

# Effect of hydrogen absorption on structure, superconductivity, magnetic susceptibility and heat capacity of $Zr_2Rh$

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## Abstract

The superconducting intermetallic compound  $Zr_2Rh$  (CuAl<sub>2</sub>-type C16 tetragonal structure with  $T_C \approx 11$  K) can be hydrided at room temperature and about 1 atm hydrogen pressure to give a composition  $Zr_2RhH_x$  ( $x = 4.25 \pm 0.25$ ) without a change in crystal structure. This is the first report on the stabilization of a hydride phase with an appreciable hydrogen content. Results of X-ray diffraction, electrical resistivity, magnetic susceptibility and heat capacity are reported on the hydride phase and compared with those of the parent compound. It is found that: (i)  $Zr_2RhH_{4.25}$  exhibits metallic behaviour similar to  $Zr_2Rh$ ; however, no superconducting transition is seen down to 1.8 K; (ii) the hydride is Pauli paramagnetic, but its susceptibility is reduced to almost one-half of the value of the parent compound; (iii) the Debye temperature of the hydride is almost twice that of  $Zr_2Rh$ , indicating stronger bonding despite the increased interatomic separation; (iv) the electronic specific heat coefficient is reduced by almost an order of magnitude on hydriding. Approximate estimates of the density of states at the Fermi level and the electron-phonon coupling constant have been obtained for the intermetallic compound and the hydride.

## 1. Introduction

Zirconium-based intermetallic compounds with the CuAl<sub>2</sub>-type C16 structure (space group  $I4/mcm$ ) have received considerable scientific attention as they can exhibit fairly high superconducting transition temperatures ( $T_C$ ). For example,  $Zr_2Rh$  shows  $T_C \approx 11$  K which is one of the highest reported values for a non-cubic binary system for conventional alloy superconductors (*i.e.* excluding the oxide superconductors). Other members of this family with appreciable superconducting transition temperatures are  $Zr_2Ir$  and  $Zr_2Co$  with  $T_C$  values of approximately 7 K and 6 K respectively [1, 2]. Systematic studies on the pseudobinary C16 intermetallic systems demonstrate a correlation between  $T_C$  and the d.c. susceptibility ( $\chi$ ) values, both showing a

maximum for approximately the same composition with an electron concentration of approximately 5.7 electrons per atom [1, 2]. This correlation between  $T_C$  and  $\chi$  could be ascribed to their similar dependence on the density of states at the Fermi level  $N(E_F)$ , which has contributions mainly from the Zr 4d states [3]. It would be interesting to investigate whether the correlation between  $T_C$  and  $\chi$  holds when changes in the density of states are brought about by hydrogen absorption. The preferential occupancy by H atoms of the interstitial sites formed by Zr atoms [4–6] is expected to bring about a change in  $N(E_F)$ .

Zirconium-based systems absorb a large quantity of hydrogen [4–16] and the resulting ternary hydrides show a rich variety of changes in their electrical and magnetic properties. These are obviously related to changes in their electronic structure. However, no theoretical estimates for the density of states (band structure) are presently available for any of the hydrides of Zr-based

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C16 compounds. Indeed, even for the intermetallic compounds (IMCs), the existing status of the band structure calculations is not adequate. Elaborate band structure calculations are presently being carried out in our laboratory.

Recently, we reported the first successful hydriding at low temperature and low hydrogen pressure of a member of this class of compounds, the high-temperature phase C16  $Zr_2Fe$  [6], and several other systems [17, 18]. Indeed, using this procedure, high hydrogen absorption could be achieved, and the resulting ternary hydrides showed different magnetic properties and a higher value of the Mössbauer isomer shift (IS) [6, 17, 18].  $Zr_2NiH_x$  is probably the most widely investigated system in this class of intermetallics. Neutron diffraction studies on  $Zr_2NiD_x$  [5] and Mössbauer investigations on  $^{57}Fe$ -substituted  $Zr_2NiH_x$  [16] and  $Zr_2FeH_x$  [6] have been used to infer H-atom occupancy. More interesting from the viewpoint of the present study are the pulsed proton nuclear magnetic resonance ( $^1H$  NMR) investigations by Aubertin *et al.* [15] on  $Zr_2NiH_x$ , for  $x=2$ , 3 and 4.5. From the experimental values of the spin lattice relaxation times and the Korringa constants, these workers have concluded that  $N(E_F)$  increases as a function of  $x$ . Assuming this to be valid for the Zr-based C16 IMCs, an enhancement of  $T_C$  may be expected on hydrogen absorption. With this in mind, we successfully carried out, for the first time, the hydriding of  $Zr_2Rh$  ( $T_C \approx 11$  K) to a composition of  $Zr_2RhH_x$  with  $x=4.25 \pm 0.25$ . In addition to the crystal cell parameter estimation at room temperature, electrical resistivity ( $\rho(T)$ ) (15–300 K), magnetic susceptibility  $\chi$  (2–300 K) and heat capacity (2–19 K) measurements were carried out on the hydrided sample. A reduction in  $\chi$  to approximately one-half of the value for the normal state  $Zr_2Rh$  is against the expectations based on the results of Aubertin *et al.* [15]. The hydrided composition, although exhibiting metallic behaviour, is not superconducting at least down to 1.8 K. From the experimental values of the coefficient of electronic heat capacity ( $\gamma$ ) and the Debye temperature ( $\theta_D$ ), approximate values of  $N(E_F)$  and the electron–phonon coupling constant have been estimated.

