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Evidence for disorder-induced enhancement of magnetic interactions in superconducting Zr–Fe metallic glass by neutron irradiation

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Abstract. The electrical resistivity, superconducting T_c, and the normal state magnetic susceptibility have been measured in neutron irradiated $Zr_{75}Fe_{25}$ metallic glass. With doses up to 7.5×10^{17} n cm^{-2} we observe small and temperature independent shifts towards increased magnetic interactions in the electron gas magnetic susceptibility and the development of a feature in the normal state resistivity close to T_c which is related to magnetic interactions. These observations give evidence for enhanced magnetic interactions due to increased disorder as predicted by interaction theories.

An interesting prediction from interaction and weak localization theories is an increased tendency towards magnetism with increased randomness in disordered systems (Fukuyama 1981, Finkel'stein 1984, Castellani *et al* 1984). In particular, in a metallic superconductor, one would expect increased disorder to give an enhanced magnetic susceptibility, develop spin fluctuations which would depress T_c, and eventually destroy superconductivity, but retain a metallic phase of unknown magnetic structure (Fukuyama 1985).

The observation of this prediction is impeded by the difficulty of varying disorder continuously. By varying the thickness of a thin film, e.g. in addition to disorder effects, one is likely to introduce effects from the slowly varying dimensionality. When comparing different three-dimensional amorphous metals, variations between sample properties of the order of several percent may mask effects from different degrees of disorder in the limited range of variation available.

We have chosen to monitor randomness by neutron irradiation of a metallic glass. By starting with a disordered metal one avoids the large effects which are associated with the destruction of a lattice. On the other hand, we can only produce a small increase in disorder and small shifts in sample properties.

Glassy $Zr_{75}Fe_{25}$ is chosen for this investigation since it is fairly close in concentration to a ferromagnetic phase boundary while still being in a superconducting phase (Batalla *et al* 1985). In this way one would expect to facilitate a transition towards increased magnetic interactions and have the advantage of an additional observable in the superconducting transition temperature.

The magnetic susceptibility of the normal state of metallic glasses may contain contributions from small amounts of clusters. Although the influence of irradiation

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on these clusters is in itself an interesting topic, it is of a different character and may instead prevent observation of the predictions from interaction theories. Therefore we later describe in detail how cluster contributions can be accurately separated from matrix properties. We find a small shift towards magnetism in the bulk magnetic susceptibility. Further evidence for increased magnetic interactions is obtained from the development of a peak in the electrical resistivity in the superconducting fluctuation region above T_c.

Samples were prepared from elements of nominally 99.8 wt% pure Zr and 99.999% Fe (both from Alfa Ventron) in a standard way by arc-melting several times in Ar gas of reduced pressure and melt-spinning in He gas. In order to produce increased disorder, fast neutrons are suitable as a radiation source since they penetrate bulk foils and presumably produce homogeneously distributed radiation damage. To ascribe the changing properties of the sample to the influence of disorder unambiguously, however, it is important that relaxation effects are minimized and that the sample temperature is not allowed to increase during irradiation. Therefore it is convenient to use a low-power reactor†. The sample container was covered with Cd to avoid activation from thermal neutrons and placed in an empty fuel element position at the reactor core edge. It was surrounded on all sides by water, the temperature of which never exceeded 25 °C. The fast neutron flux ($E_n > 1$ MeV) at the irradiation position was about 1.5×10^{11} n cm^{-2} s^{-1}. Therefore we could reach 7.5×10^{17} n cm^{-2} only after 1.5 year of irradiation and some time for intervening experiments. Assuming that the energy needed to produce a displacement of an atom from its regular position is 30 eV, we estimate that this dose corresponds, within about a factor of three, to 3×10^{20} displaced atom/cm^3. Of the order of 1% of the atoms have thus been displaced as a result of either a direct neutron–atom collision or in a cascade resulting from such a collision. The increase in disorder within the sample is therefore comparatively small.

The magnetic susceptibility, χ_m, was measured in a Faraday balance in fields up to 1.2 MA m^{-1} (1.5 T) at temperatures T from 4.3 to 300 K. χ_m was measured before neutron irradiation and after a dose of 3×10^{17} n cm^{-2}. The increase in χ_m was found to be small and therefore irradiation was continued to a higher dose. All three measurements were made on the same pieces of a sample ribbon, which allowed us to clearly identify a small but distinct enhancement of χ_m with irradiation at all values of T. Figure 1 shows χ_m plotted against T at 1 MA m^{-1} for one sample in all three states.

