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Magnetic characterization of Zr$(Cr_{1-x}Cu_x)_2$ alloys and their hydrides

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Magnetization measurements were carried out on the alloys Zr$(Cr_{1-x}Cu_x)_2$ (x=0, 0.1, 0.3, 0.5) before and after hydrogenation. All the binary and the ternary alloys, as well as their hydrides, exhibit a temperature-independent or nearly temperature-independent Pauli type of paramagnetism. Beside the Pauli paramagnetism, a ferromagnetic contribution to the total magnetization was observed for most of the alloys and their hydrides. It was also observed that hydrogen absorption enhances the Pauli paramagnetism as well as the ferromagnetism of the alloys. The rather unusual magnetic behaviour of these systems is briefly discussed in terms of 3d band filling of the transition metal, and is compared with some related systems.

1. Introduction

Zirconium-based Laves phase intermetallics react reversibly and absorb large quantities of hydrogen and have therefore attracted a great deal of attention as possible hydrogen storage materials [1–5]. Apart from their possible practical application, these materials are also of interest due to the drastic electronic modifications that occur as a result of the hydriding process. For example, in the system $Zr_{1-x}Ti_xMn_2$ which exhibits Pauli paramagnetism, upon absorption of hydrogen, paramagnetism is enhanced (low titanium concentration), or ferromagnetism or spin-glass behaviour is induced (higher concentration of titanium) [6].

It was found that partial substitution of chromium in $ZrCr_2$ by iron, cobalt, nickel or copper considerably affects the hydrogen capacity and the dissociation equilibrium pressure of $ZrCr_2$ [7–10]. It was also found that the Pauli paramagnetism of $ZrCr_2$ was changed into ferromagnetism in the system Zr$(Cr_{1-x}Fe_x)_2$, was strongly enhanced in the system Zr$(Cr_{1-x}Co_x)_2$ and was only moderately enhanced in the system Zr$(Cr_{1-x}Ni_x)_2$. Hydrogen uptake increased the magnitude of these effects.

In this paper the results of the magnetization measurements for the system Zr$(Cr_{1-x}Cu_x)_2$ and their hydrides are reported. The aim of this study was to obtain further information on the magnetic behaviour of ternary systems based on $ZrCr_2$ and their hydrides, which could help in obtaining a better understanding of their electronic structure.

2. Experimental procedure

The intermetallics compounds corresponding to the stoichiometry Zr$(Cr_{1-x}Cu_x)_2$ were prepared by arc melting. The purity of the starting materials was Zr 99.9 wt %, Cr 99.9 wt %, and Cu 99.98 wt % (all metals supplied by Ventron, Germany). One part of each sample was charged with hydrogen and the rest was used in the hydrogen-free form. The details of alloy preparation, hydrogen absorption procedure, hydrogen pressure–composition desorption measurements, as well as the apparatus used, have been described elsewhere [9, 11].

X-ray powder diffraction patterns of alloys and their hydrides were obtained using a Philips PW 1050 diffractometer equipped with a pulse height analyser; nickel-filtered CuK_α radiation was employed.

Magnetization measurements were performed on a vibrating sample magnetometer (VMS) in the Physics Department, University of Durham, as described in detail elsewhere [12, 13]. This VSM is fitted with an Oxford Instruments CF 1200 helium gas flow cryostat which allowed measurements to be made over the temperature range 4.2–330 K, in applied fields up to 12 kOe. $HgCo(CNS)_4$ was used to calibrate the system.

No special procedure was undertaken in order to prevent hydrogen release from the alloys, because the hydrides were assumed to be relatively stable. This was concluded from desorption isotherms with equilibrium pressure values of only several kilopascals at room temperature. Furthermore, no changes were observed in the X-ray patterns even after the hydrides had been exposed to air for several months.