## 2. Experimental details

$Zr_2Rh$  was prepared from pure metal constituents by argon arc melting in a water-cooled copper hearth. The nominal composition was chosen to be  $Zr_{0.67}Rh_{0.33}$  and the charge was melted several times for homogenization. X-ray diffraction (XRD) did not show any perceptible change on vacuum annealing at 1000 °C for 3 h. Unless specified, the experiments were carried out on as-cast samples. Hydriding was carried out at

room temperature, following the gaseous route, in a stainless steel reactor. The experimental apparatus and the detailed procedures of heat treatment activation for hydrogen absorption, surface poisoning and hydrogen estimation have been described previously [6, 17–23]. After activation, a known amount of hydrogen (small quantity) was introduced into the reactor system at 1–2 atm. It was found that initial hydrogen absorption required an incubation time which varied with the applied hydrogen pressure. For example, the incubation period was reduced from a few hours at 1 atm hydrogen pressure to 10–20 min at pressures higher than 5 atm. After the initial absorption was complete, a fresh charge of hydrogen into the reactor resulted in very fast absorption. Enough time was allowed between successive hydrogen introductions to minimize the local heating effects. Once the hydride with a composition  $Zr_2RhH_x$  with  $x \approx 4.25 \pm 0.25$  was formed, a further increase in hydrogen pressure up to approximately 10 atm did not lead to any detectable difference in the composition. The formation of a well-defined, single-phase ternary hydride was confirmed by XRD. No disproportionation into stable binary hydride and Rh metal was observed under the conditions employed in this work.

The hydrogen composition was estimated by decomposing a known amount of the hydride sample in a standard volume and by measuring the change in pressure. As in the case of  $Zr_2Fe$  [6], attempts to prepare a hydride with  $x < 4.25$  in the absorption mode did not succeed. For example, in one experiment, when a limited supply of hydrogen was contacted with the IMC, it was found by XRD only a fraction of the sample acquired a composition with  $x = 4.25$ , whereas the remainder was completely unhydrided IMC. All the studies described in this work pertain to the composition  $Zr_2RhH_{4.25}$ . The hydride was found to be stable for several months as demonstrated by the peak positions in the XRD pattern. The procedures for measuring the heat capacity, magnetic susceptibility and electrical resistivity are described below.

For the measurement of the electrical resistance and heat capacity, the hydrided powder sample was compacted into a pellet. In order to avoid the loss of hydrogen, no heat treatment was given to the pellet. A conventional four-probe method was used to measure the temperature dependence of the resistance. Because of the uncertainty in the degree of compactness and therefore the exact magnitude of  $\rho(T)$ , only the resistivity ratio ( $\rho(T)/\rho(300$  K)) has been estimated accurately.

A superconducting quantum interference device (SQUID) magnetometer (model MPMS, Quantum Design) was used to carry out the magnetic measurements down to 1.8 K in various fields. In order to examine the correlation between  $T_C$  and  $\chi$  on hydrogen absorption, it is important to minimize the error in the

estimation of  $\chi$  of the IMC and its hydride. Similar amounts of  $Zr_2Rh$  and  $Zr_2RhH_{4.25}$ , both in the powder form, were taken in the same quartz tube to ensure a similar demagnetization correction. Corrections for the blank tube etc. were applied to obtain the magnetic susceptibility values in the normal state. The onset of superconductivity in  $Zr_2Rh$  is indicated by a very sharp diamagnetic response in  $\chi$  at  $T_C \approx 11.2$  K (midpoint), whereas  $Zr_2RhH_{4.25}$  does not show such behaviour down to 1.8 K, the lowest temperature.

