Hydrogen in amorphous magnetic alloys

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Iron-rich $Y_{1-x}Fe_x$ amorphous alloys have been charged electrolytically with hydrogen to an H:Y ratio of approximately 3. The alloys are originally asperomagnetic, with spin freezing temperatures below 110 K, but they become soft ferromagnets on hydrogenation with Curie temperatures in excess of 400 K. The iron moment in a-$Y_{12}Fe_{88}$ changes from 1.96 to 2.24 μ_B in the hydride and the isomer shift increases by 0.15 mm/s. However, it appears that the main effect of the hydrogen is to shift a broad, mostly ferromagnetic exchange distribution with some antiferromagnetic interactions to an overwhelmingly ferromagnetic one. This is attributed to dilation of the iron–iron nearest-neighbour distances. By contrast, no significant effects on magnetic moment or exchange were detected on hydrogenating amorphous $Fe_{40}Ni_{38}Mo_4B_{18}$ (Metglas 2826 MB), but the in-plane anisotropy was modified and the soft magnetic properties degraded.

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Hydrogen can bring about important modifications in the electronic structure and magnetic properties of crystalline alloys of transition metals, especially in alloys with the rare earths, La, Y or Sc [1]. We report here its effect on some representative amorphous magnets.

In crystals there may be no change in lattice symmetry on hydrogenation, but there usually is some lattice dilation which can be regarded formally as the effect of a negative pressure. The transition metal moment is destroyed entirely in certain hydrides, whereas in others ferromagnetism appears on hydrogenation [1]. Effects in crystalline Y-Fe [2,3] and Sc-Fe [4] intermetallic compounds are less dramatic, but quite significant nevertheless. The iron moment increases by about 20% in the hydride, whereas the ferromagnetic exchange coupling, generally a sensitive function of interatomic spacing, may be either strengthened or weakened according to the alloy composition. Changes in Curie temperature of ±50% found in YFe_2 and Y_6Fe_{23} [2] were attributed by Buschow to the increase of lattice constant on hydrogenation, in view of the pressure derivatives of T_c known for these alloys [4]. Rare earth iron hydrides have H:Fe ratios of order unity, but much smaller quantities of hydrogen suffice to modify the micromagnetic behaviour of soft magnetic materials [6]. Strain fields associated with hydrogen impurities interacting with domain walls via magnetostriction can modify the hysteresis behaviour and ac losses.

Relatively little has been published on hydrogen in amorphous magnetic alloys [7], but it should act in much the same way as it does in crystals. Of particular interest is the possibility of using it to modify the exchange distribution in random, noncollinear magnets where interactions of both signs are present [8]. We present in this paper some results of a preliminary investigation of the influence of hydrogen on amorphous magnetic materials. Alloys chosen for study were iron-rich members of the amorphous $Y_{1-x}Fe_x$ series, particularly $Y_{12}Fe_{88}$, and a standard commercial ferromagnetic glass $Fe_{40}Ni_{38}Mo_4B_{18}$ (Metglas 2628MB). The Metglas alloy is a good soft ferromagnet [9], prepared in the form of a ribbon 12 x 0.04 mm by melt spinning. Our $Y_{1-x}Fe_x$ alloys were prepared by dc triode sputtering from Y-Fe targets onto a liquid nitrogen cooled substrate, yielding sheets approximately 100 x 50 x 0.02 mm

[10]. An extensive account of their magnetic properties has been given recently [10, 11]. Briefly, the iron-rich alloys, x≳0.5 resemble canonical spin glasses in some respects, whereas in other respects they behave more like normal hard ferromagnets. Their magnetic properties are attributed to random but directionally anisotropic spin freezing, asperomagnetic order, below a temperature T_M which only reaches ~110K in the amorphous alloys containing most iron. By contrast, the Curie points of crystalline YFe_3, Y_6Fe_{23} and Y_2Fe_{17} are 539 K, 476 K and 310 K respectively [12]. We suggested previously that an asymmetric distribution of direct exchange interactions, predominantly positive but with some negative, antiferromagnetic interations associated with the shortest Fe-Fe distances was the cause of their unusual magnetic behaviour [10,11]. Extreme structure-sensitivity of the magnetic order in amorphous $Y_{1-x}Fe_x$ is indicated by the variations in the properties reported by different groups, using different preparation techniques [10,11,13,16]. In this respect $Y_{1-x}Fe_x$ is quite unlike other amorphous magnetic alloy systems such as $Y_{1-x}Co_x$.