χ_m is somewhat field dependent in metallic glasses such as Zr–Fe and Zr–Co (Altounian and Strom-Olsen 1983, Hedman and Rapp 1984). This property is usually ascribed to ferromagnetic clusters in the matrix. These clusters may have a wide range of sizes, magnetization against field curves, and Curie temperatures. It turns out, however, that χ_m can be decomposed into a field independent component χ and a cluster component

$$M = \chi_m H = \chi H + \omega\sigma. \tag{1}$$

The last term represents saturated clusters of weight fraction ω and mean saturation magnetization σ. One can obtain χ and $\omega\sigma$ from fitted straight lines in plots of χ_m

† The reactor R2-0 at Studsvik, Sweden was used. This is a 1 MW light water moderated reactor with fuel elements of Materials Testing Reactor type and with natural convection cooling. The fast neutron flux measured at the sample position and at a reactor power of 500 kW was 8×10^{11} n cm^{-2} s^{-1}. The reactor was usually operated only at day time, however, and then at an average power of 100 kW.

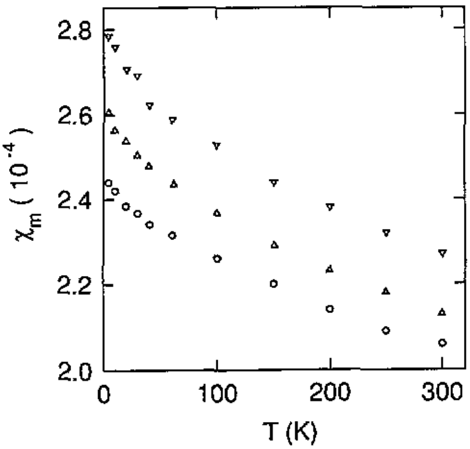

Figure 1. The measured magnetic susceptibility at $H = 1$ MA m^{-1} as a function of temperature at different radiation doses (sample no 5). ○, before irradiation; △, after 3×10^{17} n cm^{-2}; ▽, after 7.5×10^{17} n cm^{-2}. χ_m and χ in this and subsequent figures are obtained from the measured values using the density 6800 kg m^{-3} from Altounian and Strom-Olsen (1983).

against $1/H$ or M against H. This technique has a wide applicability. In particular, the detailed structure of ferromagnetic clusters does not have to be resolved. All saturated clusters are separated by equation (1), be they in the form of magnetic Zr–Fe clusters, ferromagnetic impurities of the starting materials or possible ferromagnetic impurities on the surface.

While the physical origin of $\omega\sigma$ is simple enough this may not be the case for χ, to which contributions may come from unsaturated clusters, superparamagnetic clusters, free moments, and ferromagnetic clusters above their Curie temperatures, as well as from the matrix. In the present case, the following discussion shows that the contributions to χ from clusters and free moments are small. χ thus very nearly represents the magnetic susceptibility of an ideal Zr–Fe matrix.

Before discussing the present data in detail, it should be pointed out that the decomposition of χ_m according to equation (1) has proved to be very useful in previous investigations of metallic glasses (Rapp and Hedman 1984, Flodin *et al* 1986). One example is the possibility of varying $\omega\sigma$ by more than a factor of three by using different cooling rates in metallic glasses with a similar chemical composition. The matrix properties remained unchanged as inferred, for example, from the small effects on the superconducting T_c, and the matrix susceptibility of the different samples was found to be identical to within ±2% except for the lowest temperatures (Rapp and Hedman 1984). In the present case, with measurements on the same samples, an even higher resolution in χ is expected.

The analysis of the present data is illustrated in figure 2 by the plot of M against H at four temperatures after an irradiation with 7.5×10^{17} n cm^{-2}. Straight lines were fitted to the data at fields above about 0.6 MA m^{-1}. The straight lines fit the data excellently. In similar analyses of all 33 different combinations of irradiation and measuring temperatures shown in figure 1, the relative root mean square deviation (RMS) was about 5×10^{-4}.

