The heat capacity of C15-type ZrCr$_2$H$_x$: evidence for low-energy localized excitations

LETTER TO THE EDITOR

The heat capacity of C15-type $ZrCr_2H_x$: evidence for low-energy localized excitations

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Abstract. Heat capacities $C(T)$ of C15-type $ZrCr_2H_x$ ($0 \leqslant x \leqslant 0.50$) have been measured over the temperature range 5.3–293 K. For the hydrogen-doped samples the heat capacities show considerable non-electronic contributions to the low-temperature linear $C(T)$ term and strong deviations from the Debye behaviour in the range 15–50 K. These features are consistent with the existence of additional low-energy modes related to hydrogen motion.

The intermetallic compound $ZrCr_2$ may exist in the form of two structural modifications (the hexagonal C14 or the cubic C15) both of which absorb large amounts of hydrogen. Recent nuclear magnetic resonance (NMR) experiments [1,2] have revealed the anomalously high hydrogen mobility down to low temperatures in the C15-type $ZrCr_2H_x$ ($x \leqslant 0.5$). The microscopic picture of hydrogen motion in these compounds is not yet clear. The experimental NMR relaxation data [1,2] suggest a coexistence of two types of diffusive H motion with different frequency scales (e.g. some kind of localized motion in addition to the long-range diffusion). The localized hydrogen motion which is not frozen out on the NMR frequency scale (10^7–10^{10} s^{-1}) down to $T \approx 30$ K has been found earlier in the related C5-type system $TaV_2H_x(D_x)$ [3,4]. Such localized motion may be described as hydrogen tunnelling in a double-well potential. In the present letter we report on the results of the heat capacity measurements in C15-type $ZrCr_2H_x$ showing strong effects of hydrogen motion at $T < 80$ K.

The preparation of the samples has been described in our previous papers [1,2]. Measurements were made on four $ZrCr_2H_x$ samples with $x = 0$, 0.27, 0.45 and 0.50. All the samples were prepared from the same ingot of $ZrCr_2$. According to the x-ray diffraction analysis, all the samples are single-phase compounds having the cubic C15-type structure; their lattice parameters are listed in table 1. No signs of a phase separation in $ZrCr_2H_x$ with $x \leqslant 0.5$ have been found in NMR experiments [1,2] down to 11 K; this is consistent with the tentative phase diagram of the $ZrCr_2$–H(D) system [5]. The heat capacity C was measured by the standard adiabatic method. Germanium and platinum resistance thermometers were used to measure the temperature in the ranges 5.3–20 K and 20–293 K, respectively. Experiments on the copper reference sample have shown that the

Table 1. Lattice parameters at room temperature and the low-temperature heat capacity fit parameters for $ZrCr_2H_x$ compounds.

Sample	a (Å)	δ (mJ mol^{-1} K^{-2})	θ_D (K)
$ZrCr_2$	7.210	4.8∓0.4	424∓6
$ZrCr_2H_{0.27}$	7.245	17.0∓0.3	397∓5
$ZrCr_2H_{0.45}$	7.260	15.9∓0.5	424∓7
$ZrCr_2H_{0.50}$	7.274	13.3∓0.4	428∓6

accuracy of the heat capacity measurements is about 1–2% at $T < 7$ K, 0.5% between 7 and 15 K, and 0.4% in the range 15–293 K.

Figure 1 shows the low-temperature behaviour of the heat capacity of $ZrCr_2H_x$ in the usual C/T against T^2 representation. For all the samples studied the experimental data at $T < 15$ K can be described by the expression

$$C = \gamma T + \beta T^3. \tag{1}$$

In metals γ is usually identified as the electronic specific heat coefficient proportional to the density of electron states at the Fermi level, $N(E_F)$, and

