# Phase transitions, electronic properties, and superconductivity in the system $V_2ZrH_x$

C. Geibel, W. Goldacker, H. Keiber, V. Oestreich, H. Rietschel, and H. Wühl

### Kernforschungszentrum Karlsruhe und Universität Karlsruhe, Postfach 3640, D-7500 Karlsruhe, Federal Republic of Germany

(Received 16 July 1984)

We present experimental results for the magnetic susceptibility in the temperature range between 10 and 300 K and for the low-temperature specific heat in samples of nominal composition  $V_2ZrH_x$ ,  $0 < x \le 1.22$ . These data are supplemented by results from x-ray diffraction experiments. We find that at low temperatures and for  $x \le 1.3$ ,  $V_2ZrH_x$  decomposes into  $V_2Zr$  and  $V_2ZrH_{1.3}$ . In  $V_2ZrH_{1.3}$ , the coefficient of the electronic specific heat,  $\gamma$ , is  $\sim 3.2 \text{ mJ/K}^2$  g-at. (for cubic  $V_2Zr$ ,  $\gamma \sim 23 \text{ mJ/K}^2$  g-at.) and the magnetic susceptibility at 10 K,  $\chi(10 \text{ K})$ , is  $\sim 1.8 \times 10^{-4}$  emu/g-at. [for cubic  $V_2Zr$ ,  $\chi(10 \text{ K}) \sim 3.9 \times 10^{-4}$  emu/g-at.]. Thus, a drastic reduction of the electronic density of states at the Fermi level is observed. Above 2 K,  $V_2ZrH_{1.3}$  is not superconducting (for cubic  $V_2Zr$ ,  $T_c \sim 8.7 \text{ K}$ ). Our results are discussed in the context of recent band-structure calculations for  $V_2Zr$ .

### I. INTRODUCTION

Among the superconductors with a high electronic density of states (DOS) at the Fermi level, the C15 compound V<sub>2</sub>Zr has attracted much recent attention. In bandstructure calculations,<sup>1,2</sup> the electronic DOS was found to be sharply structured near  $E_F$  with  $N(0) \sim 110$  states/spin Ry unit-cell. While this value is as high as in the high- $T_c$  A15 compound V<sub>3</sub>Si, the superconducting transition temperature is comparatively low (8.7 K). In a previous publication,<sup>3</sup> we have presented experimental results for the low-temperature specific heat and for the magnetic susceptibility for  $V_2Zr$  which, when combined with the band-structure results, are strongly indicative of  $T_c$ depression by spin fluctuations (SF). Since  $V_2Zr$  is able to absorb large amounts of hydrogen, and since from experiments on Pd it is known that hydrogenation may reduce N(0) and thus the influence of SF,<sup>4</sup> it was obvious to extend our experiments on hydrides of  $V_2Zr$ .

At room temperature,  $V_2Zr$  forms hydrogen solid solutions  $V_2ZrH_x$  with  $0 \le x \le 5$ . This has been first reported by Pebler and Gulbransen.<sup>5</sup> Subsequently, the structural properties of the  $V_2Zr$ -H(D) system have been studied extensively, mainly with regard to the sites occupied by the H(D) atoms.<sup>6</sup> More recently, from x-ray diffraction analysis, Irodova *et al.*<sup>7</sup> deduced an (x, T) phase diagram for  $V_2ZrH_x$  ( $V_2ZrD_x$ ) within the range 80 K  $\le T \le 370$  K,  $0.4 \le x \le 6$ . Unfortunately, this phase diagram is rather coarse, in particular for x < 1, where only two points are given for the deuteride (x = 0.4 and 0.9) and no information on the hydride.