M can thus be decomposed into a part χH with field independent susceptibility χ, and a part $\omega\sigma$, originating from those ferromagnetic clusters that could be saturated

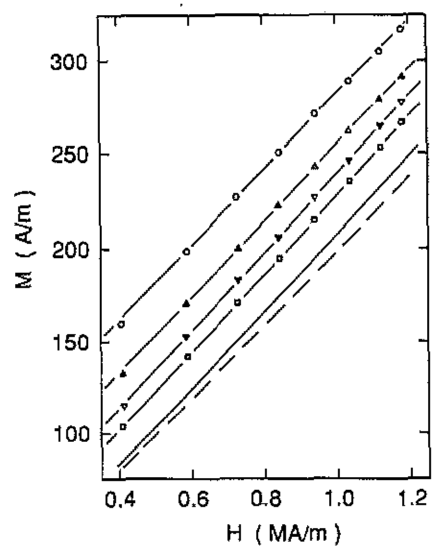

Figure 2. Analysis of equation (1) in the form of magnetization $M = \chi_m H$ against H. Data after irradiation with 7.5×10^{17} n cm^{-2} are shown at four different temperatures. ○, 4.3; Δ, 100; ∇, 200; □, 300 K. The lines through the data are fits described in the text. The straight lines in the lower portion of the figure show $M = \chi H$ against H at two temperatures: full line, 300 K, broken line, 4.3 K.

at the moderately high fields between 0.6 and 1.2 MA m^{-1}. For the present samples an upper limit for ω is 600 ppm. The results are shown in figure 3(a) for $\omega\sigma$ against T and in figure 3(b) for χ against T. The uncertainty in χ can be (over)estimated by displacing the two end points of a fitting interval in figure 2 by one RMS value in opposite directions. Such errors are contained within the data points of figure 3(b), and the uncertainty in χ is thus negligibly small.

Since our main interest is focused on the effect of neutron irradiation on the matrix susceptibility of $Zr_{75}Fe_{25}$, it is important to investigate whether all effects of unwanted ferromagnetic clusters can be separated from χ. The following three arguments all indicate that the cluster contributions to χ are negligibly small.

(i) Small clusters that behave superparamagnetically give a Curie–Weiss-like contribution to χ at low T. The same is true for free Fe moments and also for such small clusters that cannot be saturated even at the highest fields used here. Their Curie temperatures should, however, be quite low. Figure 3(b) shows in fact a rise of χ at low T, but it is small, less than the effect of irradiation and unaffected by it.

(ii) The larger clusters, which could be well separated from χ_m in their saturated states, have a wide range of Curie temperatures, Θ, which is shown by $\omega\sigma$ against T in figure 3(a). These larger clusters contribute to χ at temperatures above Θ. This contribution may be estimated by the following simple model. The $\omega\sigma$ against T curves can be considered to be distribution functions of Θ. Fe atoms with ferromagnetic moment m and paramagnetic moment p in clusters with Curie temperature Θ contribute a Curie–Weiss term $(-\Delta\omega\sigma/m)p^2/3k_B(T-\Theta)$. It is assumed that the paramagnetic Curie temperature is equal to Θ. The integration over Θ of these terms was stopped a few degrees below T in order to avoid the singularity. With $m = gS\mu_B$ and $p^2 = g^2\mu_B^2 S(S+1)$ for all the magnetic Fe atoms and with $S = 2$, the result is that the ferromagnetic clusters contribute to χ with at most 1%. This contribution is

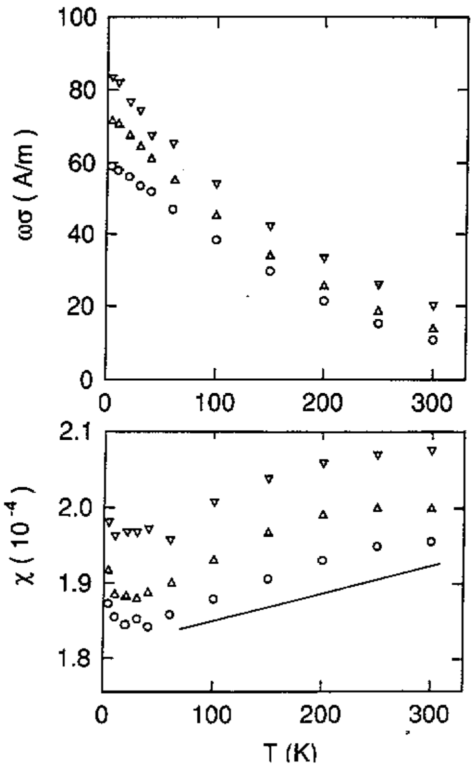

Figure 3. Results of the decomposition of χ_m: (a) cluster part, $\omega\sigma$, and (b) field independent magnetic susceptibility χ. ○, before irradiation; △, after 3×10^{17} n cm^{-2}; ▽, after 7.5×10^{17} n cm^{-2}. The slope of the straight line in the bottom of (b) is equal to that of polycrystalline Zr above 77 K (Collings and Ho 1979). This slope is roughly equal to that of the present data illustrating the well known dominance of Zr d-electrons at the Fermi surface of Zr-rich metallic glasses (Oelhafen *et al* 1979).

