρ increased as x increased in the α phase of ZrH_x (α - ZrH_x), decreased rapidly in the $\alpha + \beta$ phase and showed a parabolic change in the β phase of ZrH_x (β - ZrH_x). The change in ρ in β - ZrH_x is similar to that reported for β - TiH_x [6]. No difference was found in measured ρ for H and D. The results for 1000 K (figure 4(b)) and 950 K (figure 4(c)) were similar to that for 1050 K.

Figure 5 shows measured ρ of α - ZrH_x and α - ZrD_x at temperatures between 700 K and 1050 K. Values of ρ were found to be almost the same for H and D. We can clearly see from figure 5 a deviation from Matthiessen's rule; $d\rho/dx$ decreased as T increased. The values of ρ at $x = 0$ were slightly different from those corresponding to figure 4(a)-(c) since the measurements were made on a different sample as mentioned in the previous section.

Figure 6 shows the x - ρ relationship obtained for H at temperatures between 900 K and 1100 K. The parabolic change in ρ of β - ZrH_x will be discussed later in detail. Since we did not make measurements on the same sample as used to obtain figure 4(a)-(c), slight differences can be observed between figure 6 and figure 4(a)-(c).

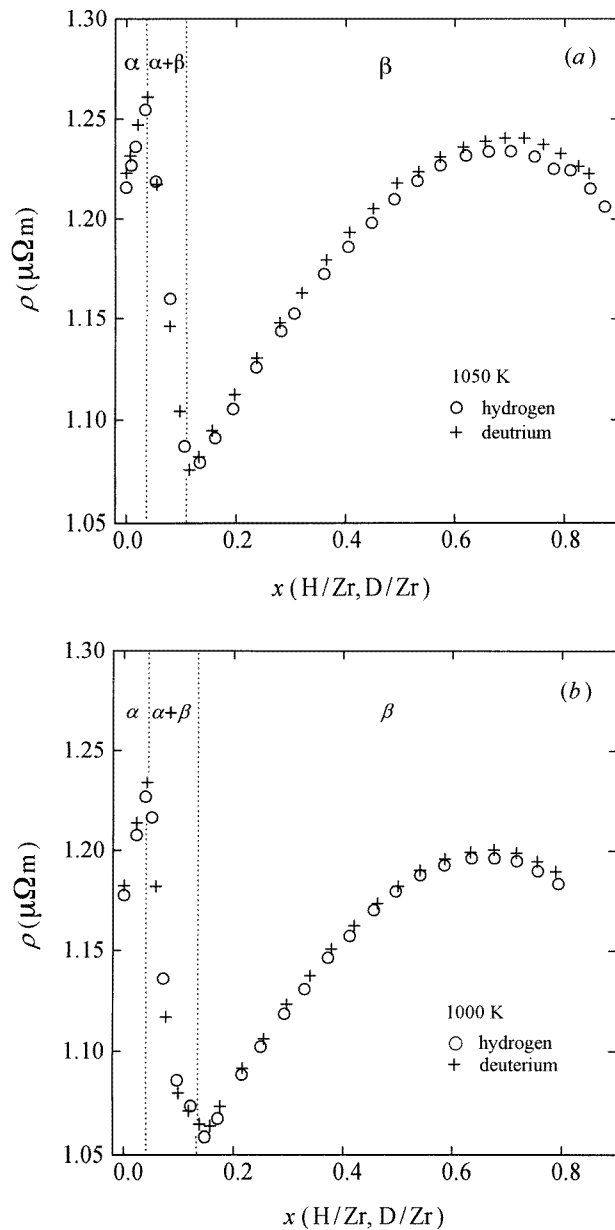


Figure 4. x - ρ relationship obtained for H and D at (a) 1050 K, (b) 1000 K and (c) 950 K. The dotted lines indicate the phase boundaries.