First attempts to introduce hydrogen into the alloys, by exposing them to hydrogen gas pressure, were unsuccesful. No change was detected in their appearance, magnetization or Mossbauer spectra after exposure to a hydrogen pressure of 1 MPa for a week, and a pressure of 15 MPa failed to induce any measurable change in a $Y_{32}Fe_{68}$. Similar treatment of crystalline Y-Fe alloys reduces them to powders of hydrides such as YFe_2H_4 [2]. The difference in behaviour of crystalline and amorphous alloys may be related to the absence of grain boundaries in the latter. We therefore resorted to a standard electrolytic procedure [17]. The sample formed the cathode of a cell with a platinum anode and an electrolyte of 0.1 M H_2SO_4 containing 10 ppm of Na AsO_3 as a hydrogen recombination poison. Currents of order 100 mA/cm^2 were passed for several minutes but it was found that hydrogenation could be achieved, albeit more slowly, without a current. The method worked best for a-$Y_{1-x}Fe_x$ alloys with x≳0.75. Less iron-rich compositions dissolved quite rapidly in the acid bath. Both Y-Fe and Metglas alloys became brittle on charging, and the tendency of the sample electrode to curl up and break effectively limited the charging time. Recovery times after charging were of the order of a week, or longer. Analysis of a
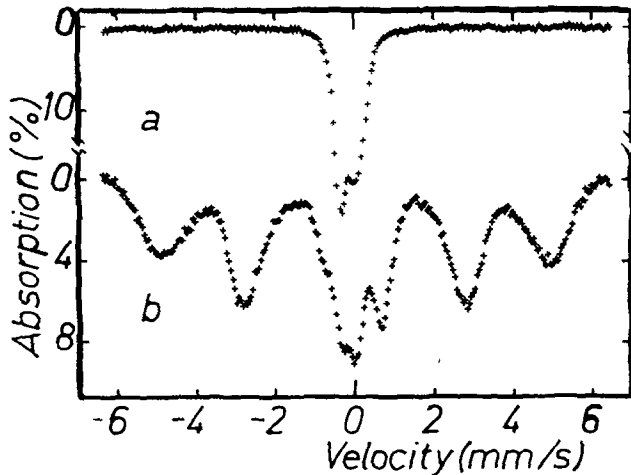
Figure 1. Mössbauer spectra at 290 K of amorphous $Y_{12}Fe_{88}$ a) before and b) after electrolytic hydrogenation.
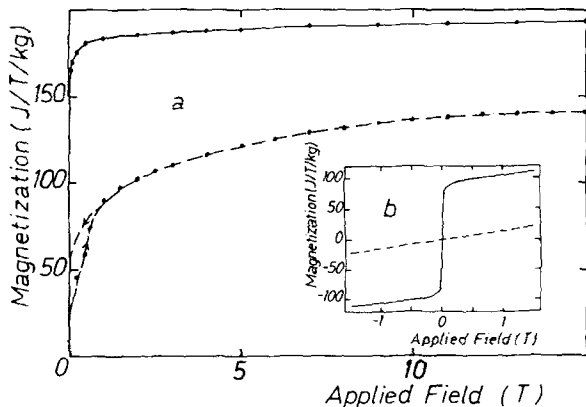

Figure 2. Magnetization curves for amorphous $Y_{12}Fe_{88}$ (dashed lines) and $Y_{12}Fe_{88}H_{36}$ (solid lines) at 4.2 K (a) and at 290 K (b). The field was applied parallel to the plane of the sample.

hydrogen-loaded a-$Y_{12}Fe_{88}$ sample by [11]B bombardment gave its hydrogen content as $Y_{12}Fe_{88}H_{36}$. X-ray analysis showed that the amorphous nature of the sample was unchanged, but there was an indication of some increase in interatomic distances. Measurements were made of the Mössbauer spectra and magnetization of a-$Y_{1-x}Fe_x$ and $Fe_{40}Ni_{38}Mo_4B_{18}$ before and after hydrogen loading.

Hydrogenation of the iron-rich a-$Y_{1-x}Fe_x$ alloys produces a remarkable change in their magnetic properties, which may be seen in the room-temperature data on a-$Y_{12}Fe_{88}$ presented in figures 1 and 2b). At this temperature, hydrogen changes the alloy from a strong paramagnet (ferromagnetic short-range correlations persist well above T_M [10]) into a true soft ferromagnet. Coercivity is only 32A/m (0.4 Oe), similar to that of untreated Metglas 2826 MB. The Mössbauer spectrum in figure 1b) shows that the bulk of the sample is magnetically ordered with an average hyperfine field B_{hf} = 32.5 T and an isomer shift δ 0.15 mm/s greater than in the unhydrogenated alloy. The relative intensity of the Δm=0 lines, 40%, shows that the moments have some tendency to lie in the plane of the film, as expected from the demagnetizing effect. Extrapolation of the hyperfine field of spectra in the temperature range 80-300 K using molecular field theory with S = 1 yields a Curie temperature of 410 K. Numerical data on the alloy before and after hydrogenation are summarized in the table. The increase in hyperfine field at T = 0 corresponds to an increase in iron moment of 8% if strict proportionality of these two quantities is initially assumed. Part of the sample (~10%) is

initially unaffected by the hydrogenation treatment, leading to superposition of a small amount of the spectrum of figure 1a), which disappears in time.

