Rigid magnetic foam-like behavior in ball-milled FeAl

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After ball-milling nonmagnetic FeAl a grain structure resembling to a rigid magnetic foam is indicated by Mössbauer spectroscopy. It consists of nanosize nonmagnetic grains with ferromagnetic boundaries formed by about two atomic layers of Fe. The magnetic behavior is uncommon: (i) the transition to the paramagnetic state is glass-like and magnetic relaxation sets in at low temperatures; (ii) the magnitude of the local Fe magnetic moments decreases linearly with temperature; (iii) in high fields a strongly anisotropic ferromagnetic behavior is observed.

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Many studies have already made evident that the magnetic properties of nanosize objects are to a large extent determined by the surface properties. Surface atoms may have magnetic anisotropies, moments, and even magnetic ordering significantly different from those of the bulk atoms due to their altered topological arrangement, reduced coordination, and increased volume. Despite this, separation of the surface effects from other special features of the nanomaterials is far from trivial. In most sample preparation techniques (evaporation, ball milling, chemical reduction, etc.) both the surface and the bulk properties are influenced by impurities, mixing, and disordering of the components. A definitive scaling with the inverse characteristic length of the nanosize objects is rarely observed. A magnetic foam without substrate, i.e., a nonmagnetic volume (bubble) surrounded by a continuous magnetic layer, would exhibit solely surface and/or thin film effects. Former studies of magnetic foams concentrated mostly on the field dependence of the coarsening of the domain patterns of fluid froths. We are not aware of any study of the fundamental magnetic properties of a frozen foam. In the following it will be shown that ball-milled FeAl is a good candidate for the material that can be termed as a rigid magnetic foam.

The structure of Fe-Al alloys is based on the bcc lattice of \( \alpha \)-Fe in a broad concentration range. Two ordered phases appear around the stoichiometric FeAl and Fe\(_2\)Al. FeAl crystallizes to a CsCl-type (B2) crystal structure, in which each Fe atom has 8 Al nearest and 6 Fe next nearest neighbors. Ordered Fe\(_2\)Al has D\(_0\)\(_3\)-type structure, where the Fe I atoms have 8 Fe nearest and 6 Al next nearest neighbors, while the atoms of the pure Fe sublattice (Fe II) are surrounded by 4 Fe I and 4 Al (forming a tetrahedron) first neighbors, and 6 Fe II next nearest neighbors. FeAl is nonmagnetic, and the bcc Fe-Al solid solution and Fe\(_2\)Al are ferromagnetic. Ferromagnetism rapidly transforms into a complex magnetic state between 30 and 50 at.\% Al content. It is often described as a spin-glass state following the hypothesis of Sato and Arrott on antiferromagnetic Fe-Al-Fe superexchange. Cold-working restores ferromagnetism due to the formation of antiphase boundaries (APB’s) and due to the effects of the local environments on the magnetic state of a given Fe atom. The magnitude of the iron magnetic moments depends on the number of iron nearest neighbors; it is about the same as in pure \( \alpha \)-Fe(2.2\( \mu_B \)) for five or more nearest Fe neighbors, and the iron atoms having less than four Fe nearest neighbors are nonmagnetic. The concentration dependence of the average magnetization yields 1.8\( \mu_B \) for the magnetic moment of Fe atoms with a 4 Fe—4 Al first neighbor environment, which is slightly larger than the room-temperature value measured by neutron diffraction in Fe\(_3\)Al [\( \mu_{Fe \, II} = (1.50 \pm 0.10) \mu_B \)]. In the stoichiometric ordered B2 structure APB (i.e., the partial replacement of an Al plane by an Fe plane) creates magnetic moments on the formerly nonmagnetic iron atoms since the number of the nearest Fe neighbors reaches 4 Fe along the boundary. Off-stoichiometry amplifies effect drastically.

The stoichiometric Fe-Al ingot was prepared by induction melting in a cold crucible. X-ray diffraction and low-temperature Mössbauer measurement confirmed the well-ordered B2 state. Mechanical milling was carried out in a vibrating frame hardened steel single ball vessel, which was continuously evacuated by a turbomolecular pump system. Annealing of the powders at 650–700 K restored the well-ordered B2 state and no composition change or contamination was detected by Mössbauer measurements.

The x-ray diffractograms were measured by a Philips X-pert powder diffractometer using Cu \( K_{\alpha} \) radiation. The grain size of the granules, \( D \), was determined from the full width at half maximum of the x-ray diffraction profiles by the modified Williamson-Hall procedure as 21±2, 13±2, and 8±1 nm after 1, 10, and 100 h of ball-milling, respectively.