overestimated since S is likely to be partly smaller than two.

(iii) We further note that in spite of the strong variation of $\omega\sigma$ by a factor of four to five with T, and the substantial variation of $\omega\sigma$ with irradiation (40% increase at 4 K and almost 100% at 300 K), the curves of χ against T are strictly parallel as detailed later. This observation gives strong evidence against spurious magnetic effects.

The enhancement of χ in figure 3(b) is fairly constant as a function of temperature. In fact the average enhancement of χ with irradiation at eleven temperatures between 4 and 300 K is 4.4 and 11.9×10^{-6} at 3 and 7.5×10^{17} n cm^{-2} respectively and the uncertainty in these mean values is only about 0.2×10^{-6}. Thus there is a small but significant upward curvature in the matrix susceptibility against irradiation dose. This is illustrated in figure 4, where data from figure 3(b) at four different temperatures have been plotted.

Ageing or oxidation effects are not expected to be observable in χ. In a previous investigation of similar Zr–Co glasses, a 3% increase in $\omega\sigma$ was observed after being stored in air for 39 months (Flodin *et al* 1986). The results for χ, however, were within a few tenths of a percent at all temperatures between 4 and 300 K. Independent evidence against the sensitivity of the matrix susceptibility to oxygen atmosphere is obtained from the similar results of χ in two different samples of the same chemical composition, where one sample had been melt-spun in nitrogen enriched air and the other in argon gas (Flodin *et al* 1986).

Therefore the increase in χ with neutron dose in figure 4 indicates a bulk phenomenon in an electron gas with an enhanced exchange interaction due to increased randomness, in agreement with interaction theories (Fukuyama 1981, 1985, Finkel'stein 1984, Castellani *et al* 1984). The shift towards magnetism is small and the weak upward curvature of the four curves in figure 4 suggests that we are far from a magnetic transition.

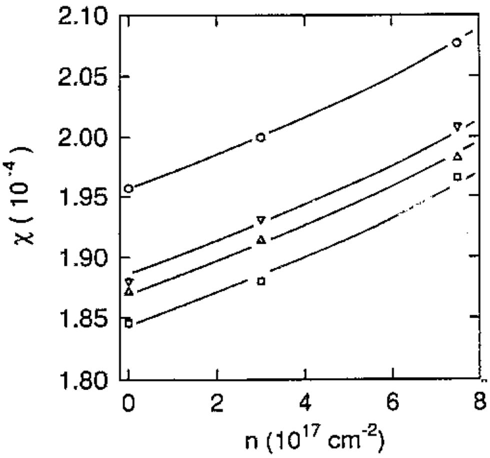

Figure 4. Matrix magnetic susceptibility χ against irradiation dose at four temperatures. △, 4.3; □, 20; ▽, 100; ○, 300 K.

Other conceivable alternative interpretations should also be examined; for example neutron irradiation might cause a structural rearrangement in the amorphous phase with an enhanced density of states and magnetic susceptibility; or the special atmosphere in the reactor might imply significantly different conditions compared with our ageing experiments. Both these possibilities seem less likely; the former due to the resistivity results described later, the latter due to the parallel shift with irradiation in figure 3(*b*). The influence from the nuclear reactions of Zr and Fe is most probably negligible. The most abundant product (initially Nb) would have a concentration below 0.01 ppm.