3. Results

It has been reported earlier [10] that chromium in $ZrCr_2$ can be replaced by copper up to the composition

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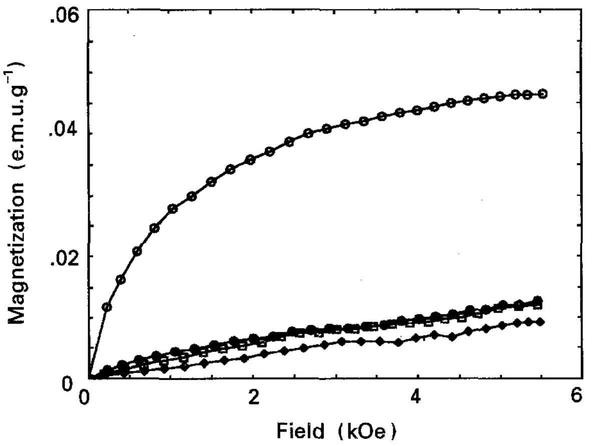

Figure 1 Magnetization versus field for the alloys $Zr(Cr_{1-x}Cu_x)_2$; x = (□) 0, (○) 0.1, (◇) 0.3 and (●) 0.5 at 300 K.

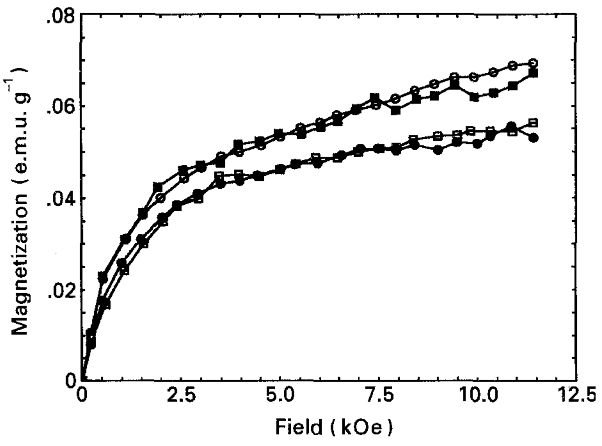

Figure 3 Magnetization versus field for (□, ●) $Zr(Cr_{0.9}Cu_{0.1})_2$ and (○, ■) $Zr(Cr_{0.7}Cu_{0.3})_2H_{2.98}$ at (■, ●) 10 K and (○, □) 300 K.

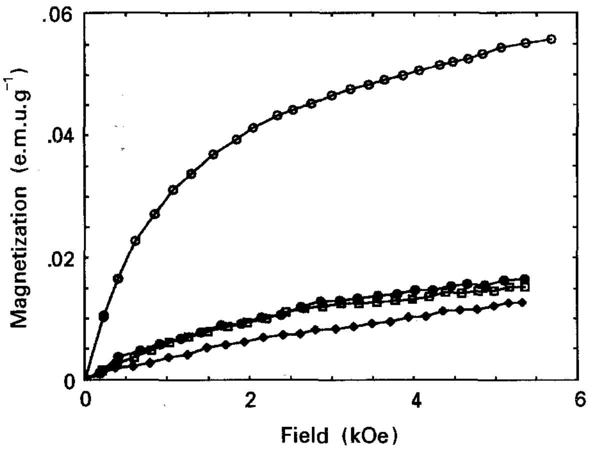

Figure 2 Magnetization versus field for the hydrides $Zr(Cr_{1-x}Cu_x)_2$; x = (□) 0, (○) 0.1, (◇) 0.3 and (●) 0.5 at 300 K.

$Zr(Cr_{0.5}Cu_{0.5})_2$. The cubic Laves structure ($MgCu_2$ type) of the binary $ZrCr_2$ is preserved in the whole ternary region. It was also reported that all the alloys react readily with hydrogen to form hydrides having two to three hydrogen atoms per formula unit. Hydrogen absorption increases the unit cell volume of the alloys by 22%–23%. It should be noted that the magnetic properties before and after hydrogenation of the other, hexagonal polymorph of $ZrCr_2$, have been reported elsewhere [14] and these data are included here for comparison.

Magnetization measurements carried out for the alloys $Zr(Cr_{1-x}Cu_x)_2$ ($x = 0, 0.1, 0.3, 0.5$) and their corresponding hydrides in the temperature range 10–300 K and in applied fields up to 12 kOe are illustrated in Figs 1–3.

