Magnetic properties of Zr(Cr$_{1-x}$Fe$_x$)$_2$ alloys and their hydrides

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Abstract

The magnetic properties of MgZn$_2$-type Zr(Cr$_{1-x}$Fe$_x$)$_2$ ($0.3 \leqslant x \leqslant 0.7$) and Zr(Cr$_{1-x}Fe_x$)$_2H_y$ ($y \sim 3$) alloys have been investigated. Arrott plots showed no evidence for ferromagnetic ordering. ZFC/FC magnetization and Mössbauer spectroscopic data indicated spin glass-like freezing. Saturation moments in the unhydrided alloys decreased with decreasing Fe concentration, vanishing for $x \approx 0.3$. Hydrogen absorption made magnetic moments increase and freezing temperatures decrease. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Laves phase; Zr–Cr–Fe alloys; Hydrides; Spin glass

The structural and magnetic properties of transition metal-based Laves phase compounds AB$_2$ have aroused long-standing interest. Although various Zr(M$_{1-x}$Fe$_x$)$_2$ alloy systems have been investigated in detail (e.g. with M = Mn, Co, Al [1]), magnetic data are rather scarce for the M=Cr alloys [2,3]. The latter materials are further noteworthy for their high hydrogen absorption capability [4]. In this paper, we report on the magnetic properties of Zr(Cr$_{1-x}$Fe$_x$)$_2$ alloys in the intermediate concentration range, and on the changes induced by absorbed hydrogen.

Zr(Cr$_{1-x}$Fe$_x$)$_2$ samples with $x = 0.3, 0.4, 0.5, 0.6$ and 0.7 were prepared by arc melting high-purity elements in stoichiometric amounts, and all were found by X-ray diffraction to be single-phased with the hexagonal MgZn$_2$ structure. Each alloy was charged to its maximum hydrogen uptake at room temperature in a Sieverts-type facility. Absorbed hydrogen contents ranged from 3.7 to 2.5 H/f.u. for increasing Fe concentration. Both vibrating-sample magnetometer (in fields up to 9 T) and ^{57}Fe Mössbauer spectroscopy measurements were carried out on powdered samples, at temperatures between 4.2 and 300 K.

Hydrogen-free alloys: M vs. H curves did not reveal ferromagnetic behavior. The magnetization increased slowly with applied field, with no tendency toward saturation. Although some hysteresis was observed for $x = 0.7$ and 0.6, the Arrott plots shown in Fig. 1 do not extrapolate to a positive M^2 for any sample, thus confirming the absence of ferromagnetic ordering. Fig. 2 shows zero field-cooled (ZFC) and field-cooled (FC) magnetization data for Zr(Cr$_{0.3}$Fe$_{0.7}$)$_2$. The departure between these curves is a signature of spin glass-like freezing occurring at $T_f = 42$ K for this alloy. The other samples behaved in a similar manner, with lower freezing temperatures.

Mössbauer spectra at 4.2 K were magnetic sextets with broad lines, and were fitted with hyperfine field (B_{hf}) distributions. Spectra were measured at increasing temperatures until the magnetic splitting collapsed to zero. The vanishing of the average B_{hf} indicated spin freezing (SF) at the Mössbauer measuring time scale $\approx 10^{-9}$ s, therefore the corresponding SF temperatures were slightly higher than those obtained from static magnetization measurements. Saturation magnetic moments were estimated by extrapolating the $T = 4.2$ K magnetization curves to $(1/H) \to 0$. Results are shown in Fig. 3,

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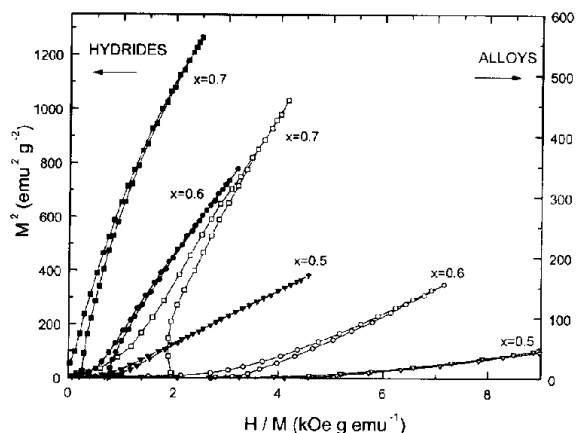
Fig. 1. Arrott plots at $T = 4.2$ K for $Zr(Cr_{1-x}Fe_x)_2$ (open symbols, right-hand scale) and $Zr(Cr_{1-x}Fe_x)_2H_y$ (closed symbols, left-hand scale).
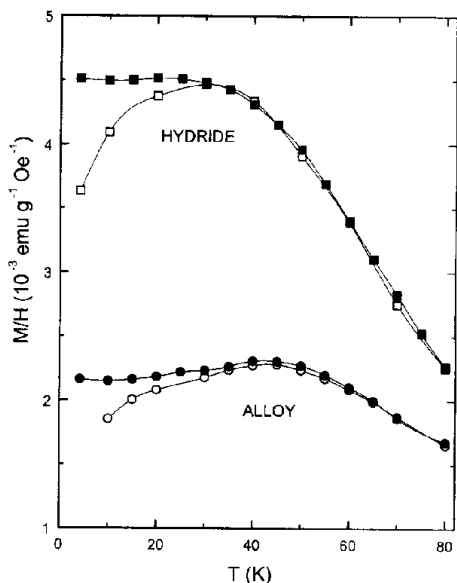