The heat capacity ( $C_v$ ) in the range 2–19 K was measured using the semi-adiabatic heat pulse method on an automated apparatus. As in the case of  $\rho(T)$ , a compacted pellet (without subsequent heat treatment) was used for the heat capacity measurements of  $Zr_2RhH_{4.25}$ . A distinct discontinuity in  $C_v$  was clearly found for  $Zr_2Rh$  at  $T_C = 11.2$  K. The corresponding hydride did not show any discontinuity down to 2 K.

### 3. Results and discussion

#### 3.1. Hydriding of $Zr_2Rh$

Figures 1(a) and 1(b) show the XRD patterns of  $Zr_2Rh$  and  $Zr_2RhH_{4.25}$  respectively. As in the case of the IMC, all the X-ray peaks for the hydride can be indexed on the basis of a tetragonal unit cell, with least-square-fitted values:  $a = 6.497$  Å,  $c = 5.614$  Å for  $Zr_2Rh$ ;  $a = 6.810$  Å,  $c = 5.603$  Å for  $Zr_2RhH_{4.25}$ . The striking feature of the X-ray data is that the volume expansion (9.65%) due to hydriding is highly anisotropic: whereas the  $a$  parameter shows considerable expansion ( $\Delta a/a = 4.8\%$ ), the  $c$  axis of the unit cell contracts slightly ( $\Delta c/c = -0.2\%$ ). The preferential expansion in the plane perpendicular to the  $c$  axis gives some indication about the selective site occupancy by H atoms in the hydride phase. Some of these aspects were mentioned in our earlier work [6]. However, an exact explanation must await the experimental determination of the H-atom site occupancies. Another striking result of this X-ray study is the unusually low value of the volume per H atom ( $V_H = 1.35$  Å<sup>3</sup>), which is almost one-half of that reported for most hydride systems [12, 19–22, 24, 25]. A low value of  $V_H$  has also been found in our recent work on the Al-rich  $Ce(Fe_{1-y}Al_y)_2H_x$  system [18] and in  $Zr_3FeH_x$  by Aubertin *et al.* [14]. These workers did not find any perceptible change in cell parameters as well as Mössbauer isomer shift in  $Zr_3FeH_x$  for  $x \leq 3$ . A systematic study of the volume expansion as a function of H-atom content is planned to obtain a better understanding of this aspect.

Our values for the cell parameters of  $Zr_2Rh$  are in agreement with earlier reports [1]. For the hydride, to our knowledge this is the first time appreciable hydrogen absorption in  $Zr_2Rh$  has been reported. It should be

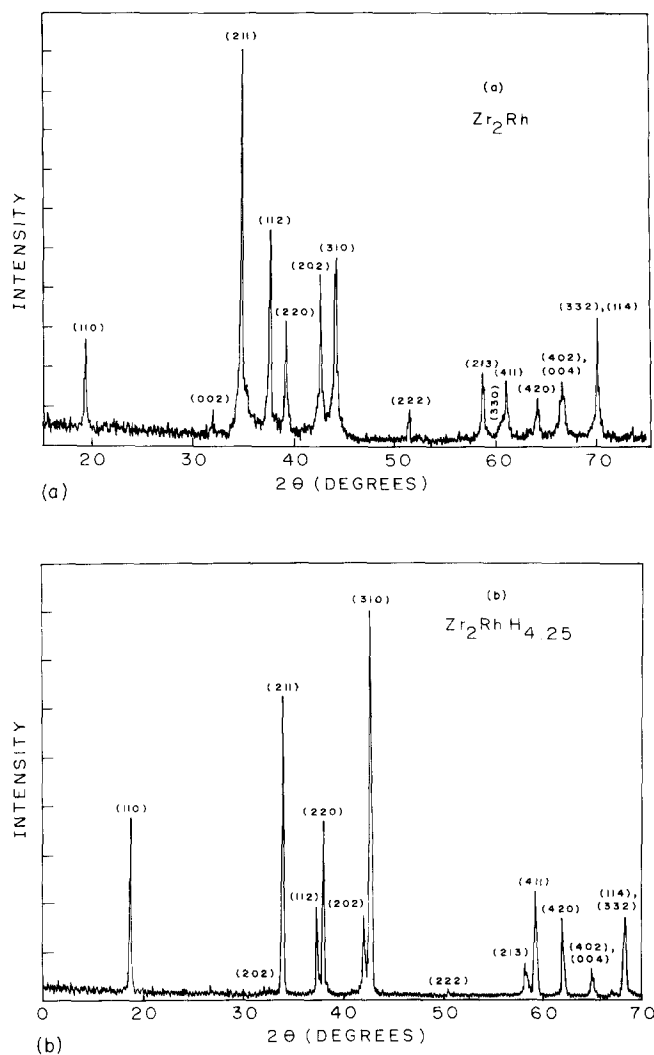


Fig. 1. X-ray diffraction pattern of  $Zr_2Rh$  (a) and  $Zr_2RhH_{4.25}$  (b) using  $Cu K\alpha$  radiation.