All the systems investigated are paramagnetic. Most of the samples do not show a linear dependence of magnetization versus field, indicating there is a ferromagnetic component superimposed on a Pauli paramagnetic component. This is most pronounced for the alloy $Zr(Cr_{0.9}Cu_{0.1})_2$ and its hydride. The possibility of ferromagnetic impurities in raw materials has been investigated by measuring their magnetic properties under the same conditions as the alloys and their hydrides. It was undoubtedly confirmed that all the materials were of high magnetic purity, i.e. their magnetization versus field dependence was found to be always linear. Contamination of the alloys and their hydrides with ferromagnetic impurities during preparation and investigation was also rejected, because several batches of prepared alloys exhibit nearly the same ferromagnetic effects. One further point is that the ferromagnetic effect was enhanced after hydrogen uptake (Table I).

It is assumed that the apparent susceptibility, $\varkappa_{app}$, consists of two terms; a temperature-independent term, $\varkappa_0$, and a term which is the result of the ferromagnetic effect, σ_s/H. The saturation magnetization, σ_s, was determined by extrapolation of the linear behaviour of magnetization versus field, H, at high fields to zero field. The experimental values of susceptibility at fields above 5 kOe were fitted according to $\varkappa_{app} = \varkappa_0 + \sigma_s/H$. The relevant magnetic data are summarized in Table I.

4. Discussion

The results of this study indicate that all the samples, the host metals and the hydrides, are paramagnetic. The magnetization is temperature independent or nearly independent down to about 30 K. Below 30 K, a gradual increase in magnetization is observed. However, this is not completely valid for the $Zr(Cr_{0.9}Cu_{0.1})_2$ alloy and its hydride (Fig. 3), i.e. the samples that exhibit the greatest ferromagnetic effect. Fig. 4 illustrates the magnetization versus temperature curves for the $Zr(Cr_{0.7}Cu_{0.3})_2$ alloy and its hydride. In this region, none of the systems studied exhibits a Curie–Weiss behaviour. A possible source of the increase of magnetization below 30 K could be the presence of various oxygen contents retained within the sample, resulting in a pronounced change in magnetization as a consequence of the change of physical condition (liquid–solid), and/or the allotropic forms of oxygen. Namely, it is well known that the three solid and two liquid forms of oxygen exhibit different magnetic properties.

Taking all this into account, it was concluded that the samples exhibit Pauli paramagnetism. The samples also have a ferromagnetic component superimposed on the Pauli paramagnetic component, which is

TABLE I Magnetic data for the $Zr(Cr_{1-x}Cu_x)_2$ alloys and hydrides

Composition	Unit cell parameters (nm)	Susceptibility, $\varkappa_0$ (10^{-3} e.m.u. mol^{-1})	Saturation magnetization, σ_s (10^{-3} e.m.u. mol^{-1})	Reference
$ZrCr_2$	hex $a = ?$ $c = ?$	0.40	–	[15]
$ZrCr_2H_{3.8}$	hex $a = ?$ $c = ?$	1.16	–	[15]
$ZrCr_2$	$a = 0.5107$ $c = 0.8274$	0.83	–	[8]
$ZrCr_2H_{4.2}$	$a = 0.5470$ $c = 0.8944$	1.23	–	[8]
$ZrCr_2$	$a = 0.7200$	0.88	–	[8]
$ZrCr_2H_{4.1}$	$a = 0.7755$	0.97	–	[8]
$ZrCr_2$	$a = 0.5104$ $c = 0.8292$	0.41	–	[14]
$ZrCr_2H_{3.44}$	$a = 0.5388$ $c = 0.8835$	1.03	–	[14]
$ZrCr_2$	$a = 0.7213$	0.31	1.34	P.W.[a]
$ZrCr_2H_{3.7}$	$a = 0.7732$	0.35	5.94	P.W.
$Zr(Cr_{0.9}Cu_{0.1})_2$	$a = 0.7194$	0.32	38.30	P.W.
$Zr(Cr_{0.9}Cu_{0.1})_2H_{2.98}$	$a = 0.7693$	0.45	43.21	P.W.
$Zr(Cr_{0.7}Cu_{0.3})_2$	$a = 0.7200$	0.34	0.34	P.W.
$Zr(Cr_{0.7}Cu_{0.3})_2H_{2.25}$	$a = 0.7690$	0.52	0.44	P.W.
$Zr(Cr_{0.5}Cu_{0.5})_2$	$a = 0.7203$	0.32	3.60	P.W.
$Zr(Cr_{0.5}Cu_{0.5})_2H_{2.06}$	$a = 0.7742$	0.40	5.50	P.W.