Regarding the electronic properties of  $V_2ZrH_x$ ( $V_2ZrD_x$ ), no experimental information has been published so far, but there are investigations on the related systems  $V_2HfH_x(V_2HfD_x)$  and  $V_2Zr_{0.5}Hf_{0.5}H_x$ ( $V_2Zr_{0.5}Hf_{0.5}D_x$ ). Däumer *et al.*<sup>8</sup> found that the superconducting transition temperature  $T_c$  (measured inductively) decreases with increasing x in both systems, and the same has been reported by Duffer *et al.*<sup>9</sup> for  $V_2HfH_x(V_2HfD_x)$ . For  $V_2Zr_{0.5}Hf_{0.5}H_x$ ( $V_2Zr_{0.5}Hf_{0.5}D_x$ ), Rao *et al.*<sup>10</sup> observed a large "isotope effect." Actually, for  $0.8 \le x \le 1.2$ , they found the hydride still superconducting while the deuteride was not. No satisfying explanation of this observation has been given.

In this paper, we report on measurements of the magnetic susceptibility and of the low-temperature specific heat in compounds of nominal composition  $V_2ZrH_x$  with  $0 \le x \le 1.22$ . The measurements were accompanied by x-ray diffraction analysis in the temperature range 20 K  $\le T \le 295$  K. From the results of the x-ray analysis and from the magnetic susceptibility, a tentative phase diagram for  $V_2ZrH_x$  has been deduced for  $x \le 1.3$  and 20 K  $\le T \le 295$  K.

The present work is a continuation of our previous publication<sup>3</sup> on  $V_2Zr$ , and the reader is referred to that reference for details regarding the preparation and characterization of  $V_2Zr$  and the experimental facilities used for measurements of the specific heat and of the magnetic susceptibility. The preparation of the hydrides is described in Sec. II and the x-ray diffraction analysis in Sec. III. In Sec. IV we present the specific heat and in Sec. V the magnetic susceptibility data. A discussion of our results follows in Sec. VI.

### **II. HYDROGENATION**

Hydrides were prepared by exposing the  $V_2Zr$  ingots to a hydrogen atmosphere of 1 to 20 mbar. The hydrogen was purified in a palladium cell. At room temperature, the reaction is very fast and leads to a disintegration of the ingots into fine powder. In order to get compact samples, the  $V_2Zr$  ingots were heated to 700 °C before introducing hydrogen. At this temperature, the dissociation pressure of the hydride is higher than the applied pressure and the hydrogen is slowly absorbed during cooling.

We obtained compact  $V_2ZrH_x$  samples of 100 to 500 mg in the composition range  $0.36 \le x \le 1.22$ . The hydrogen content was determined from the volume and pressure of the absorbed hydrogen as well as from the weight gain. Within the experimental accuracy of about 1 at. %, both methods led to the same result.

#### **III. X-RAY DIFFRACTION INVESTIGATIONS**

The structure of the samples was investigated by means of x-ray powder diffraction measurements in the temperature range between 20 and 300 K. A vertically arranged diffractometer with Bragg-Brentano geometry was used. On the detector side, a quartz monochromator was applied to suppress  $\text{Cu-K}_{\alpha_2}$  radiation. The sample was positioned in vacuum on the cold finger of an Oxford continuous-flow cryostat. The temperature was measured with a CLTS resistance strain gauge sensor which was also used for the temperature control circuit. The stability and accuracy were better than  $\pm 1$  K.

The lattice constants and the phase transitions were studied by monitoring the (2,2,0), (3,1,1), and (2,2,2) reflexes as a function of temperature. In addition, the complete diffraction pattern was scanned at 300 and 20 K. Silicon powder mixed to the samples was used as standard. As a representative example we have chosen  $V_2ZrH_{0.57}$  to discuss our results. In Fig. 1, the lattice parameter  $a_0$  as a function of temperature is shown for this sample. At 300 K, hydrogen forms a homogeneous solid solution. Thus, a single cubic phase is observed, its lattice parameter being increased in comparison to V<sub>2</sub>Zr. Below 260 K, segregation leads to two distinct cubic phases which differ in hydrogen concentration and thus in  $a_0$ . Since in  $V_2ZrH_x$  the lattice parameter  $a_0$  is a linear function of x, the composition of these two phases can be determined from the measured  $a_0$ .<sup>5</sup> The only correction to be applied is the temperature dependence of  $a_0$  which was assumed to be the same as for  $V_2Zr$ . At our lowest temperature T = 20 K,  $x \equiv x_0 = 1.3 \pm 0.1$  was found for the hydrogen-rich phase and x < 0.05 for the hydrogenpoor phase.