\( ^{57} \)Fe Mössbauer spectra were recorded by a constant acceleration spectrometer between 4.2 and 300 K, and in external magnetic fields using a 7 T Janis superconducting magnet. Standard procedures were used for the evaluation of the spectra: the ordered B2 component is fitted with a single Lorentzian line and after subtracting this curve from the measured spectra, the remaining part was described by binomial distributions. The magnetization measurements were
portionality coefficients may differ\textsuperscript{18} for the D\textsubscript{0}	extsubscript{3} and the B\textsubscript{2} phases. To the magnetic moment of the individual neighbors, the proportionality is shown by the full line. The nonmagnetic Fe atoms also experience hyperfine fields though substantially smaller than the magnetic Fe atoms, and the low-field part of the hf distribution in Fig. 1 is to be attributed to the nonmagnetic Fe atoms with magnetic moments. In Fe-Al alloys with bcc structure the iron hyperfine fields and magnetic moments are not directly proportional. The nonlocalized contribution of Fe atoms with localized moments and that of Fe atoms with 4 Al–4 Fe nearest neighbors in Fe\textsubscript{3}Al (Ref. 19), respectively. The positions of the second and fifth lines for the high field peak in the spectra of the 100 h sample in 0 T and 5 T field are marked as well.

The magnetic iron atoms mostly belong to the grain boundaries in the ball-milled samples. Their percentage \( p_{M} \) is determined as the spectral weight belonging to the high-field part of the hf distribution marked by shadowing in Fig. 1. \( p_{M} \) correlates well with the inverse of the average grain size (Fig. 2). The slope of this correlation is proportional to the thickness of the boundary region, \( d \). The proportionality coefficient is dependent on the shape of the grains; in the simplest cases (sphere or cube) it is \( 6d \). In our case this relation gives \( d \approx 0.8 \) nm for the average thickness of the grain boundaries. It may be somewhat overestimated due to the well-known bias of x-ray diffraction by the contribution of larger grains and to some disorder within the grains.

The average hf of the high-field part of the distribution, \( B_{hf} \), is attributed to Fe atoms with 4 Fe and 4 Al nearest neighbors. It is somewhat lower than the hf of Fe II in Fe\textsubscript{3}Al (23.4 T, extrapolated from the room-temperature value\textsuperscript{19}) in line with a smaller delocalized contribution. In Fe\textsubscript{3}Al the neighbors of Fe II atoms have 8 Fe neighbors (Fe I) and larger magnetic moments, while in the ball-milled samples the number of Fe environments with 5 or more Fe nearest neighbors is small. (In a completely disordered FeAl alloy this contribution would be around 36\%). In the ball-milled alloys the hf of the Fe I sites of Fe\textsubscript{3}Al with 8 Fe neighbors [32.6 T (Ref. 19)] is not present and \( B_{hf} \) is slightly increasing with increasing amount of the magnetic Fe atoms (i.e., with milling time). As a consequence the average iron moment is increasing since more formerly nonmagnetic atoms will have magnetic moments, which supports the above assignment. The simplest explanation is the formation of antiphase grain boundaries. If two bcc iron layers are surrounded on both sides by Al layers, then each Fe atom will have 4 Fe–4 Al nearest neighbor environments. The absence of a single line in the Mössbauer spectrum of the 100 h ball-milled sample indicates the disordering of the B2 structure for ball milling.

Figure 3 shows the results of the SQUID measurements. In small magnetic fields the magnetization shows a broad peak as a function of temperature both in field- and in zero-field-cooled states. The thermomagnetic curve for the 1 h ball-milled sample not shown is similar but on a smaller scale to that of the 10 h ball-milled one. This feature resembles the freezing of a spin glass. However, the zero-field Mössbauer measurements (Fig. 4) show no magnetic character around the temperature of the peaks. Indeed, the Mössbauer spectra show no well-defined transition from the magnetic to the nonmagnetic state: superparamagnetic relaxation
creases linearly with temperature. However, the magnetization cannot be saturated even in 5 T magnetic fields. It means that already small magnetic fields influence greatly the magnetic state of these ball-milled samples, respectively. It starts already at 12 K and 50 K for the 1 h and 100 h ball-milled samples, respectively. Star and empty circles mark the values for 100 h ball-milled FeAl, respectively. The inset shows the external field dependence of $B_{m}$ (dots) at 4.2 K; it is corrected for the applied field and the canting angle as explained in the text ($B_{m}^{+}$, circles).