The low temperature electrical resistance is shown in figure 5, before irradiation and after a dose of 7.5×10^{17} n cm^{-2}. Irradiation causes a peak in the normal state resistivity, ρ, close to T_c. At the lower irradiation dose no peak was observed†. Peaks in ρ due to spin fluctuations have been observed at 20–40 K in Fe–Zr metallic glasses for larger Fe concentrations, in the region around the critical concentration for ferromagnetism (Strom-Olsen *et al* 1985). The present anomaly is larger, sharply peaked and occurs just above T_c and is similar to that observed recently in glassy superconducting Cu–Zr alloys with small amounts of magnetic impurities (Lindqvist *et al* 1990). The resistivity in an almost superconducting matrix is not expected to be sensitive to small clusters. This is confirmed, for example, by the negligible sensitivity of T_c to large cluster variations (Rapp and Hedman 1984). Furthermore, $\omega\sigma$ in Zr–Cu

† At the lower irradiation dose, the measurements were only made in an ^{4}He cryostat to 1.5 K, where the resistance had decreased to 96% of its value at 4.2 K.

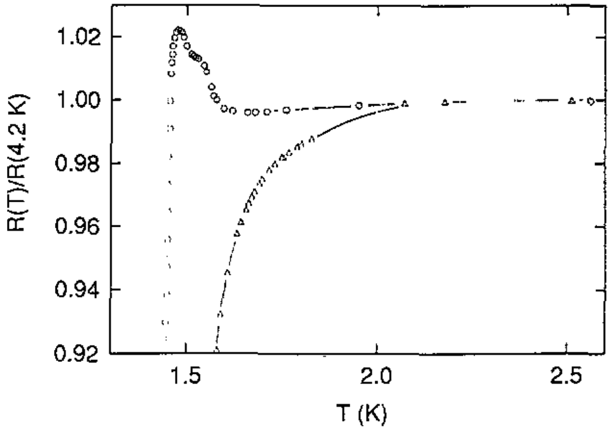

Figure 5. The electrical resistance in the region above the superconducting transition temperature (sample no 6). Δ, before irradiation; ○, after 7.5×10^{17} n cm².

is typically an order of magnitude smaller than in Zr–Fe and not correlated with the magnitude of the peak (Hedman *et al* in preparation). Therefore this peak is a bulk effect. Although the origin of the peak is not yet known, the results by Lindqvist *et al* (1990) clearly indicate that it is due to magnetic interactions. We conclude that the present resistivity results give evidence for enhanced magnetic interactions with irradiation. This result is independent of the analysis for the magnetic susceptibility and thus strengthens our conclusions.

It can be seen from figure 5 that T_c decreases slightly with irradiation. The temperature difference between resistive midpoints is 0.14 K corresponding to 10% depression. The width of the transition is about 0.06 K for both samples in figure 5. Increased disorder can increase or decrease T_c depending on the competing effects in the electron–phonon interaction (Belitz 1987). In a previous study of a neutron-irradiated Mo–Ru–B metallic glass (Kramer *et al* 1979), T_c was found to increase by 2% for a radiation dose more than 10 times larger than that used by us. The presently observed decrease in T_c is consistent with the observations of increased magnetic interactions, and the general trend for T_c predicted by interaction theories (Fukuyama 1985). However, due to the competing effects mentioned, we cannot draw any firm conclusions from the change of T_c alone.

Resistivity increases with disorder, but the observation of this effect may be hampered by difficulties with the geometrical form of metallic glass samples. For instance, Kramer *et al* (1979) observed no significant enhancement of ρ with neutron irradiation within their measurement accuracy of 10%. We measured the resistance on the same sample pieces but the positions of the potential edges were not marked before irradiation. Therefore the results are estimated to be accurate only to about 1%, corresponding to variations of dimensions over the length of the sample. Nevertheless, for both sets of samples (nos 5 and 6), we could observe an increase of about $4 \pm 2\%$ in ρ, after irradiation with 7.5×10^{-17} n cm^{-2}, thus confirming that irradiation has produced some increased disorder. For 3D metals, the depression of T_c scales roughly as ρ^2 (Beasley *et al* 1984). Our results of 4% resistivity increase and 10% decrease of T_c are roughly in line with this expectation but this observation cannot be emphasized presently with few data and the possibility that other effects could influence T_c.

In conclusion we have found some evidence for a disorder-induced enhancement of magnetic interactions in glassy $Zr_{75}Fe_{25}$. Increased randomness is produced by moderate fast neutron irradiation and leads to an increase in ρ and a decrease in T_c. Enhanced magnetic interactions are inferred from two independent observations: i.e. an increase in the exchange enhancement of the magnetic susceptibility; and the development of magnetic interactions in the electrical resistivity in the superconducting fluctuation region.

Acknowledgments

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