Below 200 K, line splitting is observed for some of the reflections of the hydrogen-rich phase. The new diffrac-



FIG. 1. Lattice parameters for  $V_2ZrH_{0.57}$  as a function of temperature; the transformation from the cubic to the rhombohedral phase of  $V_2Zr$  has not been observed in our x-ray diffraction measurements.

tion pattern can be indexed on the basis of a tetragonally distorted cell with  $c/a=0.992\pm0.001$  at 20 K. This phase transition is probably induced by an ordering of the hydrogen atoms in the same way as has been found for  $V_2ZrD_{4,0}$ .<sup>6</sup>

We did not observe the phase transition cubic $\rightarrow$ rhombohedral in our x-ray pattern for the V<sub>2</sub>Zr portion, although a transition clearly shows up in the magnetic susceptibility data (see Sec. V). As already discussed in the foregoing work on V<sub>2</sub>Zr,<sup>3</sup> this transition is likely to be suppressed in the surface layer probed by x-ray radiation.

The results for the other samples look very similar to those shown in Fig. 1 except for the fact that changes in x lead to changes in the temperature where the segregation takes place and to changes in the respective amounts of  $V_2Zr$  and  $V_2ZrH_{1.3}$  at low temperatures. In Fig. 2, we have summarized our results by drawing a tentative (x, T) phase diagram for T between 20 and 300 K and for  $x \le 1.3$ . The hydrogen concentration at the phase boundary was determined from the lattice constants as already described above.

At 20 K, two phases are present, pure  $\alpha V_2Zr$  and tetragonal  $\beta V_2ZrH_{1.3}$ . Above about 100 K, the solubilities of hydrogen in the  $\alpha$  phase and of hydrogen vacancies in the  $\beta$  phase increase noticeably. At about 200 K, the  $\beta$ phase transforms into cubic  $\alpha' V_2ZrH_x$  which differs from the  $\alpha$  phase by an increased hydrogen content and enlarged lattice constant. Above about 260 K, the miscibility gap between the  $\alpha$  and  $\alpha'$  phase is closed leading to a homogeneous solid solution of hydrogen in  $V_2Zr$ .

Our results are similar to those by Irodova *et al.*<sup>7</sup> for  $V_2ZrD_{0.4}$ . These authors found a decomposition into  $V_2Zr$  and  $V_2ZrD_{\sim 1.0}$  below 180 K and a transition of the



FIG. 2. Tentative (x, T) phase diagram for  $V_2ZrH_x$ . The diagram has been deduced mainly from our x-ray results on  $V_2ZrH_{0.57}$  (closed circles), the x values of these data points have been determined from the lattice parameters shown in Fig. 1 as outlined in the text. The points denoted by an open circle and a triangle were taken from data for x=0.80 and 1.22, respectively. Since for the tetragonal phase, the relation between lattice parameters and hydrogen content x is not known, the corresponding relation for the cubic phase was taken which implies some uncertainty in the right-hand side of the phase boundary (broken line).

deuteride to a tetragonal phase with  $c/a \sim 0.993$ , i.e., with about the same distortion as we found for the hydride.

# IV. SPECIFIC HEAT

Specific-heat data were taken in a heat-pulse calorimeter<sup>3</sup> for temperatures within the range between 2 and 13 K. The data are plotted as C/T versus  $T^2$  in Fig. 3. Above  $T_c$ , they were fitted to

$$C_N(T) = \gamma T + \beta T^3 + \alpha T^5 \tag{1}$$

under the usual entropy constraint.<sup>3</sup> The resulting constants  $\gamma$  and  $\Theta_D = (12\pi^4 n k_B / 5\beta)^{1/3}$  are listed in Table I.