$$\beta = (12/5)\pi^4 Rz\theta_D^{-3}$$

with R, z and θ_D being the gas constant, the number of atoms in as formula unit and the limiting Debye temperature, respectively. The values of γ and θ_D resulting from the least-squares fit of equation (1) to the data are presented in table 1.
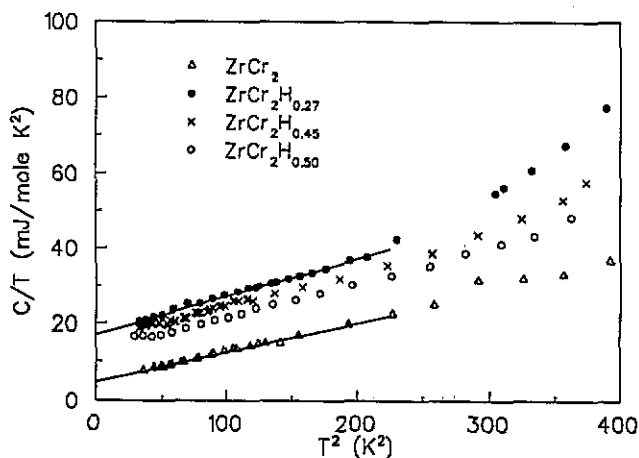
Figure 1. Low-temperature behaviour of C/T as a function of T^2. Solid lines represent least-squares fits of equation (1) to the data for $ZrCr_2$ and $ZrCr_2H_{0.27}$.

As can be seen from this table, the concentration dependence of γ appears to be non-monotonic. Furthermore, there is a strong difference between the apparent γ values for the hydrogen-free and hydrogen-doped samples. On the other hand, the measurements of the magnetic susceptibility, the proton Knight shift and the electronic contribution to the

proton spin relaxation rate [1, 2] unambiguously show that $N(E_F)$ in $ZrCr_2H_x$ increases monotonically with increasing x. This is also consistent with the results of the x-ray photoelectron spectroscopy [6] and the band structure calculations [7]. Similar behaviour of $N(E_F)$ as a function of x has been observed for the isoelectronic system $TiCr_2H_x$ [8]. This means that the apparent values of γ for $ZrCr_2H_x$ with low x should contain considerable non-electronic contributions (most probably related to hydrogen motion).

The linear (or nearly linear) contributions to $C(T)$ of non-electronic origin are known to exist in glasses [9]. They can be accounted for by the two-level system (TLS) model [10] implying the tunnelling of atoms in a double-well potential. However, the microscopic description of TLS in glasses remains to be elucidated. It is generally assumed that the existence of the double-well potentials is due to the disorder in glasses, so that a rearrangement of a group of atoms can switch the system between the adjacent local energy minima. For a metal–hydrogen system is it natural to relate TLS to the motion of a single H atom. The relevant example is the tunnelling of H in the double-well potential near O and N impurities in niobium [11]. For a number of metal–hydrogen systems double-well potentials are expected to be intrinsic [4, 12, 13].
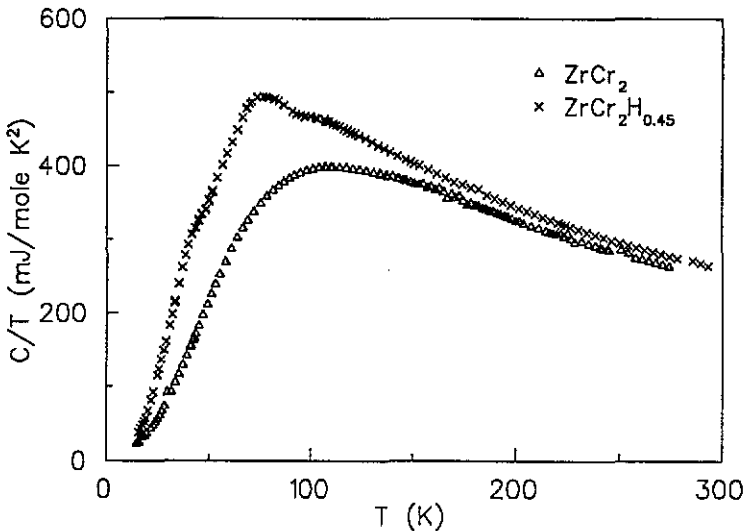

Figure 2. Temperature dependence of C/T for $ZrCr_2$ and $ZrCr_2H_{0.45}$.

Figures 2 and 3 show the temperature dependence of C/T for $ZrCr_2H_x$ in the range 15–293 K. For the hydrogen-free $ZrCr_2$ the behaviour of C/T is typical of crystalline solids. However, for the hydrogen-doped samples marked anomalies in C/T are observed. First, there are strong deviations from Debye behaviour of the heat capacity above 16 K (see also figure 1), the rise in C/T being more pronounced for the samples with lower x. This may be correlated with the fact that the low-temperature hydrogen mobility in $ZrCr_2H_x$ increases with decreasing x [2]. It should be noted that optical vibrations of hydrogen cannot give significant contributions to $C(T)$ in this temperature region since their characteristic energy is too high, being of the order of 0.15 eV [14].