Fig. 2. Zero field-cooled (open symbols) and field-cooled (closed symbols) M/H vs. temperature for $Zr(Cr_{0.3}Fe_{0.7})_2$ (bottom) and $Zr(Cr_{0.3}Fe_{0.7})_2H_{2.5}$ (top). The applied field was 2 kOe.
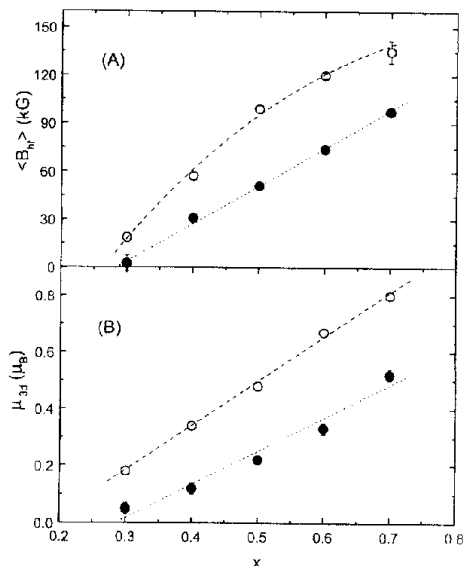

Fig. 3. Average hyperfine field at $T = 4.2$ K (A) and magnetic moment per 3d atom at $T = 4.2$ K (B) as a function of Fe concentration. Closed symbols: $Zr(Cr_{1-x}Fe_x)_2$, open symbols: $Zr(Cr_{1-x}Fe_x)_2H_y$.

as well as the average B_{hf} at 4.2 K. Both data are closely proportional to each other, tending to zero for $x \approx 0.3$. It is not known whether these moments can be assigned to Fe atoms only, as the existence of Cr moments cannot be ruled out.

The $Zr(Cr_{0.5}Fe_{0.5})_2$ alloy has been reported to be ferromagnetic with $T_C = (30 \pm 3)$ K and $\mu_s = 0.18$ μ_B/Fe atom [3]. From our results it is clear that spin glass-like phenomena, rather than long-range ferromagnetic ordering, are occurring in this system. This conclusion is fur-

ther supported by AC susceptibility results reported in Ref. [5].

Hydrides: Similar measurements were performed on $Zr(Cr_{1-x}Fe_x)_2H_y$ samples and the results are summarized as follows. (a) M vs. H curves were steeper than for unhydrided alloys, but no ferromagnetic behavior was detected, as evidenced by the Arrott plots shown in Fig. 1. (b) Spin freezing temperatures were lowered upon hydriding. This is illustrated by the ZFC/FC magnetization data in Fig. 2, and was corroborated by Mössbauer measurements. (c) The magnetic moment per 3d atom increased significantly upon hydrogen uptake and the onset of magnetism apparently shifted to a lower Fe concentration (Fig. 3B). The Fe hyperfine fields were likewise enhanced (Fig. 3A), but the proportionality between B_{hf} and μ_{3d} did no longer hold. This could be an indication of a significant Cr contribution to the magnetization in the hydrides.

The magnetic moment increase upon hydrogen absorption is a commonly observed effect, particularly in $Zr(M_{1-x}Fe_x)_2$ alloys [3,6]. It can be understood as a consequence of 3d band narrowing caused by cell volume expansion. On the other hand, the observed decrease of spin-freezing temperatures must be due to a weakening of exchange coupling between atomic moments. A similar trend, including suppression of ferromagnetism, was observed for $Zr(Al_{1-x}Fe_x)_2$; for $Zr(Mn_{1-x}Fe_x)_2$, in contrast, hydrogen absorption caused T_C to increase [6]. It thus appears that the hydrogen effect on exchange interactions is of a complex nature, in

which the role of a second 3d element is not fully understood.

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