For  $V_2Zr$  (x = 0), the specific heat shows two distinct superconducting transitions at 8.7 and 8.0 K. As has been outlined in Ref. 3, these transitions have to be assigned to the cubic (8.7 K) and rhombohedral (8.0 K) phase, respectively, of this compound. For increasing x, the twin discontinuity smears out and looses in height, but remains detectable up to x=0.80. For x=1.22, only one broad transition can be observed between 7.0 and 8.7 K.

The specific-heat results can be interpreted with the help of the phase diagram plotted in Fig. 2. At low temperatures, a sample of initial composition  $V_2ZrH_x$  has decomposed into  $V_2ZrH_{1.3}$  with concentration c = x/1.3 and into  $V_2Zr$  with concentration 1-c. The twin discontinuity is produced by  $V_2Zr$ , its height being governed by



FIG. 3. Specific-heat data plotted as C/T versus  $T^2$  for samples of composition  $V_2ZrH_x$ ; the solid lines represent guides to the eye. Inset: The low-temperature data for x=1.22 on a larger scale.

TABLE I. Specific-heat coefficient  $\gamma$  and Debye temperature  $\Theta_D$  for compounds of nominal composition V<sub>2</sub>ZrH<sub>x</sub>; the sample with x = 0 transformed almost completely into the rhombohedral phase of V<sub>2</sub>Zr which has  $\gamma \sim 16$  mJ/K<sup>2</sup> g-at. according to Ref. 3.

x	$\frac{\gamma}{(mJ/K^2 \text{ g-at.})}$	$\Theta_D$ (K)
0.33	13.2	210
0.57	11.3	220
0.80	9.1	243
1.22	5.2	305

1-c. No further discontinuity is observable, indicating that  $V_2ZrH_{1.3}$  is not superconducting above 2 K.

From the values for  $\gamma$  listed in Table I, the individual  $\gamma$  for V<sub>2</sub>ZrH<sub>1.3</sub> could be extracted by decomposing the specific heat into separate contributions from V<sub>2</sub>Zr and V<sub>2</sub>ZrH<sub>1.3</sub>. However, this way demands the proper knowledge of the phase boundary, in particular for the samples with lower x. A more direct and more reliable estimate for  $\gamma$  in V<sub>2</sub>ZrH<sub>1.3</sub> can be obtained by extrapolating the low-temperature part of the *C/T* curve for x=1.22 (see inset in Fig. 3) down to T=0. This gives  $\gamma(V_2ZrH_{1.3}) \sim 3 \text{ mJ/K}^2 \text{ g-at.}$ 

Actually, because of the small remainder (~6%) of superconducting V<sub>2</sub>Zr, this number has to be divided by 0.94 which leads to  $\gamma \sim 3.2 \text{ mJ/K}^2 \text{ g-at}$ . The error bar for this result is mainly determined by the uncertainty in the determination of the phase boundary at  $x_0 \sim 1.3$ . If we estimate this uncertainty in  $x_0$  by  $\pm 0.1$  (see Sec. III), as our final result we find  $\gamma = 3.2 \pm 0.3 \text{ mJ/K}^2 \text{ g-at}$ . in  $V_2 \text{ZrH}_{1.3}$ .

### V. MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility  $\chi(T)$  was determined from magnetization measurements in a Faraday balance in the same way as already described in Ref. 3. The measurements were performed at temperatures between 10 and 300 K. The results are shown in Fig. 4.