Second, for $x = 0.27$ and 0.45 there are additional shoulder-like anomalies near 40 K. Figure 4 shows the temperature dependence of $(C - \gamma T)/T^3$ for $ZrCr_2$ and $ZrCr_2H_{0.27}$ below
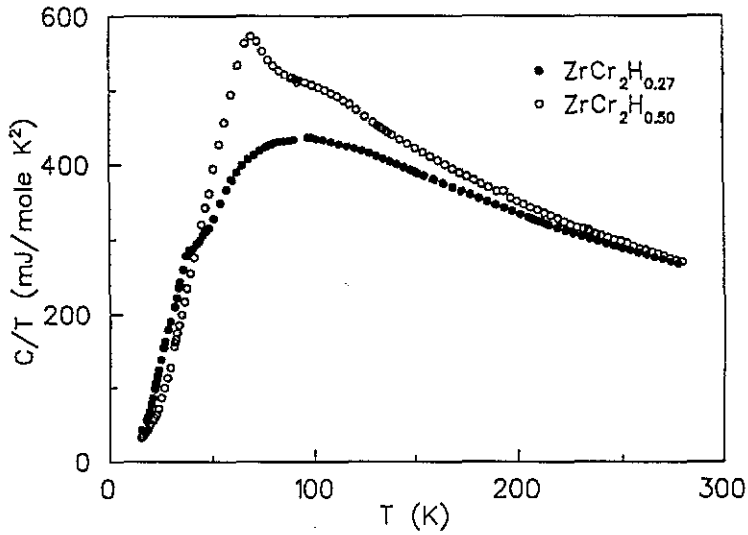
Figure 3. Temperature dependence of C/T for $ZrCr_2H_{0.27}$ and $ZrCr_2H_{0.50}$.
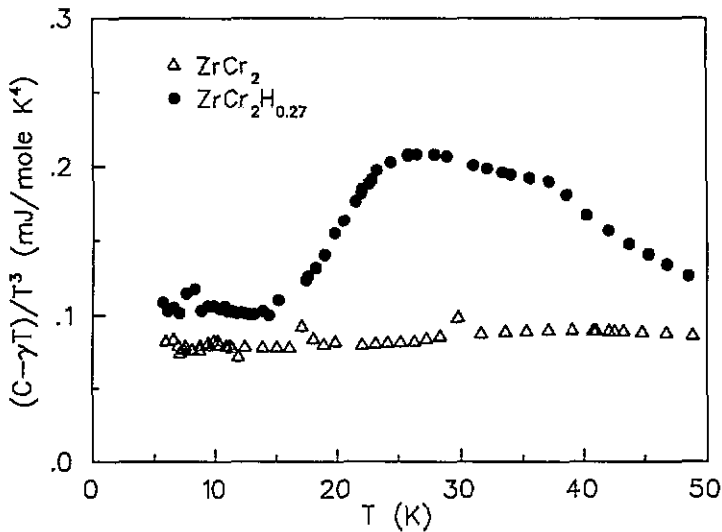

Figure 4. Temperature dependence of $(C - \gamma T)/T^3$ for $ZrCr_2$ and $ZrCr_2H_{0.27}$.

50 K. These axes are convenient for the analysis of deviations from the Debye behaviour of $C(T)$. As can be seen from figure 4, the effects of hydrogen doping are dramatic. For $ZrCr_2H_{0.27}$ the value of $(C - \gamma T)/T^3$ shows a maximum near 25 K. Similar maxima in C/T^3 near 10–20 K are typical of glasses [9]; they can be ascribed to the soft localized vibrational states [15].

A rough estimate of the density of such soft localized modes n may be obtained by comparing the energy of a single mode with the total excess vibrational energy. The energy of the soft mode is expected to be of the order of $4.9k_BT_{max}$ [16], where T_{max} is the

temperature of the $(C - \gamma T)/T^3$ maximum. The total excess vibrational energy can be estimated from the heat capacity data by subtracting the Debye contribution and integrating over the temperature range of the anomaly. For $ZrCr_2H_{0.27}$ such an estimate in the range 15–50 K gives $n = 0.1$ (per formula unit). This value is of the same order of magnitude as the hydrogen concentration ($x = 0.27$) in the sample.