3.2. Possible origins of ρ in the Zr-H system

Any deviation from perfect periodicity in the structure of ZrH_x can cause electrical resistance. A possible origin of ρ is the deviation due to the presence of H atoms in the crystal lattice of Zr. We can assume that Zr and ZrH have perfect crystal lattices and cause no resistance at 0 K. H atoms in ZrH_x , however, cause resistance since most ZrH_x

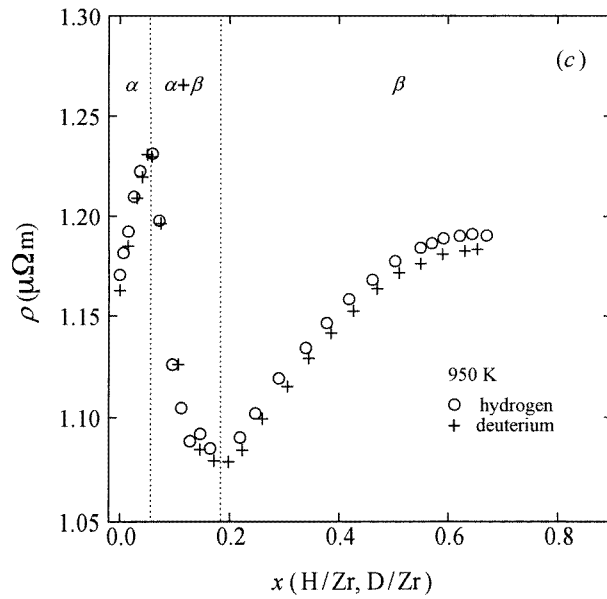
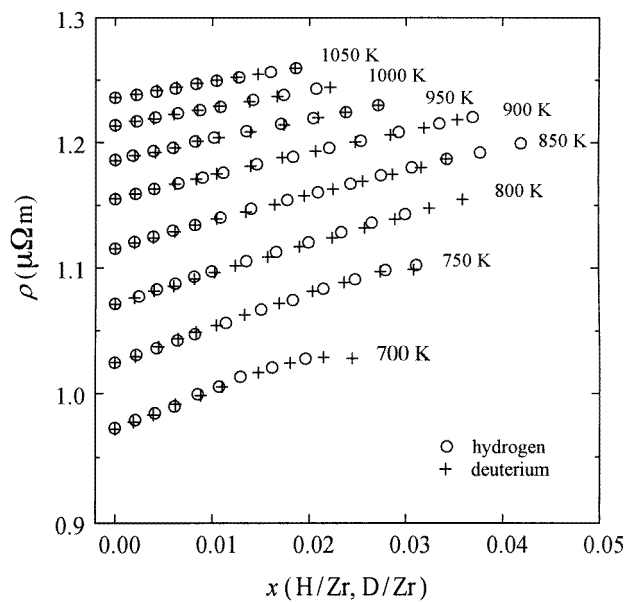


Figure 4. (Continued)

Figure 5. x - ρ relationship for H and D in the α phase at the temperatures shown in the figure.

is nonstoichiometric and H atoms are no longer in a perfectly periodic arrangement. In fact, H atoms are known to occupy randomly the interstitial sites of the crystal lattice of α - and β -Zr [1, 17]. Interstitial H atoms, which we hereafter refer to as H atoms, thus form electron scatterers when x is small and vacant interstitial sites, in addition to the H atoms, form electron scatterers when x approaches unity, as in the case of ρ in alloys [11].

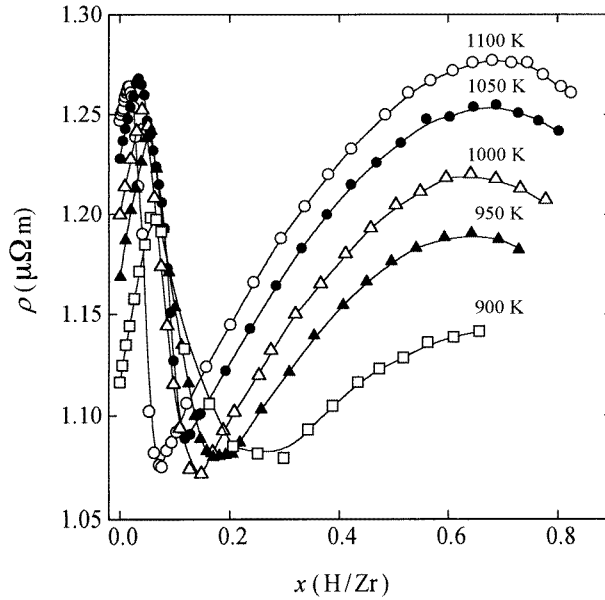


Figure 6. x - ρ relationship for H at the temperatures shown in the figure. The solid lines are only for clarity of the figure.