In interpreting these results, let us start with the sample with x = 0 (i.e.,  $V_2Zr$ ). For this sample,  $\chi(T)$  shows a marked step below 130 K. As has been discussed extensively in Ref. 3, this decrease is due to the transformation from the cubic to the rhombohedral phase. For increasing x, the step looses in height and is barely recognizable for the sample with x=1.22. This can easily be understood with the aid of the phase diagram shown in Fig. 2: At 130 K, hydrides with  $0 < x \le 1.3$  have almost completely decomposed into  $V_2Zr$  and  $V_2ZrH_{1.3}$ . Thus, since the step is produced by  $V_2Zr$ , its height is proportional to the amount of  $V_2Zr$  which decreases with increasing x.

For x=0.36, 0.57, and 0.80, two more features appear, namely, a further step around 200 K and a broad maximum around 260 K. We relate the further step to the transformation of the cubic  $\alpha'$  phase into the tetragonal  $\beta$ phase on cooling, and the maximum to the decomposition into the  $\alpha$  and  $\alpha'$  phase, in accordance with our phase dia-



FIG. 4. Magnetic susceptibility  $\chi$  as a function of temperature for samples of composition V<sub>2</sub>ZrH<sub>x</sub>.

gram. For x=1.22, the maximum has completely disappeared since for this concentration, the decomposition temperature has dropped to about 150 K. In principal, some additional structure should now be expected at this lower temperature. However, since we are very close to the low-temperature phase boundary  $x_0=1,3$ , the decomposition can have only little effect and thus remains undetectable.

#### VI. DISCUSSION

It was a major goal of our experiments to induce changes in the electronic density of states in  $V_2Zr$  by adding hydrogen and to observe their effects on the electronic properties of this material. Our intent was to do this in a quasicontinuous way of changing the hydrogen concentration x in small steps. However, it turned out that at low temperatures, this was impossible because of the decomposition of  $V_2ZrH_x$  into  $V_2Zr$  and  $V_2ZrH_{1.3}$ . So, information on the electronic properties at low temperatures can be provided for these two components only.

 $V_2Zr$  has already been discussed extensively in Ref. 3. Here, let us briefly summarize our results for  $V_2ZrH_{1.3}$ and contrast them with those for cubic  $V_2Zr$ :  $V_2ZrH_{1.3}$  is not superconducting above 2 K (cubic  $V_2Zr$ :  $T_c = 8.7$  K). Its coefficient of the electronic specific heat,  $\gamma$ , is about 3.2 mJ/k<sup>2</sup>g-at., which is smaller by a factor of about 7 than in cubic  $V_2Zr$  ( $\gamma \sim 23$  mJ/K<sup>2</sup>g-at.). At 10 K, the value of the magnetic susceptibility  $\chi$  is  $1.8 \times 10^{-4}$ emu/g-at. [cubic  $V_2Zr$ :  $\chi(10) \sim 3.9 \times 10^{-4}$  eu/g-at.]. Around 200 K,  $V_2ZrH_{1.3}$  transforms from the cubic into a tetragonally distorted phase with  $c/a \sim 0.992$ . This phase transition is accompanied by a decrease in  $\chi$  of about  $0.2 \times 10^{-4}$  emu/g-at.

From the experimental result for  $\gamma$ , one can estimate the value of the electronic band-structure DOS at the Fermi level, N(0), via the relation  $\gamma = (1+\lambda)N(0)$  $\times 2\pi^2 k_B^2/3$ . As will be outlined below, for V<sub>2</sub>ZrH<sub>1,3</sub> the influence of spin fluctuations should be negligible and  $\lambda$ can be identified with the electron-phonon coupling strength. Since  $T_c < 2$  K in this compound,  $\lambda$  cannot exceed 0.4 by much if the Coulomb interaction  $\mu^*$  is assumed to be  $\sim 0.1$ . As a first guess we assume  $\lambda \sim 0.4$ which leads to  $N(0) \sim 37$  states/spin Ry unit-cell. Thus, compared to its value in  $V_2Zr$  (~110 states/spin Ry unitcell),<sup>1,2</sup> N(0) is lower by a factor of 3. It is tempting to interpret this within a rigid band model on the basis of the band-structure calculations of Refs. 1 and 2 performed for  $V_2$ Zr. In these references, a wide valley slightly above  $E_E$ has been predicted for the electronic DOS, its value fluctuating around 50 states/spin Ry unit-cell. If the absorbed hydrogen atoms are assumed to deliver their electrons to the conduction bands of  $V_2Zr$ , the total number of electrons per unit-cell (which contains two formula units) will be increased by 2.6 and  $E_F$  shifted into the valley, thus explaining the lowering of N(0) in V<sub>2</sub>ZrH<sub>1.3</sub>.