noted that an earlier report [26] on the hydriding of various Zr–Rh alloys also included the composition  $Zr_2Rh$ . An approximate estimate of the maximum amount of hydrogen absorbed by  $Zr_2Rh$  in that work [26] is less than 1% of that reported in this study. This is mainly because of the different hydriding conditions employed in the two investigations. For example, in ref. 26, hydrogen absorption was carried out at very high temperature (1050 °C), compared with room temperature (25 °C) in our case. In view of the very different hydrogen absorption in these two cases, it is important to elaborate the role of the relevant hydriding parameters in the formation of the end products.

Although the equilibrium plateau pressures of many ternary hydrides at hydriding temperature are orders of magnitude lower, most studies are reported at high  $H_2$  gas pressure and high temperature. These high values help to dissociate the molecular hydrogen at the surface and facilitate faster permeation of H atoms

into the bulk to convert the IMC into its hydride. (Effectively, the activation energy for hydriding is reduced at higher hydrogen pressure [27].) However, as  $H_2$  absorption itself is an exothermic process, the stabilization of the ternary hydride often requires the withdrawal of excess heat. Failure to withdraw the excess heat rapidly can result in disproportionation, leading to the formation of binary hydride, particularly when one of the constituents of the IMC belongs to group III (e.g. Sc, Y), group IV (e.g. Ti, Zr) or the rare earth series. The elements of these groups show great affinity towards  $H_2$  and form very stable crystalline binary hydrides with large negative heats of formation (see, for example, table 1 of Buschow *et al.* [8]). Thus, depending on the hydriding parameters, an IMC with a composition  $R_mT_n$  (where R is one of the elements of the above groups and T is a transition metal atom) may transform into a crystalline ternary hydride, amorphous ternary hydride or crystalline binary hydride ( $RH_x$ ) together with T metal or a T-rich IMC [6, 8, 17, 18, 27]. The rate of diffusion of the T atoms, relative to that of the H atoms, at the hydriding temperature is the crucial factor in deciding the final products. Some of these aspects, including the phenomenon of hydrogen-induced amorphization (HIA), have been discussed in recent papers [6, 17, 18, 27, 28]. In this context, it may be emphasized that the hydriding of the isostructural compound  $Zr_2Fe$  [6] required not only low temperature and low  $H_2$  pressure, but also fast withdrawal of exothermic heat, which was achieved by employing a copper reactor. Another factor which is quite important from the viewpoint of final product formation is the stability of the IMC itself [6, 17, 18, 27, 28]. It has been suggested that weaker bonding between the constituents of the IMC favours binary hydride formation, whereas stronger bonding gives rise to crystalline ternary hydride phase formation. Intermediate stability of the IMC favours hydrogen-induced amorphization. The Debye temperature ( $\theta_D$ ) of a metallic system gives a rough measure of the bond strength of its constituents: a higher value represents a stronger bonding. The relatively low value of  $\theta_D$  for  $Zr_2Rh$  (approximately 214 K, estimated from the heat capacity data in the normal state, see Section 3.4) points to a rather weak bonding between the Zr and Rh atoms in this structure. This also implies that, in order to stabilize the crystalline ternary hydride of this compound, milder hydriding conditions are essential. In our opinion, the earlier attempt to hydride at 1050 °C [26] should have resulted in disproportionation and not in ternary hydride formation. No phase analysis of the products was reported in ref. 26. This is further supported by the observations that, on  $H_2$  absorption, there is almost no change in the superconducting transition temperature ( $T_C$ ), and only a fraction (about 10%) of the IMC becomes

hydrided. We also surmise that the relative ease of crystalline ternary hydride formation of  $Zr_2Rh$  at room temperature, in spite of the low  $\theta_D$  value, is related to the low diffusivity of Rh atoms in the hydride matrix.