Figure 3 shows the external field dependence of $B_{m}$ (dots) at 4.2 K; it is corrected for the applied field and the canting angle as explained in the text ($B_{m}^{+}$, circles). The inset of Fig. 5 shows that this expectation is well fulfilled. $I_{2,5}$ is a measure of the iron magnetic moments in 0 T ($B_{m}$) and in 5 T ($B_{m}^{+}$, circles) for the 100 h (a) and 10 h (b) ball-milled FeAl, respectively. The inset shows the external field dependence of $B_{m}$ (dots) at 4.2 K; it is corrected for the applied field and the canting angle as explained in the text ($B_{m}^{+}$, circles).

mation on the direction of the Fe magnetic moments is given by the relative intensity of the second and fifth lines, $I_{2,5}$, of the spectra (corresponding to the $\Delta m=0$ nuclear transitions). $I_{2,5} = 4 \sin^2 \theta/(1+\cos^2 \theta)$, where $\theta$ is the angle between the magnetic moment and the magnetic field $B_{ext}$ applied parallel to the $\gamma$-beam direction. $I_{2,5}$ found without applied field (Fig. 1) corresponds to a random Fe spin orientation. For complete saturation, i.e., when all the magnetic moments are collinear to $B_{ext}$, $I_{2,5} = 0$. Despite that this state was not reached at 4.2 K even in 7 T (our highest available external field), $I_{2,5}$ continuously decreased for increasing $B_{ext}$, signaling the gradual alignment of the canted magnetic moments. If a linear extrapolation is justified, at least 14 T and 18 T would be necessary to reach saturation for the 100 h and 10 h ball-milled samples, respectively. Similar strong magnetic anisotropy is reported for ferromagnetic clusters along the APB in off-stoichiometric Fe-Al alloys. The $hf$ is oriented antiparallel to the magnetic moment. In the collinear ferromagnetic state the absolute value of the $hf$ should decrease with the value of the applied field when it is larger than the demagnetizing field. In the case of a canted moment the decrease is $B_{ext}\cos \theta$. Obviously, the $hf$ of antiferromagnetically coupled moments should increase with this amount. Thus the increase of the standard width of the distribution around $B_{m}$ should occur if magnetic moments with random directions were present as in a spin glass. Experimentally a decreasing width with increasing $B_{ext}$ was found, which is expected for a strong random anisotropy dominated ferromagnet. (For the example shown in Fig. 1 the standard width of the distribution around $B_{m}$ should occur if magnetic moments with random directions were present as in a spin glass. 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\( \theta \) angle between the magnetic moment and applied field as 
\[ \bar{\mu}_{Fe} = \mu_{Fe} p_M \cos \theta. \]
All these quantities depend on the applied field and the temperature, which explains the complex behavior of the average magnetization shown in Fig. 3. At low temperature and in 5 T the measured average magnetization is \( \bar{\mu}_{Fe} = 0.87 \) and 0.45 \( \mu_B/\text{Fe atom} \) for the 100 and 10 h ball-milled samples, respectively. The Mössbauer measurements yield \( p_M = 0.62 \) and 0.41, \( \cos \theta = 0.79 \) and 0.63 for the two samples and the calculated moments are \( \bar{\mu}_{Fe} = 1.78 \) and 1.73 \( \mu_B \), respectively. These experimentally determined magnetic moment values support the conclusion drawn from the hf properties that the iron atoms in the grain boundaries have four iron nearest neighbors.

The most straightforward interpretation of our results is that ball-milling results in the formation of a magnetic shell around the nonmagnetic grain containing two adjacent iron layers. Obviously this shell is not necessarily perfect, it can be somewhat disordered as the inner part of the grains, too.

The strong magnetic anisotropy [substantially stronger than that of \( \alpha \)-Fe or Fe\(_2\)Al (Ref. 9)] directs the magnetic moments along the plane of the shell. In zero external magnetic field this arrangement forms no net magnetization. Since there is no preferred direction of the magnetization, it is very sensitive for small perturbations. It means that for increasing temperature the ferromagnetic ground state quickly disappears without a detectable transition temperature. On the other hand, even small magnetic fields can break this symmetry, causing the appearance of a net moment. The behavior of the system is ferromagnetic but saturation is not reached even in large fields because of the spherical distribution of the magnetic anisotropy directions.

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