Another possible origin of ρ is the deviation due to phonons in ZrH_x at finite temperatures. The large difference in the mass of H and Zr atoms allows us to regard the acoustic phonon with the large dispersion as vibration of Zr atoms and the optical phonon with the small dispersion as independent vibration of H atoms. We can therefore apply the Debye model to the vibration of Zr atoms and the Einstein model to that of H atoms. Other possible origins such as grain boundaries and dislocations in the sample will not be considered in the present study in view of the fact that the change in measured ρ was much larger than the difference in ρ in different samples.

We can thus discuss ρ of ZrH_x in terms of three contributions:

$$\rho = \rho_0 + \rho_{\text{H vib}} + \rho_{\text{Zr vib}} \quad (1)$$

where ρ_0 is the residual resistivity due to the presence of H atoms and $\rho_{\text{H vib}}$ and $\rho_{\text{Zr vib}}$ are the resistivities due to the vibrations of H and Zr atoms, respectively. It should be noted that $\rho_{\text{Zr vib}}$ depends on x . This can be seen from the fact that the elastic constants of ZrH_x change with x [18] and characteristics of the acoustic phonon in ZrH_x are closely related to the elastic constants as discussed, e.g. for V, Nb and Ta hydrides and deuterides [19].

3.3. Resistivity of α - ZrH_x and α - ZrD_x

Measured ρ increases linearly with x (figure 5) except at above $x \approx 0.02$ at 700 K, where the $\alpha/\alpha + \delta$ phase boundary seems to have some effect on ρ . The linear increase in ρ corresponds to the linear increase in ρ_0 and implies that each H atom forms an independent electron scatterer. There is no appreciable difference in measured ρ for H and D. This fact, together with the smaller scattering potential of H than of Zr, implies that electrons are scattered mainly from the strain of the Zr lattice induced around H atoms, not from H atoms, as previously suggested for V, Nb and Ta [10]. The induced strain is expected to

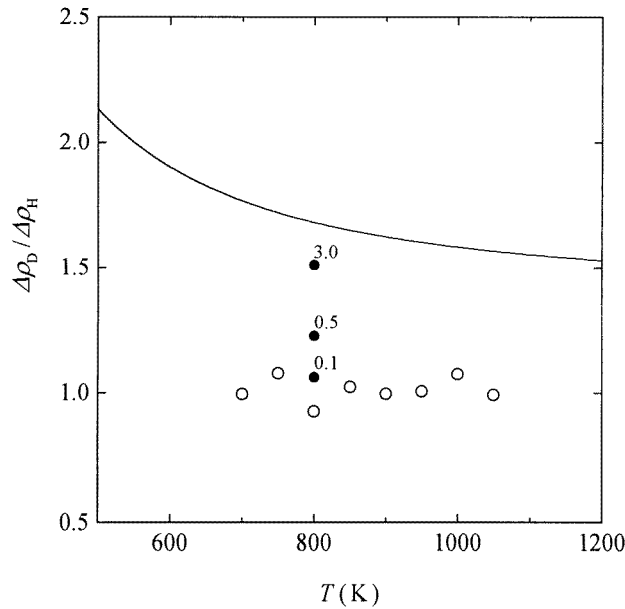


Figure 7. Ratio of the increase in ρ due to D absorption to that due to H absorption in the α phase. The open circles indicate the ratio of the increases for $x = 0 \rightarrow 0.01$; the filled circles indicate the ratio for the values of $\rho_{\text{H vib}}/(\Delta\rho_0 + \Delta\rho_{\text{Zr vib}})$ shown in the figure (see the text for details). The solid line is the ratio computed for equation (2) using $\hbar\omega_{\text{H}} = 2^{1/2}\hbar\omega_{\text{D}} = 0.144$ eV.

be almost the same in ZrH_x and ZrD_x from the fact that H atoms cause only one per cent larger expansion of Pd lattice than D atoms [20], and gives almost the same ρ_0 for H and D.