### 3.2. Electrical resistivity of $Zr_2RhH_{4.25}$

Hydrogen absorption brings about an overall change in the properties of the intermetallics, including the temperature dependence of  $\rho(T)$  [8, 17, 29]. As stated earlier, owing to the inadequate compacting of the hydrides, only the resistivity ratio  $\rho(T)/\rho(300\text{ K})$  has been estimated. Figure 2 shows the variation of the resistivity ratio for the temperature range 15–300 K. A monotonic increase in this ratio, with temperature, is typical of metallic behaviour. From these studies, it is concluded that the hydriding of  $Zr_2Rh$ , at least up to the composition  $Zr_2RhH_{4.25}$ , retains the metallic behaviour of the IMC. (The present study is confined to this composition only, since other compositions could not be prepared in the absorption mode.) The absence of superconductivity, down to at least 1.8 K, has been inferred from the susceptibility and heat capacity measurements. It may be noted from Fig. 2 that the linear temperature dependence of  $\rho(T)$  shows a small kink around 80 K. At present, it is not possible to make any definite comments on this aspect. This could possibly be related to the diffusion characteristics of H atoms in the hydride matrix.

### 3.3. Magnetic properties of $Zr_2Rh$ and $Zr_2RhH_{4.25}$

Figures 3(a) and 3(b) show the temperature dependence of magnetization in the temperature range close

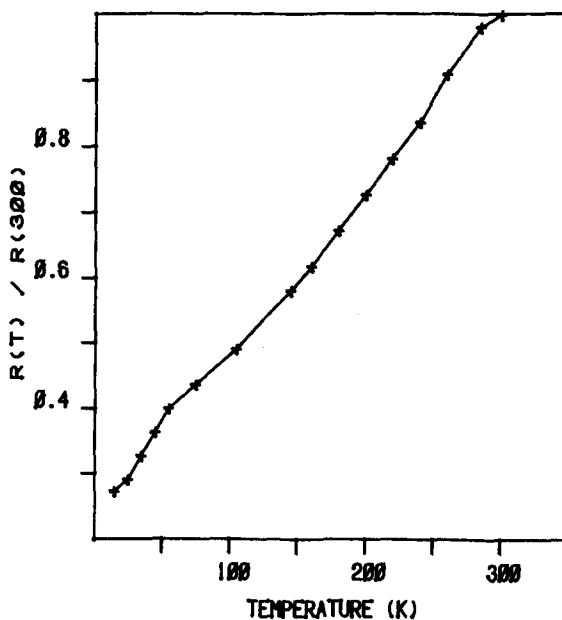


Fig. 2. Temperature dependence of the resistivity ratio for  $Zr_2RhH_{4.25}$ .

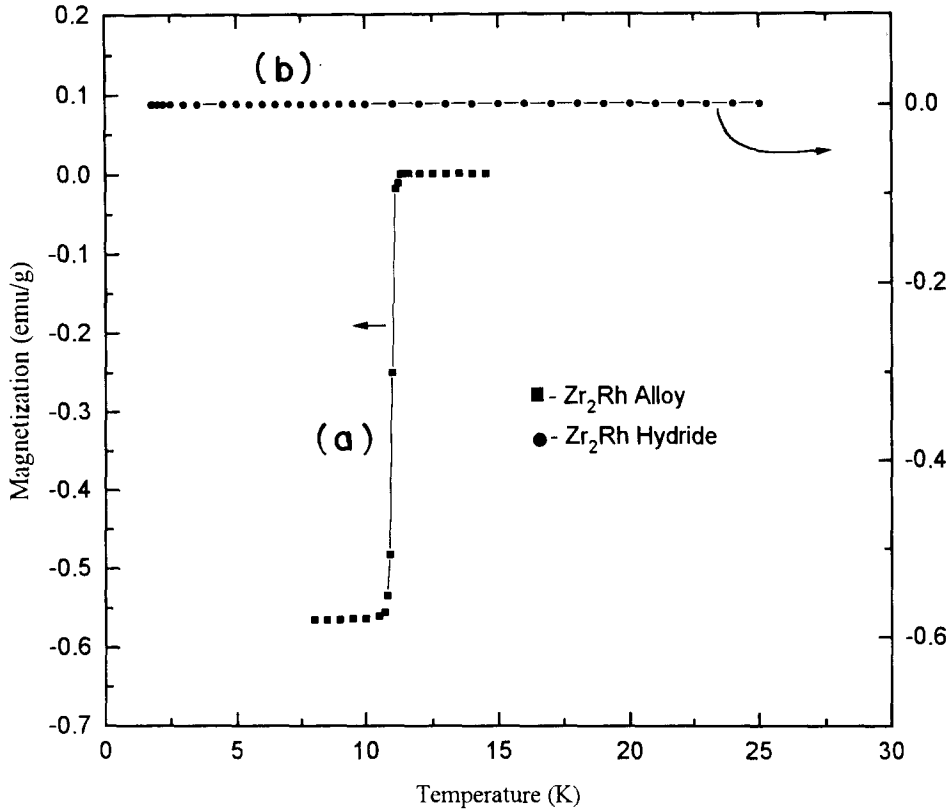


Fig. 3. Temperature dependence of magnetization of  $Zr_2Rh$  (a) and  $Zr_2RhH_{4.25}$  (b) in a magnetic field of 0.1 T.