Magnetization curves at 4.2 K in fields up to 15 T shown in figure 2a) highlight the qualitative change in the magnetic order that is brought about by hydrogen. The curve for untreated $Y_{12}Fe_{88}$ shows the features expected of an asperomagnet, namely i) a large fraction of the saturation magnetization is readily induced by the applied field, ii) the reduced remanence (M_r/M_s = 0.31) has a typically ferromagnetic value yet iii) the magnetization cannot be properly saturated in any laboratory field. The saturation magnetization M_s, estimated by extrapolating the magnetization curve to $1/B_0$ = 0, corresponds to an average moment of 1.96 μ_B/Fe. The curve for a-$Y_{12}Fe_{88}H_{36}$ is typically ferromagnetic, apart from the slight high-field slope which is attributed to a residue of unconverted material. The moment per iron atom in the ferromagnetic, hydrogenated material obtained by extrapolating the nearly horizontal section to B_0 = 0 is 2.24 μ_B/Fe. The increase in iron moment with hydrogen derived from the 4.2 K magnetization curves is consistent with that deduced from the hyperfine fields extrapolated to T = 0 $B_{hf}(0)$, although the effect is rather less than it is in crystalline Y-Fe compounds. For instance the iron moment changes from 1.45 μ_B in YFe_2 to 1.83 μ_B in YFe_2H_4, and the isomer shift increases by 0.46 mm/s [3]. The smaller proportion of hydrogen in the amorphous alloy may account for the smaller increases in moment and isomer shift.

Turning now to the Metglas alloy, we could find no sign of any change in magnetization, hyperfine field or Curie temperature in the hydrogenated sample. However Mössbauer spectra at 80K, shown in figure 3, indicate that there has been some effect on the macroscopic anisotropy. The relative intensity of the Δm = 0 transitions changes from 43% in the untreated ribbon to 37% after hydrogen treatment, suggesting a departure from a domain structure with the magnetization lying mainly in the ribbon plane to one where the directions of the moments in the domains are more dispersed. The effect is evident on comparing the relative intensities of lines 5 and 6 in the spectra of figure 3. Furthermore, the initial permeability of the ribbon is reduced and the coercivity increased on hydrogenation by about a factor of three. No measurement was made of the hydrogen content of the sample, but it is believed to be much less than in the iron-rich $Y_{1-x}Fe_x$ alloys. Figure 4 shows the effect of hydrogen on the hysteresis

These experiments point the way to further work with hydrogen in amorphous magnetic alloys. The major effect in amorphous $Y_{1-x}Fe_x$ alloys appears to be the strengthening of ferromagnetic exchange interactions relative to antiferromagnetic ones which transforms the iron-rich alloys from asperomagnets to soft ferromagnets, and raises the magnetic ordering point by a factor of 4. There is no evidence that random local anisotropy plays any significant part in determining the magnetic properties of the series. By analogy with the crystalline Y-Fe hydrides, the effect on the exchange distribution is probably the result of increased Fe-Fe nearest neighbour distances, rather than a hydrogen-induced change in the electronic structure of iron. An increase in iron moment cannot in itself be responsible for a change in character of the magnetic order. The prospect therefore emerges of using hydrogen as a way of modifying the exchange distribution P(J) of concentrated amorphous alloys in a controlled way. This should prove valuable in studying further the problem of magnetic order arising from an asymmetric random exchange distribution, and the passage from spin-glass-like to ferromagnetic ground states. Insofar as the Metglas alloys are concerned, we have seen that their soft magnetic properties may be degraded by hydrogen, but a detailed examination of the domain structures is needed to explain the obervations properly.

Table: Magnetic properties of a-$Y_{12}Fe_{88}$ before and after hydrogenation

	$B_{hf}(0)$ T	$\mu_o{}^c$ m_B/Fe	$\mu_s{}^d$ μ_B/Fe	T_M K	T_c K	Order	δ^e mm/s
$Y_{12}Fe_{88}$	30.1 ± 0.2^a	2.08	1.96 ± 0.08	109 ± 4	–	asperomagnetic	-0.19
$Y_{12}Fe_{88}H_{36}$	32.5 ± 1.5^b	2.24	2.24 ± 0.05	–	410 ± 20	ferromagnetic	-0.04

