LETTER TO THE EDITOR

Comment on the hyperfine field of amorphous iron

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Abstract. It is shown that, contrary to the supposition of Takács and Hargitai, there is no conclusive experimental evidence for a substantially reduced atomic magnetic moment in amorphous iron.

The atomic magnetic moment of pure amorphous iron has been assumed to be substantially reduced in comparison with that of the body centred cubic (bcc) phase. It was claimed (Takács and Hargitai 1983, to be referred to as TH) that the iron hyperfine fields in amorphous Fe–B alloys cannot be interpreted correctly without taking this reduction into account.

According to these authors, the hyperfine field of iron atoms with and without boron nearest neighbours must be treated separately. In analogy to the sensitive atomic volume dependence of iron magnetic moments in crystalline materials (Andersen et al 1977) TH assume that $H$, the hyperfine field of an iron atom without boron neighbours, is empirically related to $V/Z$, the average Voronoi polyhedron volume belonging to one neighbour:

$$H = H_1 + \beta V/Z.$$  \hspace{1cm} (1)

Here $V$ is the volume of the Voronoi polyhedron of the central iron atom and $Z$ is the total coordination number determined from the pyramidal volume contributions defined by the faces of the polyhedron and the central atom (Carter 1976). $H_1$ and $\beta$ are parameters to be determined experimentally from the hyperfine field distribution of pure amorphous iron.

These parameters are estimated by TH from the Mössbauer measurements of a sputtered amorphous film (Bjarman et al 1980). In this way an anomalously low average hyperfine field (20 T) and a large width of the hyperfine field distribution (comparable to that of Fe–10 at% B amorphous alloy) are attributed to pure amorphous iron.

In the following we will show that these values are in variance with both the general trends found in different crystalline materials which are used by TH to suggest equation (1) and with the available experimental data.

Figure 1 shows the absolute values of the saturation magnetic moment and hyperfine field for several different crystalline iron structures as a function of both $V$ and $V/Z$. Here HCP indicates the hexagonal phase of iron attained by high pressure. This remains

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Figure 1. Absolute values of the saturation magnetic moments and the hyperfine fields (full and empty symbols, respectively) for the different modifications of iron as a function of (a) average atomic volume and (b) \( V/Z \) (for explanation see text). The full curve is for guidance only. The circle indicated by TH/BKW corresponds to the hyperfine field value attributed to the Mössbauer measurement of Bjarmann et al (1980) by TH. The broken and chain lines are explained in the text.

non-magnetic down to 30 mK under a pressure of 21.5 GPa according to the Mössbauer studies of Cort et al (1982). The lattice parameters are \( a = 2.461 \, \text{Å}, c/a = 1.603 \) (Mao et al 1967). The existence of two face centred cubic (FCC) phases is reported for iron from different extrapolations. The FCC phase (FCC <) with the low lattice parameter \( (a = 3.547 \, \text{Å}, Kaufman and Ringwood 1961) \) is obtained from the extrapolation of the data of Fe–C, Fe–N and Fe–Mn alloys, in good agreement with the data of FCC iron precipitated in a copper matrix. This latter material has been found to be antiferromagnetic both from neutron and Mössbauer measurements (Abrahams et al 1962, Johanson et al 1970, Gonser et al 1963). The FCC phase (FCC >) with the large lattice parameter \( (a = 3.64 \, \text{Å}, Kaufman et al 1963) \) is extrapolated from different FCC alloys: Fe–Pt, Fe–Pd and Fe–Ni. They are ferromagnetic with a large iron magnetic moment. Despite the difficulties and uncertainties in the extrapolations the trends mentioned above are well established by several different experimental methods including magnetisation, neutron and Mössbauer measurements. The BCC iron phase is the well-known low-temperature modification with \( a = 2.866 \, \text{Å} \) and \( \mu_{Fe} = 2.22 \mu_B \) (Mao et al 1967).

For a BCC lattice the coordination number determined from the definition of Carter
(1976) is \( Z = 12.3 \) (L. Takács, private communication), very close to that of close-packed structures. Because of this, similar trends are expected in the function of both \( V \) and \( V/Z \). The data in figure 1(a) follow the theoretical trends for the volume dependence of the magnetic moment very closely in the close-packed crystalline structures calculated by Andersen et al. (1977). It is clear from figure 1 that both \( \mu_{Fe} \) and \( H_{Fe} \) are monotonously increasing functions of \( V \) (or \( V/Z \)) which saturate, and a linear approach of these functions (equation (1)) has a limited validity range.

A lower bound for the average volume of amorphous iron \( \bar{V} = 12.2 \, \text{Å}^3 \) is obtained from the upper limit of the packing fraction \( \eta = 0.67 \) (determined from the mass density of Fe–B alloys, Shirakawa et al. 1981) and the suggested atomic diameter of Fe; \( r = 2.5 \, \text{Å} \) (TH). The dense random packing model of Takács (1980) uses \( \eta = 0.64 \), resulting in \( V = 12.6 \, \text{Å}^3 \). The peak value of the volume distribution published by Srolovitz et al. (1981) gives \( \bar{V} = 12.3 \pm 0.2 \, \text{Å}^3 \), which is also a lower estimation of \( \bar{V} \) because of the marked asymmetry of the distribution. A value of \( V/Z = 1.058 \, \text{Å}^3 \) is calculated by TH for dense random packing models.

All of these values are larger than those of the crystalline modifications, even above the values of bcc iron. Figure 1 and equation (1), providing the empirical relation of TH, thus imply that the magnetic moment and hyperfine field of amorphous iron should be at least as high as these parameters of bcc iron.