We next discuss $\rho_{\text{H vib}}$. In $\alpha\text{-ZrH}_x$, H atoms randomly occupy tetrahedral sites of the Zr lattice [1, 17]. Applying the Einstein model to the vibration of H atoms as mentioned above, we can write $\rho_{\text{H vib}}$ as [21]

$$\rho_{\text{H vib}} = A \frac{\hbar\omega}{k_{\text{B}}T} \frac{1}{\exp(\hbar\omega/k_{\text{B}}T) - 1} \frac{1}{1 - \exp(-\hbar\omega/k_{\text{B}}T)} \quad (2)$$

where $\hbar\omega$ is the energy of vibration of H atoms, k_{B} is the Boltzmann constant and A is a constant determined from the magnitude of interaction between electrons and the vibration of H atoms. Using equations (1) and (2) we can estimate the magnitude of $\rho_{\text{H vib}}$ relative to ρ from the difference in increases in ρ , $\Delta\rho_{\text{H}} (= \Delta\rho_0 + \rho_{\text{H vib}} + \Delta\rho_{\text{Zr vib}})$ and $\Delta\rho_{\text{D}} (= \Delta\rho_0 + \rho_{\text{D vib}} + \Delta\rho_{\text{Zr vib}})$, due to the addition of H and D atoms to Zr because $\Delta\rho_0$ and $\Delta\rho_{\text{Zr vib}}$ are the same for H and D. Figure 7 shows the comparison of $\rho_{\text{D vib}}/\rho_{\text{H vib}}$ computed for equation (2) and $\Delta\rho_{\text{D}}/\Delta\rho_{\text{H}}$ obtained from figure 5. The solid line in figure 7 shows $\rho_{\text{D vib}}/\rho_{\text{H vib}}$ computed for equation (2) using the value $\hbar\omega_{\text{H}} = 2^{1/2}\hbar\omega_{\text{D}} = 0.144$ eV [17]. The open circles indicate the values of $\Delta\rho_{\text{D}}/\Delta\rho_{\text{H}}$ for the increases $\Delta\rho_{\text{H}}$ and $\Delta\rho_{\text{D}}$ corresponding to the change $x = 0 \rightarrow 0.01$ in figure 5. Statistical errors in the values of $\Delta\rho_{\text{D}}/\Delta\rho_{\text{H}}$ range from ± 0.03 at 900 K to ± 0.17 at 700 K. From the fact that $\rho_{\text{D vib}}/\rho_{\text{H vib}} > 1.5$ and $\Delta\rho_{\text{D}}/\Delta\rho_{\text{H}} \sim 1$ (figure 7), we can see that $\rho_{\text{H vib}}$ makes only a small contribution to $\Delta\rho_{\text{H}}$. To estimate the contribution we have calculated values of $\Delta\rho_{\text{D}}/\Delta\rho_{\text{H}}$ at 800 K for $\rho_{\text{H vib}}/(\Delta\rho_0 + \Delta\rho_{\text{Zr vib}}) = 0.1, 0.5$ and 3.0 . They are shown in figure 7 by the filled circles with the values of $\rho_{\text{H vib}}/(\Delta\rho_0 + \Delta\rho_{\text{Zr vib}})$ on them. The values of

$\Delta\rho_D/\Delta\rho_H$ obtained experimentally (open circles) compare well with the value calculated for $\rho_{H\text{vib}}/(\Delta\rho_0 + \Delta\rho_{Zr\text{vib}}) = 0.1$, implying that A in equation (2) is small, i.e. the electron–optical phonon interaction is small in $\alpha\text{-ZrH}_x$.

The small contribution of $\rho_{H\text{vib}}$ suggests that a cause of the deviation from Matthiessen’s rule (DMR) observed for $\alpha\text{-ZrH}_x$ is the dependence of $\rho_{Zr\text{vib}}$ on x and T . $d\rho_0/dx$ is unlikely to depend strongly on T because the expansion of the Zr lattice due to H absorption is almost independent of T [22] and the strain around H atoms is therefore unlikely to depend strongly on T . However, it seems that more experimental and theoretical study [11, 23] is needed to discuss in detail the DMR in $\alpha\text{-ZrH}_x$. For example, atomic correlations, i.e. H–H correlations in the present study, may become significant [11] in $\alpha\text{-ZrH}_x$ even at small x because $\alpha/\alpha + \beta$ and $\alpha/\alpha + \delta$ phase boundaries occur at rather small x (figure 2). The strain of the Zr lattice resulting from the H–H correlations forms electron scatterers different from the independent scatterers discussed above, and may lead to the DMR.