a   Measured at 4.2 K.
b   Extrapolated from data in the range 80–300 K.
c   Average iron moment obtained from $B_{hf}(0)$, assuming a conversion factor of $14.5T/\mu_B$ [11].
d   Average iron moment obtained from magnetization curves at 4.2 K, as described in the text.
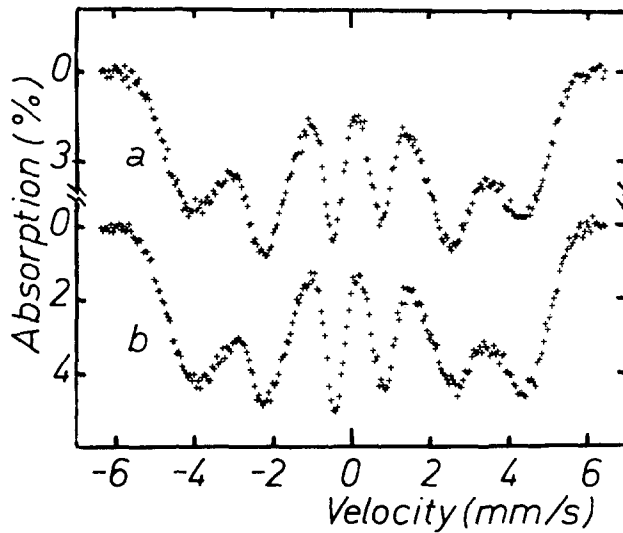e   Isomer shift at 290 K relative to iron metal.

Figure 3.   Mössbauer spectra of a-$Fe_{40}Ni_{38}Mo_4B_{18}$ at 80 K a) before and b) after hydrogenation.

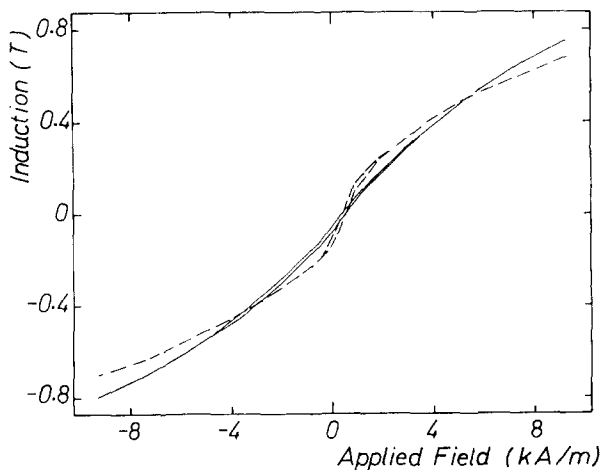Figure 4.   Magnetization curves of a-$Fe_{40}Ni_{38}Mo_4B_{18}$ at 290 K before hydrogenation (dashed line) and after hydrogenation (solid line).

REFERENCES

[1]   W.E. Wallace, Topic in Applied Physics Vol. 28: 'Hydrogen in Metals I'. G. Edfeld J. Volkl eds., (Springer, Berlin) Chap. 7 (1978).

[2]   K.H.J. Buschow, Solid State Comm. 19, 421 (1976).

[3]   K.H.J. Buschow and A.M. van Diepen, Solid State Comm. 19, 79 (1976).

[4]   P.H. Smit, H.C. Donkersloot and K.H.J. Buschow J. Appl. Phys. 53, 2460 (1982).

[5]   M. Brouha, K.H.J. Buschow and A.R. Miedema, IEEE Trans. Mag. MAG 10, 182 (1974).

[6]   H. Kronmuller, Topics in Applied PHysics Vol. 28 'Hydrogen in metals I' G. Adefeld and J. Volkl eds. (Springer,Berlin) Chap. 11 (1978).

[7]   B.S. Berry and W.C. Pritchet J. Appl. Phys. 52, 1865 (1981).

[8]   J.M.D. Coey, J. Appl. Phys 49, 1646 (1978).

[9]   Allied Chemical Data Sheet on Metglas 2826MB (1979).

[10]   J.M.D. Coey, D. Givord, A. Lienard, and J.P. Rebouillat J. Phys. F. 11 2707 (1981).

[11]   J. Chappert, J.M.D. Coey, A. Lienard and J.P. Rebouillat J. Phys. F 11 2727 (1981).

[12]   D. Givord, F. Givord and R. Lemaire, J. Physique 32, C1-668 (1971).

[13]   J.J. Rhyne, J.H. Schelleng and N.C. Koon, Phys. Rev. B. 10 4672 (1974).

[14]   D.W. Forrester, N.C. Koon, J.H. Schelleng J. Appl. Phys. 50, 7336 (1979).

[15]   J.J. Croat and J.F. Hubst J. Appl. Phys. 53 2294 (1982).

[16]   Y. Nishihara, T. Katayama and S. Ogawa, J. Appl. Phys. 53, 2285 (1982).

[17]   B.J. Berkowitz, J.J. Burton, S.R. Helms and R.S. Polizzatti, Scri Met 10, 871 (1976).