to  $T_C$  for the IMC and its hydride, recorded in a magnetic field of 0.1 T. A very sharp drop in the magnetic susceptibility, indicating a transformation from Pauli paramagnetic to diamagnetic behaviour at the superconducting transition temperature, is clearly shown in Fig. 3(a). The value of  $T_C$  (11.2 K) found from this study matches exactly that obtained from the heat capacity data and is within the narrow range of values reported for  $Zr_2Rh$  in Table 1 of ref. 1. As-cast samples are reported to show slightly higher  $T_C$  values in this class of IMCs; our  $T_C$  value for  $Zr_2Rh$  is in accord with this trend. The variation in magnetization in Fig. 3(b) shows no transition down to 1.8 K. This clearly indicates that the absorption of  $H_2$  by  $Zr_2Rh$ , at least for the composition  $Zr_2RhH_{4.25}$ , yields a non-superconducting compound or reduces  $T_C$  to less than 1.8 K.

The magnetic susceptibilities of  $Zr_2Rh$  and  $Zr_2RhH_{4.25}$  were determined at 20 and 300 K, in the normal state, in magnetic fields from 0.01 to 0.5 T. The magnitude of  $\chi$  was found to be almost independent of the applied field. Our values of molar susceptibility, at 20 K, are found to be approximately  $3.7 \times 10^{-4}$  and  $1.8 \times 10^{-4}$  e.m.u. mol $^{-1}$  respectively. It is thus found that, on hydrating, the magnitude of  $\chi$  is reduced to almost half the value of  $Zr_2Rh$ . Since powdered samples were used in this study, the emphasis is more on the relative

changes, on hydrating, rather than on the exact magnitudes. As expected for Pauli paramagnetic systems, the room temperature  $\chi$  values for both the IMC and its hydride were only about 10%–20% lower than the 20 K values. The value of the normal state  $\chi$  for the IMC in this work is similar to that reported in ref. 1.

We now attempt to determine whether the reduction in the magnitude of  $\chi$  on hydrating to  $x = 4.25$ , to almost half the value of the parent compound, can be qualitatively related to the reduction in the density of states at the Fermi level. Following McCarthy [1], the experimental value of the susceptibility can be written as

$$\chi = \chi_{\text{spin}}^d + \chi_{\text{spin}}^s + \chi_L + \chi_{\text{dia}} + \chi_{\text{orb}} \quad (1)$$

where  $\chi_{\text{spin}}^d$  and  $\chi_{\text{spin}}^s$  are the separable d electron and s electron Pauli spin susceptibilities given by the expressions

$$\chi_{\text{spin}}^d = 2\mu_B^2 N_d \quad \text{and} \quad \chi_{\text{spin}}^s = 2\mu_B^2 N_s$$

where  $\mu_B$  is the Bohr magneton and  $N_d$  and  $N_s$  are the d electron and s electron contributions, respectively, to the density of states at the Fermi level. (A comparison of these expressions with those given by Switendick [29] implies that  $N_d$  and  $N_s$  should include the enhancement of susceptibility due to electron–phonon interaction.) The last three terms in eqn. (1) are the

Landau diamagnetic term, diamagnetic contribution from the closed electronic shells and the orbital paramagnetic susceptibility respectively.

The major variations in  $\chi$ , on alloying, have been mainly ascribed to the changes in  $\chi_{spin}^d$  by McCarthy [1], who also concluded that, in the pseudobinaries of  $Zr_2Rh$ ,  $T_C$  correlates with  $\chi$ . Switendick [29], on the other hand, has stressed that the susceptibility is only partly given by the Pauli contribution and that its variation on hydriding only remotely reflects the density of states information. In the next section, it is shown that, on hydriding  $Zr_2Rh$ , the electronic heat capacity (and therefore  $N(E_F)$ ) reduces by almost an order of magnitude, whereas our normal state susceptibility value reduces by a factor of approximately two only. It should be noted that the reduction in  $N(E_F)$  is contrary to the expected increase deduced from the pulsed  $^1H$  NMR results on the hydrides of  $Zr_2Ni$  [15].