Table 1. Values of E_F , $n(E_F)$, $\langle v_F^2 \rangle^{1/2}$ and λ for $\beta\text{-Zr}$ and $\beta\text{-ZrH}$. The values of λ for Zr site and H site correspond to λ_H and λ_{Zr} , respectively, in equation (3).

	E_F (Ryd)	$n(E_F)$ (states Ryd ⁻¹ /cell/spin)	$\langle v_F^2 \rangle^{1/2}$ (m s ⁻¹)	λ
Zr	0.660	10.65	4.50×10^5	0.922
ZrH	0.695	11.04	4.23×10^5	0.050 (H site) 0.659 (Zr site)

3.4. Electron states in $\beta\text{-Zr}$ and $\beta\text{-ZrH}$

To discuss ρ of $\beta\text{-ZrH}_x$, where x is not always small, we have to consider the effect of the presence of H atoms on $\rho_{Zr\text{vib}}$. In this section, quantities that are closely related to ρ and used to discuss it are estimated from energy band calculations of $\beta\text{-Zr}$ and $\beta\text{-ZrH}$.

The electron states are computed by using the augmented plane-wave method [24] with the exchange–correlation potential based on the local density approximation [25]. We use the simplest version of the method because we only need a crude estimate of the quantities. By reproducing the reported electron states of $\alpha\text{-Zr}$ [26, 27] and $\beta\text{-Zr}$ [28], we confirm that the method gives correctness and enough accuracy for the present purpose. In the computation of $\beta\text{-ZrH}$, H atoms are assumed to occupy periodically the tetrahedral site in bcc $\beta\text{-Zr}$ as in $\beta\text{-Ti}$ [17]. We have also made calculations for $0 < x < 1$ using the virtual crystal approximation [11]. All values calculated for $0 < x < 1$ are found to fall between those for $\beta\text{-Zr}$ and $\beta\text{-ZrH}$ as expected and they are not discussed here.

Table 1 lists the result of the computation of the Fermi energy E_F , the density of states $n(E_F)$ at E_F , the square root of the squared average of the Fermi velocity $\langle v_F^2 \rangle^{1/2}$ and the electron–phonon coupling constant λ . Using the result of the energy band calculations, we have computed $\langle v_F^2 \rangle^{1/2}$ from $v_k = (1/\hbar)\partial E/\partial \mathbf{k}$ and λ from $\lambda = n(E_F)\langle I^2 \rangle / (M\langle \omega^2 \rangle)$ [29] where M is the mass of the H or Zr atom, $\langle \omega^2 \rangle$ is the squared average of phonon frequency and $\langle I^2 \rangle$ is the squared average of electron–phonon matrix elements at the Fermi surface and is computed from the phase shift, the partial density of states etc [30], which are obtained in the course of the energy band calculations. Since the mass greatly differs for H and Zr, we can write for ZrH_x [9, 31, 32]

$$\lambda = \frac{n(E_F)\langle I_H^2 \rangle}{M_H\langle \omega_H^2 \rangle} + \frac{n(E_F)\langle I_{Zr}^2 \rangle}{M_{Zr}\langle \omega_{Zr}^2 \rangle} \equiv \lambda_H + \lambda_{Zr}. \quad (3)$$

In the computation of λ , we have used the values $\hbar\langle\omega_{\text{H}}^2\rangle = 0.12$ eV, which is the same as for $\beta\text{-TiH}_x$ [17], and $\hbar\langle\omega_{\text{Zr}}^2\rangle = 0.015$ eV, which we have estimated from the reported value obtained from the inelastic neutron scattering measurement [33]. The values listed in table 1 will be used in the next section to discuss the x dependence of ρ_0 , $\rho_{\text{H vib}}$ and $\rho_{\text{Zr vib}}$ of $\beta\text{-ZrH}_x$.