[a] P.W., present work.

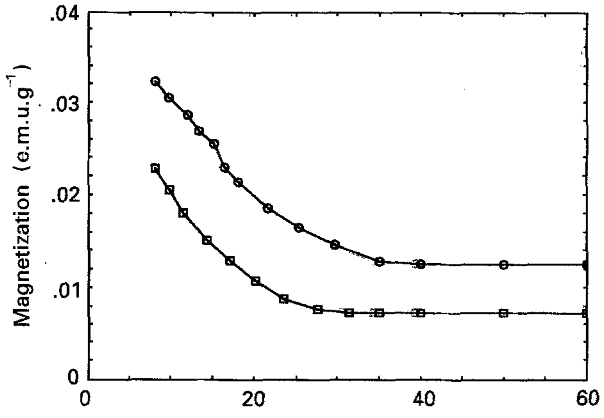

Figure 4 Magnetization versus temperature for (□) $Zr(Cr_{0.7}Cu_{0.3})_2$ and (○) $Zr(Cr_{0.7}Cu_{0.3})_2H_{2.25}$ at 5 kOe.

most pronounced for the alloy $Zr(Cr_{0.9}Cu_{0.1})_2$. Hydrogen absorption increases the Pauli type of paramagnetism as well as the ferromagnetic component of the alloys (Table I).

Before we attempt to discuss the results obtained for the ternary alloys and their hydrides, it is as well to compare the susceptibility values for both polymorphs of $ZrCr_2$ and their hydrides with the values obtained by other authors (Table I). Our results on the hexagonal $ZrCr_2$, which have been published elsewhere [14], indicate that this polymorph has a 33% larger susceptibility value than the cubic one. However, hydrogen uptake strongly enhances the paramagnetism of the hexagonal phase, but moderately enhances the paramagnetism of the cubic phase. This difference in behaviour may either originate with slight differences in the electron structure of the cubic and hexagonal $ZrCr_2$ (c/a ratio differs from the ideal value 1.667) or with chromium atoms residing on the zirconium sites in the cubic $ZrCr_2$. This will be discussed later. The susceptibility values for the hexagonal $ZrCr_2$ (Table I; [14]) are in good agreement with the values given by Jacob *et al.* [15] but not with the values found by Hirosawa *et al.* [8] which are larger by a factor of 2. After hydrogenation, our susceptibility values for the hexagonal phase [14] are in good agreement with the values given by both authors. It is interesting to point out that hydrogen uptake increases the susceptibility of the cubic $ZrCr_2$ only moderately. This is in agreement with the available data in the literature, i.e. with those given by Hirosawa *et al.* [8], but they reported values which are greater by a factor of 3.

The temperature-independent Pauli paramagnetism most likely originates with the 3d band electrons. These values do not change significantly with substitution of chromium by copper. Probably two opposite effects take place, i.e. copper atoms increase the local electron density of state of chromium, but at the same time the concentration of chromium decreases because the concentration of copper is increased. After hydrogenation, the Pauli paramagnetism of $Zr(Cr_{1-x}Cu_x)_2$ alloys is increased as a consequence of an increase in the electron density of states.

The most interesting feature observed in these systems is the unexpected induction of weak ferromagnetism. This was observed in virtually all the alloys investigated and increased after hydrogenation. The ferromagnetic component is temperature independent, which means that the temperature region investigated lies well below the Curie temperature. An explanation for the presence of ferromagnetism in these alloys does not seem to be easy and straightforward. However, we believe that some semiqualitative discussion can be given.