This expectation is confirmed by the Mössbauer investigation of 2–5 at\% O\(_2\) and Ar stabilised amorphous iron films where 35.5 T was obtained for the mean hyperfine field of amorphous iron (Litterst et al. 1978). This value is plotted in figure 1 at the amorphous mark and agrees very well with the curve determined by the crystalline data. Since the largest part of the volume distribution curve of amorphous iron (Srolovitz et al. 1981) covers the saturation range of figure 1(a), a rather narrow hyperfine field distribution is expected in good agreement with the result of Litterst et al. (1978). So far as we are aware no other hyperfine field data have been published on amorphous iron films with similarly low impurity content. It is also reassuring that the average magnetisation results of Felsch (1969) for samples with comparable impurity content and the polarised neutron scattering and saturation magnetisation data of Schweizer (1982) on amorphous Fe produced by electrical discharge-induced decomposition also indicate a similarly high value of atomic magnetic moment.

It is somewhat unexpected in this context that the room-temperature Mössbauer spectrum of Bjarmann et al. (1980) on a sputtered amorphous film is taken by TH as representing pure amorphous iron. They attribute \( \bar{H} = 20 \, \text{T} \) for the saturation value of the average iron hyperfine field and \( \sigma_H = 4 \, \text{T} \) for the mean square deviation of the hyperfine field distribution. The broken line in figure 1(b) corresponds to equation (1) using the parameters of TH \( (H_1 = -32.9 \, \text{T}, \beta = 50 \, \text{T} \, \text{Å}^{-3}) \) evaluated from the above data. In a later work Bjarmann and Wäpppling (1981) reported the hyperfine field distribution and temperature dependence of the average value of their sample. From these data \( H = 24 \, \text{T} \) and \( \sigma_H = 6 \, \text{T} \) values are extrapolated to \( T = 0 \). The chain line in figure 1(b) corresponds to equation (1) with \( H_1 = -55.5 \, \text{T} \) and \( \beta = 75 \, \text{T} \, \text{Å}^{-3} \) evaluated from these latter values. If these new \( H_1 \) and \( \beta \) parameters were to be used in equation (1) together with the \( \langle V/Z \rangle \) values published by TH, a significant change would occur in the calculated \( P(H) \) distributions of amorphous Fe–B alloys. For example, at 12 at\% B content, the centre of the hyperfine fields of iron atoms without boron neighbours, the relative amount of which is 21\% at this concentration, shifts from the 25.0 T calculated by TH to 31.4 T.

The fundamental problem, however, is the relevance of this sputtered film to pure amorphous iron. Back-scattering analysis of the sputtered amorphous film with 4 MeV
\( \alpha \) particles has revealed approximately 10 at% carbon content (Bjarman and Wäppling 1981). In the Fe–B system, samples with very similar metalloid content have also been investigated (Schaafsma et al. 1980, Chien and Unruh 1982). It is well established that the iron hyperfine field still increases at this composition with decreasing boron content. The width of the hyperfine field distribution is practically composition independent in the whole investigated (9–30 at%) boron concentration range. The identification of the width of the hyperfine field distribution of an iron–10 at% metalloid sample with the volume fluctuations of pure amorphous iron is unfounded.

In conclusion we have no knowledge of any hyperfine field data which would indicate a significantly reduced magnetic moment for pure amorphous iron. On the contrary, the agreement of different methods even using materials prepared under significantly different conditions is especially convincing for the existence of a magnetic moment within 10% for the BCC Fe value for moderately (2–5 at%) impurity stabilised amorphous Fe. The magnetic properties of nominally pure amorphous iron represent one of the most interesting (and probably one of the most difficult) problems of amorphous magnetism. Since the pioneering measurements of Felsch (1969) it seems to be well-established that the magnetic moment is approximately constant near to the value of bcc iron above 2 at% impurity content (Si) and then quickly decreases to a value of about 1.8 \( \mu_B \) at 0.2 at% Si. The decrease is suggested as indicating the low magnetic moment of the pure amorphous iron. Despite the existence of a genuine reduction of atomic magnetic moment being neither well documented experimentally nor understood theoretically, the assumption (Wright 1976, 1977) seems to be justified that the reduction might be associated with mixed magnetism, i.e. the pure amorphous Fe may not be a simple ferromagnet. The average magnetisation data extrapolated for the case of ‘pure’ amorphous iron from samples under 2 at% impurity content are by no means conclusive for the atomic magnetic moments. Since the measurements of Felsch (1969) were performed in small external magnetic fields (max. 700 Oe) and the coercive field increases with decreasing impurity content suggesting increased magnetic anisotropy, the determination of atomic magnetic moments from these measurements may well be problematic. Similar trends indicating reduced magnetisation are also to be found in several measurements which are connected indirectly with the magnetisation such as low-angle electron diffraction (Bostanjoglou and Giese 1976) and Hall effect (Raeburn and Aldridge 1978) measurements. In these cases the problem of magnetic anisotropy also prevents an unambiguous determination of the saturation moment. Even if apparent saturation is attained the extrapolation of average magnetisation to individual atomic moments is a highly questionable procedure without having detailed data on the magnetic state of the amorphous films. The reduction in iron magnetisation is probably caused by the onset of mixed magnetism (Wright 1977) due to the stresses and anisotropies. Unfortunately no direct measurement of local magnetic moment (i.e. neutron investigation or hyperfine field data) is available for this composition range.

The 2 at% critical concentration mentioned earlier corresponds to about 50 atoms influenced by a single impurity thereby demonstrating that this is not a nearest neighbour effect. That is, even if the behaviour of atomic magnetic moments below and above this concentration were found to be qualitatively different (for which there is no conclusive experimental verification) it is difficult to see the physical meaning of the simple interpolation between the two incompatible regimes.

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