We here mention the following two points concerning the computation result above. Firstly, all the quantities were computed up to $x = 1$ and for the β phase. At larger x , the β phase transforms to the fct δ phase (figure 2) and the electron states change accordingly. The calculated electron states of ZrH_2 [32] show that ρ_{H} is small in the δ phase as well. Observed ρ in the δ phase, however, indicates a considerable contribution of the optical phonon [2]. In the present study we cannot comment on this discrepancy. Secondly, we should be careful about the applicability of the energy band calculation to the discussion of ρ of ZrH_x . If the mean free path of electrons that participate in ρ becomes comparable to the lattice constant of Zr, then the electrons are in a localized state and the band picture is no longer applicable directly to ρ of ZrH_x [11]. The values of ρ obtained in the present study seem somewhat smaller than those in which the localized electron state plays a major role. The DMR and the decrease in $d\rho/dT$ in Zr at high temperatures (figure 3) observed in the present study, however, suggest invalidation of the applicability of the band picture and necessity to consider, e.g. the hopping conduction mechanism [12, 13].

3.5. Resistivity of $\beta\text{-ZrH}_x$

The residual resistivity ρ_0 can be written as

$$\rho_0 = \frac{3}{2} \frac{1}{e^2 \langle v_{\text{F}}^2 \rangle n(E_{\text{F}}) \tau} \quad (4)$$

where τ is the relaxation time. This is the same equation as given in Ziman [21]. When H atoms and vacant interstitial sites are regarded as electron scatterers as mentioned above, τ can be written as [11]

$$\frac{1}{\tau} = Bx(1-x)n(E_{\text{F}}) \quad (5)$$

where B is a constant. From equations (4) and (5) we see that ρ_0 depends on x through the terms $x(1-x)$ and $\langle v_{\text{F}} \rangle^2$. However, $\langle v_{\text{F}} \rangle^2$ can be regarded as constant for $0 \leq x \leq 1$ because the values of $\langle v_{\text{F}} \rangle^2$ at $x = 0$ and 1 do not differ considerably (table 1) and the E_{F} value can be found from the energy band calculations to lie in the region where the energies of s and d bands do not change considerably for $0 \leq x \leq 1$. We therefore have a parabolic change in ρ_0 :

$$\rho_0 = B'x(1-x) \quad (6)$$

where B' is a constant.

The contribution of $\rho_{\text{H vib}}$ to ρ can be regarded as small because only a small difference is found in measured ρ for H and D (figure 4). The energy band calculation result shows that $\lambda_{\text{H}} \ll \lambda_{\text{Zr}}$ (table 1), supporting the small contribution of $\rho_{\text{H vib}}$ up to $x = 1$. This is the same conclusion as obtained for $\alpha\text{-ZrH}_x$. At larger x , however, we cannot completely exclude possible importance of $\rho_{\text{H vib}}$ as pointed out for ZrH_2 [2]. The optical phonon has been shown to play an important role in ρ for $x > 0.7$ in the Pd-H system as well [8, 9].

We now discuss the contribution of $\rho_{\text{Zr vib}}$ to ρ . At $x = 0$ and 1, ρ consists only of $\rho_{\text{Zr vib}}$ as mentioned above and $\rho_{\text{Zr vib}}$ at $x = 0$ and 1, which we hereafter refer to as $\rho_{\text{Zr vib}}$ and $\rho_{\text{ZrH vib}}$, respectively, have different values (figure 6). However, the difference, which

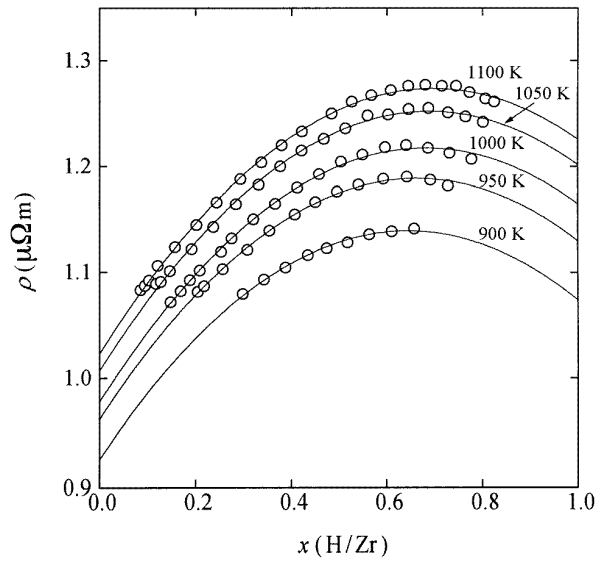


Figure 8. Result of the fit of equation (8) (solid lines) to measured ρ for β -ZrH (open circles). The open circles have been taken from figure 6.