For the samples with $x = 0.45$ and 0.50 the additional feature of $C(T)$ is observed near 70 K (figures 2 and 3). The behaviour of $C(T)$ in this region resembles the well known '50 K anomaly' in the heat capacity of concentrated $PdH_x(D_x)$ [17]. Neutron scattering experiments in PdD_x [18] have shown that this anomaly originates from hydrogen ordering. Similar anomalies in $C(T)$ related to low-temperature hydrogen ordering have recently been observed in C15-type $TaV_2H_x(D_x)$ [19]. In the case of $TaV_2H_x(D_x)$ the low-temperature phase transition is found to be 'weak', i.e. it is not accompanied by a change in the host lattice structure. For $ZrCr_2H_x$ the corresponding anomalies in $C(T)$ are even weaker. Thus one can hardly expect the formation of a phase with long-range order in $ZrCr_2H_x$ with $x \leqslant 0.5$; some kind of short-range order seems to be more probable. As has been noted previously [19], a direct relation may exist between the localized motion of H atoms and the low-temperature phase transition. Such a relation is known to exist, for example, in ferroelectrics of the KH_2PO_4 (KDP) type [20] where a proton can move between two equilibrium sites in the potential of the hydrogen bond.

In conclusion, our measurements have revealed glass-like features in the heat capacity of $ZrCr_2H_x$ with $0 < x \leqslant 0.5$ including considerable non-electronic contributions to the low-temperature linear $C(T)$ term and strong deviations from Debye behaviour in the range 15–50 K. These features suggest the existence of additional low-energy modes due to hydrogen motion; they may be related to the anomalously high hydrogen mobility in $ZrCr_2H_x$. To the best of our knowledge, this is the first time that such a glass-like behaviour of $C(T)$ has been observed in a crystalline metal–hydrogen system with considerable hydrogen content. The microscopic picture of hydrogen motion in this system may be clarified by neutron scattering experiments. Since the low-temperature anomalies are likely to imply hydrogen tunnelling, one may expect strong effects of hydrogen isotope substitution. Heat capacity measurements on $ZrCr_2D_x$ are in progress now.

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] Skripov A V, Belyaev M Yu, Rychkova S V and Stepanov A P 1989 *J. Phys.: Condens. Matter* **1** 2121
[4] Skripov A V, Rychkova S V, Belyaev M Yu and Stepanov A P 1990 *J. Phys.: Condens. Matter* **2** 7195
[5] Somenkov V A and Irodova A V 1984 *J. Less-Common Met.* **101** 481
[6] Schlapbach L, Osterwalder J and Riesterer T 1984 *J. Less-Common Met.* **103** 295
[7] Gupta M and Schlapbach L 1988 *Hydrogen in Intermetallic Compounds I* ed L Schlapbach (Berlin: Springer) p 139
[8] Bowman R C, Lynch J F and Johnson J R 1982 *Mater. Lett.* **1** 122
[9] Hunklinger S and Raychaudhuri 1986 *Prog. Low Temp. Phys.* **9** 267
[10] Phillips W A 1987 *Rep. Prog. Phys.* **50** 1657
[11] Wipf H, Steinbinder D, Neumaier K, Gutsmiedl P, Magerl A and Dianoux A J 1987 *Europhys. Lett.* **4** 1379
[12] Anderson I S, Berk N F, Rush J J, Udovic T J, Barnes R G, Magerl A and Richter D 1990 *Phys. Rev. Lett.* **65** 1439
[13] Svare I, Torgeson D R and Borsa F 1991 *Phys. Rev. B* **43** 7448

[14]   Richter D, Hempelmann R and Bowman R C 1992 *Hydrogen in Intermetallic Compounds II* ed L Schlapbach
          (Berlin: Springer) p 97
[15]   Buchenau U, Galperin Yu M, Gurevich V L and Schober H R 1991 *Phys. Rev.* B **43** 5039
[16]   Junod A 1980 *Solid State Commun.* **33** 55
[17]   Nace D M and Aston J G 1957 *J. Am. Chem. Soc.* **79** 3623
[18]   Ellis T E, Satterthwaite C B, Mueller M H and Brun T O 1979 *Phys. Rev. Lett.* **42** 456
[19]   Skripov A V, Mirmelshtein A V and Belyaev M Yu 1992 *Solid State Commun.* **81** 689
[20]   Blinc R and Zeks B 1974 *Soft Modes in Ferroelectrics and Antiferroelectrics* (Amsterdam: North-Holland)