The ferromagnetism may be associated with small amounts of chromium atoms residing on the zirconium sites in the crystal structure. These chromium atoms carry magnetic moments as a result of better 3d band filling. This is the consequence of a larger electron transfer from zirconium to chromium (difference in electronegativity!) due to more surrounding zirconium atoms. All other chromium atoms residing on the expected small atom sites in the structure are surrounded with fewer zirconium atoms and the electron transfer is less pronounced. As a result, the later chromium atoms exhibit paramagnetism only. Consequently, ferromagnetic clusters exist in the structure, embedded in a paramagnetic matrix. The observed irregular variation in ferromagnetism with the composition could be explained by different amounts of chromium atoms residing on the zirconium sites. Some of our results on non-stoichiometric $ZrCr_2$ [16] support this assumption as do data published on the related systems based on $ZrMn_2$ [4] and $ZrCo_2$ [17].

The occurrence of ferromagnetism in cubic $ZrCr_2$ but not in hexagonal $ZrCr_2$ could also be explained in this way, i.e. the much larger deviation from stoichiometry, which is possible in the cubic structure [16], favours chromium atoms residing on zirconium sites.

It is worth comparing the results reported here with the results reported on related systems. In the system $Zr(Cr_{1-x}Fe_x)_2$ it was found that small quantities of iron induce Curie–Weiss behaviour at the same time as the temperature-independent Pauli susceptibility encountered for pure $ZrCr_2$, while higher iron quantities induce magnetic order [15]. In the system $Zr(Cr_{1-x}Co_x)_2$, the susceptibility of $ZrCr_2$ is enhanced by cobalt substitution, but is much weaker than in systems containing iron. At higher cobalt contents ($x = 0.5$) the total susceptibility is found to be a sum of the Pauli and Curie–Weiss contributions [8, 15]. Finally, in the system $Zr(Cr_{1-x}Ni_x)_2$, small quantities of nickel ($x \geq 0.375$) induce a Curie–Weiss contribution superimposed on the temperature-independent susceptibility term. However, this contribution is much weaker than in the system containing cobalt [14]. Hydrogen uptake always increased the magnitude of the observed effects.

The system $Zr(Cr_{1-x}Cu_x)_2$ does not strictly follow the observed trend in magnetic behaviour, because the transition metal changes from iron to copper in the 3d transition metal period. Rather, it behaves similarly to the $Zr(Cr_{1-x}Co_x)_2$ system, where small quantities of cobalt and hydrogen uptake were found to induce ferromagnetism with a very small saturation magnetic moment (0.01 μ_B formula unit) [15], or as in the systems based on $ZrMn_2$ where hydrogen absorption or substitution of zirconium with titanium induces weak ferromagnetism, which is not observed for binary $ZrMn_2$ [6, 15].

However, the possibility that the ferromagnetism observed in the system described in this paper is associated with small quantities of a second ferromagnetic phase (high T_c) not detectable by X-rays could not be completely ruled out, although optical metallographic investigations of the alloys prior to hydrogenation confirmed their single-phase nature. A more detailed investigation on the non-stoichiometric $ZrCr_2$, as well as on systems based on $ZrMn_2$ could probably shed more light on the interesting magnetic behaviour of these systems.

5. Conclusion

As a conclusion of the magnetic study of the $Zr(Cr_{1-x}Cu_x)_2$ alloys and their hydrides, we can say that all the alloys and their hydrides exhibit a temperature-independent or nearly temperature-independent Pauli paramagnetism. This paramagnetism probably originates with the 3d band electrons of chromium. In addition to the Pauli paramagnetism, a ferromagnetic contribution to the total magnetization was also observed and is most pronounced for the $Zr(Cr_{0.9}Cu_{0.1})_2$ alloy and its hydride. The weak ferromagnetism may be associated with small quantities of chromium atoms residing on the zirconium sites in the crystal lattice and carrying magnetic moments. These moments are a result of a larger electron transfer from zirconium to chromium atoms compared with the electron transfer from zirconium to chromium atoms residing on the expected small atoms sites of the structure. After hydrogen uptake, the Pauli paramagnetic component, as well as the ferromagnetic component, is enhanced.

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