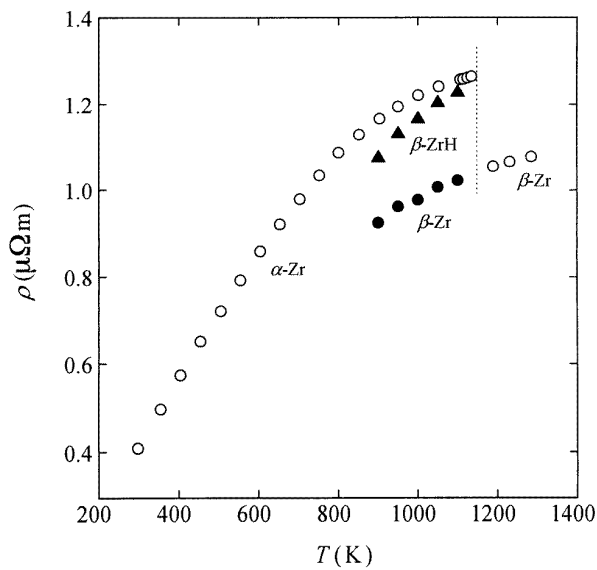


Figure 9. Values of ρ obtained from figure 8 for β -Zr (filled circles) below the α/β phase transition temperature and for β -ZrH (filled triangles) below the $\beta/\beta + \delta$ phase transition temperature. The open circles indicate the measured values taken from figure 1 and the dotted line the α/β phase transition temperature of Zr.

arises from the dependence of E_F , $\langle v_F \rangle$ and λ on x , is not large. We therefore assume a linear change in ρ for $0 \leq x \leq 1$ and have

$$(1 - x)\rho_{Zr \text{ vib}} + x\rho_{ZrH \text{ vib}}. \quad (7)$$

Equation (1) is now written, by using equations (4) and (5), as

$$\rho = B'x(1-x) + (1-x)\rho_{\text{Zr vib}} + x\rho_{\text{ZrH vib}}. \quad (8)$$

Figure 8 shows the result of a fit of equation (8) to measured ρ of $\beta\text{-ZrH}_x$. The fit has first been made for 1100 K with x as an independent variable and with $\rho_{\text{Zr vib}}$, $\rho_{\text{ZrH vib}}$ and B' as parameters and then for other temperatures with $\rho_{\text{Zr vib}}$ and $\rho_{\text{ZrH vib}}$ as parameters and with the value of B' ($= 0.517 \pm 0.012 \mu\Omega \text{ m}$) fixed at the value determined for 1100 K. Statistical errors for the values of $\rho_{\text{Zr vib}}$ and $\rho_{\text{ZrH vib}}$ range from $\pm 0.001 \mu\Omega \text{ m}$ for $\rho_{\text{Zr vib}}$ at 1050 K to $\pm 0.003 \mu\Omega \text{ m}$ for $\rho_{\text{ZrH vib}}$ at 1150 K. The result of the fit is excellent and suggests that the assumption made to obtain equation (6), i.e. periodic arrangement of H atoms in $\beta\text{-ZrH}$, is reasonable.

From the result of the fit in figure 8 we obtain ρ of $\beta\text{-Zr}$ at temperatures below the α/β phase transition (figure 9). The values of ρ of $\beta\text{-Zr}$ obtained in this way (solid circles) are in agreement with those extrapolated from measured ρ (open circles) and tend to decrease with decreasing T like those of $\alpha\text{-Zr}$. This is in contrast to the result reported for $\beta\text{-Ti}$, for which the ρ value does not decrease with decreasing T [6]. A similar result is obtained also for ρ of $\beta\text{-ZrH}$ below the $\beta/\beta + \delta$ phase transition temperature (triangles).

4. Conclusions

We have measured ρ of ZrH_x and ZrD_x and computed the quantities that are closely related to ρ with the help of the energy band calculations of ZrH_x . The linear increase in measured ρ of $\alpha\text{-ZrH}_x$ with x is due to the independent electron scatterers formed by H atoms. The parabolic change in measured ρ of $\beta\text{-ZrH}_x$ is due to the vacant interstitial sites in it as well as to H atoms. The optical phonon does not contribute appreciably to ρ for $0 \leq x < 0.9$, because there is almost no difference in measured ρ and computed λ_{H} is much smaller than λ_{Zr} . We have estimated the values of ρ of $\beta\text{-Zr}$ below the α/β transformation temperature and of $\beta\text{-ZrH}$ below the $\beta/\beta + \delta$ phase transition temperature.