### 3.4. Heat capacity of $Zr_2Rh$ and $Zr_2RhH_{4.25}$

Figure 4(a) shows the heat capacity of  $Zr_2Rh$  in the form  $C_v/T$  vs.  $T^2$ .  $C_v$  is given by the following expression

$$C_v = \gamma T + \beta T^3 \quad (2)$$

Our results, both qualitative and quantitative, are in agreement with those of Kuentzler and Waterstrat [30, 31]. The heat capacity exhibits a jump at the transition to the superconducting state, at the same temperature at which the diamagnetic response of the magnetic susceptibility is observed. The  $C_v/T$  vs.  $T^2$  plot is linear for temperatures above  $T_C$ , up to about 15 K. A slight deviation from linearity is observed for  $T > 15$  K. An extrapolation of the least-squares linear fit of the heat capacity data to eqn. (2), in the range of  $T^2$  values from 132 to 222  $K^2$ , yields  $\gamma$  ( $=C_v/T$ , at 0 K) = 68  $mJ mol^{-1} K^{-2}$  (22.7  $mJ (g atom)^{-1} K^{-2}$ ). On the other hand, a  $\gamma$  value of 78  $mJ mol^{-1} K^{-2}$  is obtained if the least-squares fit also includes the data above 15 K, where a slight downturn is observed. It should be noted that the heat capacity of the annealed  $Zr_2Rh$  sample (1000 °C for 3 h) showed a downturn at a lower temperature above  $T_C$ , although  $T_C$  remained almost unaffected. For the subsequent discussions, we will use the  $\gamma$  value derived from the data below 15 K.

The value of  $\beta$ , the coefficient of the lattice heat capacity, is found from the slope of Fig. 4(a) (see eqn. (2)). The Debye temperature is derived using the following relationship

$$\begin{aligned} \beta &\approx (12\pi^4/5)N_A k_B (1/\theta_D^3) \\ &= (1.945 \times 10^6/\theta_D^3) mJ (g atom)^{-1} K^{-4} \quad (3) \end{aligned}$$

where  $N_A$  and  $k_B$  represent the Avogadro number and Boltzman constant respectively. Using eqn. (3), we obtain  $\theta_D = 214$  K. Assuming an idealized transition

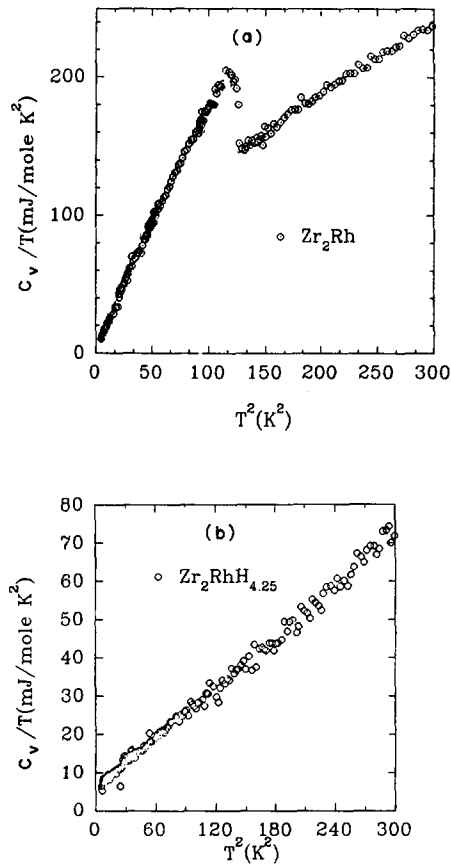


Fig. 4. Temperature dependence of the heat capacity of  $Zr_2Rh$  (a) and  $Zr_2RhH_{4.25}$  (b) in the form  $C_v/T$  vs.  $T^2$ .

occurring at 11.2 K, with zero width, the jump in the heat capacity at  $T_C$  is  $\Delta C_v/T_C = 72 mJ (mol)^{-1} K^{-2}$ . For  $\gamma = 68 mJ (mol)^{-1} K^{-2}$ , we find the ratio  $\Delta C_v/\gamma T_C = 1.06$ . This is fairly close to the value reported by Kuentzler and Waterstrat [30], but is less than the BCS predicted value of 1.4. Anomalously small specific heat jumps have been reported in the superconductors  $YGe_{1.62}$ ,  $LaSi_2$  and  $LaGe_2$  [32] where  $(\Delta C/\gamma T)_{T-T_C} = 0.80, 0.90$  and  $0.76$  respectively. It was claimed that the anomaly may be due to two-band or large anisotropy effects.

Figure 4(b) depicts the heat capacity of the hydrided sample. No phase transition is observed down to 2 K, which is in agreement with the magnetic susceptibility data. For the hydrided sample, a least-squares linear fit of the  $C_v/T$  vs.  $T^2$  data to eqn. (2) in the range 2–14 K yields the following values:  $\gamma = 6 mJ (mol)^{-1} K^{-2}$ ,  $\beta = 0.0312 mJ (g atom)^{-1} K^{-4}$  and  $\theta_D = 396$  K. It should be noted that the  $\gamma$  value of  $Zr_2RhH_{4.25}$  is reduced by a factor of more than 11, whereas  $\theta_D$  is almost doubled.