The large decrease of N(0) is also reflected in the magnetic susceptibility  $\chi$  which at low temperatures is lowered by more than a factor of 2. This regards the total susceptibility which consists of a spin contribution  $\chi_s$  and an orbital contribution  $\chi_0$ . Since  $\chi_0$  is generally less sensitive of changes in N(0), the effect on  $\chi_s$  should be even larger. One may obtain a guess on  $\chi_s$  from the estimate for N(0) by use of the relation  $\chi_s = 2\mu_B^2N(0)S$ , where the Stoner enhancement factor S is defined through S = 1/(1-N(0)U). Assuming U to be unaffected by hydrogenating and equal to  $\sim 0.5 \times 10^{-2}$  Ry (value for cubic V<sub>2</sub>Zr, see Ref. 3), from  $N(0) \sim 37$  states/spin Ry unit-cell we find  $\chi_s \sim 0.4 \times 10^{-4}$  emu/g-at. which is about one fifth of the value in V<sub>2</sub>Zr ( $2.1 \times 10^{-4}$  emu/g-at.).<sup>3</sup></sup>

Let us turn to superconductivity. As has been discussed in Ref. 3, for  $V_2Zr$  there are strong indications that superconductivity is affected by spin fluctuations. It was our hope to get more insight into these physics by inducing *small* changes in N(0) through hydrogenation. However, the smallest feasible change in N(0) was a decrease to about one third of its initial value, leading to a very different system. There, because of the low value of the spin susceptibility  $\chi_s$ , the influence of spin fluctuations can safely be assumed to be negligible, but at the same time, the electron-phonon coupling strength  $\lambda$  has been lowered from somewhere between 1.4 and 2.4 (theoretical estimates for  $\lambda$  in  $V_2Zr$ , Refs. 1 and 2) to a value of 0.4 or even less.

A final remark regards the large isotope effect in  $V_2Z_{0.5}Hf_{0.5}H_x(D_x)$  reported in Ref. 10. For the  $V_2ZrH_x(D_x)$  system, such an effect can indeed be predicted: According to Ref. 7, in the deuteride the phase boundary  $x_0$  is close to 1 whereas in the hydride we found  $x_0 \sim 1.3$ . Now, for x somewhere between 1 and 1.3,  $V_2ZrH_x$  decomposes into  $V_2ZrH_{1.3}$  ( $T_c < 2$  K) and

 $V_2Zr$  ( $T_c = 8.7$  K) whereas  $V_2ZrD_x$  represents already a homogeneous solid solution of deuterium with low or vanishing  $T_c$ . If  $T_c$  is measured inductively (as was the case in the measurements of Ref. 10), even small portions of  $V_2Zr$  may still feign bulk superconductivity, and for x within the range between  $\sim 1$  and  $\sim 1.3$ , the hydride appears to be a bulk superconductor with  $T_c = 8.7$  K in contrast to the deuteride with  $T_c < 2$  K. Since in many respects, the  $V_2Zr$  system is very similar to the  $V_2Zr_{0.5}Hf_{0.5}$  system, our explanation of the isotope effect is likely to hold for this latter case, too.

# ACKNOWLEDGMENT

We are grateful to Dr. G. R. Stewart and Dr. H. Schmidt for continued interest in this work and valuable discussions.

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