References

- [1] Zurek E, Abriata A, San-Martin A and Manchester F D 1990 *Bull. Alloy Phase Diagrams* **1** 385–95
- [2] Bickel P W and Berlincourt T G 1970 *Phys. Rev. B* **2** 4807–13
- [3] Aladjem A 1996 *Solid State Phenomena (Diffusion and Defect Data B 49–50)* ed F A Lewis and A Aladjem (Switzerland: Scitec Publications) p 281
- [4] Mishima Y, Ishino S and Nakajima S 1968 *J. Nucl. Mater.* **27** 335–44
- [5] Kandasamy K and Surplice N A 1985 *J. Phys. D: Appl. Phys.* **18** 1377–84
- [6] Ames S L and McQuillan A D 1956 *Acta Metall.* **4** 602–10
- [7] Szökefalvi-Nagy A, Huang X Y and Kirchheim R 1987 *J. Phys. F: Met. Phys.* **17** 427–31
- [8] Burger J P 1981 *Metal Hydrides* ed G Bambakidis (New York: Plenum) p 243
- [9] Papaconstantopoulos D A, Klein B M, Economou E N and Boyer L L 1978 *Phys. Rev. B* **17** 141–50
- [10] Watanabe K and Fukai Y 1980 *J. Phys. F: Met. Phys.* **10** 1795–1801
- [11] Rossiter P L 1987 *The Electrical Resistivity of Metals and Alloys* (London: Cambridge University Press) pp 50, 160, 236, 300, 373
- [12] Lee P A and Ramakrishnan T V 1985 *Rev. Mod. Phys.* **57** 287–337
- [13] Mott N F 1990 *Metal–Insulator Transitions* 2nd edn (London: Taylor and Francis) p 45
- [14] Naito S 1983 *J. Chem. Phys.* **79** 3113–20
- [15] Naito S, Yamamoto M and Hashino T 1990 *J. Phys.: Condens. Matter* **2** 1963–70
- [16] Hörz G, Hammel M and Kanbach H 1975 *J. Nucl. Mater.* **55** 291–8
- [17] Khoda-Bakhsh R and Ross D K 1982 *J. Phys. F: Met. Phys.* **12** 15–24
- [18] Ashida Y, Yamamoto M, Naito S, Mabuchi M and Hashino T 1996 *J. Appl. Phys.* **80** 3254–8
- [19] Springer T S 1978 *Hydrogen in Metals I* ed G Alefeld and J Völkl (Berlin: Springer) p 90

- [20] Schirber J E and Morosin B 1975 *Phys. Rev. B* **12** 117–18
- [21] Ziman J M 1971 *Principles of the Theory of Solids* 2nd edn (London: Cambridge University Press) pp 218, 225
- [22] Ohta Y, Naito S and Hashino T 1981 *Denki Kagaku* **49** 772–6 (abstract, figure captions and table in English)
- [23] Bass J 1972 *Adv. Phys.* **21** 431–604
- [24] Loucks T L 1967 *Augmented Plane Wave Method* (New York: Benjamin)
- [25] Pendrew J P and Zunger A 1981 *Phys. Rev. B* **23** 5048–79
- [26] Jespen O, Andersen O K and Machintosh A R 1975 *Phys. Rev. B* **12** 3084–103
- [27] Blaha P, Schwarz K and Dederichs P H 1988 *Phys. Rev. B* **38** 9368–74
- [28] Myron H W, Freeman A J and Moss S C 1975 *Solid State Commun.* **17** 1467–70
- [29] McMillan W L 1968 *Phys. Rev.* **167** 331–44
- [30] Gaspari G D and Gyorffy B L 1972 *Phys. Rev. Lett.* **28** 801–5
- [31] Klein B M and Papaconstantopoulos D A 1976 *J. Phys. F: Met. Phys.* **6** 1135–43
- [32] Gupta M and Burger J P 1981 *Phys. Rev. B* **24** 7099–111
- [33] Chen Y, Fu C L, Ho K M and Harmon B N 1985 *Phys. Rev. B* **31** 6775–7