In a purely free-electron approximation,  $\gamma$  should scale with  $\chi$  as both depend on the electronic density of states at the Fermi level. However, it is found for  $Zr_2Rh$  that, although both  $C_v$  and  $\chi$  show a reduction

on hydriding, the extent of reduction is very different. As stated earlier, Switendick [29] showed that the change in  $\chi$  on hydriding is only remotely connected with the density of states contribution. This is because the contribution from the last three terms in eqn. (1) is not small enough to be negligible. We will therefore use the heat capacity data to obtain an approximate estimate of  $N(E_F)$ . The relation between  $C_v$  and  $N(E_F)$  is given by [29]

$$N(E_F) = 3\gamma/2\pi^2k_B^2(1 + \lambda) \quad (4)$$

where the electron-phonon coupling constant  $\lambda$  can be obtained from the expression given by Rowell [33] (often adopted for strong coupling superconductors)

$$\lambda = (20T_C/\theta_D) + 0.25 \quad (5)$$

or from McMillan's formula [34]

$$\lambda = \{\mu \ln(\theta_D/1.45T_C) + 1.04\} / \{(1 - 0.62\mu) \times \ln(\theta_D/1.45T_C) - 1.04\} \quad (6)$$

where  $\mu$  reflects the electron-electron interaction and has a value of approximately 0.1. Equation (6) is considered to be more appropriate for weak and intermediate coupling strengths, *i.e.*  $\lambda < 1$ . For  $Zr_2Rh$ , eqns. (5) and (6) lead to  $\lambda = 1.3$  and 1.0 respectively. In the absence of  $T_C$  measurements for the hydride phase ( $T_C < 1.8$  K), only an upper limit can be fixed for  $\lambda$ . This gives  $\lambda \leq 0.4$  for  $Zr_2RhH_{4.25}$ . Using these  $\lambda$  values and experimental  $\gamma$  estimates, as mentioned earlier,  $N(E_F)$  is derived using eqn. (4):  $N(E_F)_{Zr_2Rh} \approx 6-7$  states  $eV^{-1}$  (formula unit) $^{-1}$ ;  $N(E_F)_{Zr_2RhH_{4.25}} < 1$  state  $eV^{-1}$  (formula unit) $^{-1}$ .

The reduction in  $T_C$  for  $x = 4.25$  can be ascribed to the considerable decrease in  $N(E_F)$  as well as electron-phonon coupling (as obtained from the heat capacity measurements).  $N(E_F)$  changes inferred from the magnetic susceptibility data are inadequate to explain such large  $T_C$  changes. It should be noted that more quantitative estimates would require a better understanding of the electronic structure of the IMC and its hydride. Some progress has been made in this direction in our laboratory.

#### 4. Conclusions

The intermetallic compound  $Zr_2Rh$  can be hydrided at room temperature and at low hydrogen pressure (approximately 1–2 atm) to a composition  $Zr_2RhH_x$  ( $x = 4.25 \pm 0.25$ ), without a change in the crystal structure. This is the first report on the stabilization of a hydride compound with an appreciable hydrogen content. The stabilization of the ternary hydride phase, in spite of the rather weak bonding between the constituent

metal atoms of  $Zr_2Rh$ , indicated by the low  $\theta_D$  value, has been ascribed to the low diffusivity of Rh atoms in the hydride matrix. It is found that: (i)  $Zr_2RhH_{4.25}$  shows metallic conductivity; however, hydriding either makes the compound non-superconducting or its  $T_C$  value is reduced to less than 1.8 K; (ii) the hydride retains Pauli paramagnetic behaviour, but the magnitude of the susceptibility is reduced to almost one-half that of  $Zr_2Rh$ ; (iii) the Debye temperature of  $Zr_2RhH_{4.25}$  (396 K) is almost twice that of  $Zr_2Rh$  (214 K), indicating stronger bonding between the constituent atoms in the hydride phase despite the increased interatomic separation between the Zr and Rh atoms. The suppression of the superconducting properties on hydriding, notwithstanding the increase in  $\theta_D$ , is ascribed to the reduction in  $N(E_F)$  as well as  $\lambda$  (obtained from the heat capacity data). The magnetic susceptibility measurements do not represent the exact variation of  $N(E_F)$  on hydriding. However, a more quantitative understanding requires elaborate electronic band structure calculations of  $Zr_2Rh$  and its hydride.

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