Determination of the size of Fe grains in Ag by Mössbauer spectroscopy

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The decrease of the average magnetic grain size with increasing Ag spacer thickness was deduced recently [J. Balogh, D. Kaptás, L. F. Kiss, T. Pusztai, E. Szilágyi, Á. Tunyogi, J. Swerts, S. Vandezande, K. Tenst, and C. Van Haesendanck, Appl. Phys. Lett. **87**, 102501 (2005)] from bulk magnetic properties of Fe/Ag granular multilayers. Now we show detailed Mössbauer spectroscopy measurements that support this finding and determine the hyperfine fields of Fe atoms in the grain boundaries. The grain size estimated by a simple model from the grain boundary fraction agrees well with that obtained from the external field dependence of the hyperfine field in the superparamagnetic state.

Understanding of the complex nonequilibrium morphologies that can be formed during thin film deposition[1] in various systems is a great challenge. Thin epitaxial Fe layers on Ag,[2] Fe/Ag multilayers,[3] and codeposited granular alloys[4] have been studied since long. The description of the giant magnetoresistance[5,6] and the appearance of the perpendicular magnetic anisotropy[3] in multilayers at certain Fe layer thickness would require a better knowledge of the sample structure and morphology. Cross-sectional transmission electron microscopy (TEM) investigations of Fe/Ag multilayers have been published recently[6] and made it clear that the grain-size distribution and morphology remain hidden even for high resolution TEM in the few monolayer Fe thickness range due to the fcc or fct structure of the small Fe grains. Mössbauer spectroscopy being sensitive to the local surrounding can be helpful, but a systematic investigation of the grain-size dependence of the static hyperfine field distribution is lacking.

Granular Fe/Ag multilayers with discontinuous Fe layers show superparamagnetic properties.[7] The temperature and magnetic field dependences of the bulk magnetization and the blocking temperature (T_B) are determined by the grain size of the magnetic particles. If exchange and dipolar interactions between the particles are negligible, the grain size can be determined within the framework of a simple superparamagnetic model.[8] A decrease of the average magnetic grain size with increasing Ag spacer thickness in Fe/Ag granular multilayers was deduced[7] from the decrease of the blocking temperature and from the temperature and magnetic field dependences of the magnetization. However, the possible effect of interactions on the superparamagnetic properties, and consequently, on the deduced grain sizes, is not well understood.[8] The supposition that the reduction of the magnetic grain size is only apparent and the magnetic properties change due to a decreased interaction because of the larger spacer thickness was ruled out in an indirect way; samples[7] containing both granular layers and interleaved thicker ferromagnetic layers were studied. The ferromagnetic layers have not modified either the blocking temperature or the perpendicular alignment of the granular layers, thus it was concluded[7] that interactions across the nonmagnetic spacer

were negligible. To explain these results, a detailed understanding of the layer growth and morphology would be necessary. In a systematic study of thicker Ag/Fe bilayers, the surface roughness and the magnetic properties were shown to depend on the Ag thickness.[9] A preferential nucleation of the magnetic clusters on a wavy surface might explain the influence of the spacer layer on the magnetic grain size.

In the present work, the average cluster size of the granular samples is determined from in-field Mössbauer spectroscopy measurements above T_B. The static hyperfine field (HF) distributions evaluated from measurements at 4.2 K in various applied fields are also found to reflect the grain-size difference. Since the ground state static HF is not influenced by magnetic or exchange interactions between the grains, it is an important check of the grain size determined from the dynamic properties.

The two granular multilayers studied,
(A) [0.2 nm ^{57}Fe/2.6 nm Ag]$_{75}$ and
(B) [0.2 nm ^{57}Fe/5.4 nm Ag]$_{75}$,
were prepared by vacuum evaporation onto Si(111) wafers, as described in Ref. 7. The bulk magnetization measurements with a superconducting quantum interference device (SQUID) indicated[7] that the average cluster moments are 600 and 200μ_B (about 270 and 90 Fe atoms if the atomic moment is 2.2μ_B), in accordance with the 40 and 12 K values of T_B for samples A and B, respectively. For the purpose of transmission Mössbauer spectroscopy measurements, the samples were removed from the substrate with a Scotch tape and the removed pieces were cut into 8×8 mm^2 squares and stacked. The sample removal does not affect the following results; our low temperature spectra reproduce quite well those of Refs. 3 and 10 on samples grown over different substrates and recent low temperature conversion electron Mössbauer spectroscopy measurements[11] on single Fe layer samples. The measurements were done with a standard constant acceleration spectrometer and a Janis cryostat equipped with a 7 T superconducting magnet. The hyperfine field distributions were evaluated by allowing binomial distribution shapes.[12] Isomer shifts are given relative to α-Fe at the respective temperature.
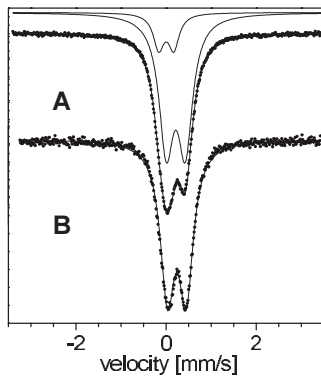
FIG. 1. Room temperature Mössbauer spectra of the two Fe/Ag granular multilayer samples: (A) [0.2 nm ^{57}Fe/2.6 nm Ag]$_{75}$ and (B) [0.2 nm ^{57}Fe/5.4 nm Ag]$_{75}$. Sample A was fitted by two subspectra as indicated in the figure.

At room temperature, the spectrum of sample B can be well described with a symmetrical quadrupole doublet, as is shown in Fig. 1. The isomer shift, IS=0.24($\pm$0.01) mm/s, and the quadrupole splitting, Q=0.42($\pm$0.01) mm/s, are both unusually large as to belong to bcc-Fe, and the evaluated full linewidth, 0.38($\pm$0.02) mm/s, indicates a distribution of the IS and Q values. Fitting by two independent lines gives IS =0.03 and 0.45 mm/s, values close to those of superparamagnetic bcc-Fe clusters[13] and individual Fe atoms dissolved in the fcc-Ag matrix,[14] but this description is not consistent with the low temperature data. As will be shown later, no component with IS as high as 0.45 mm/s is observed in the 4.2 K spectra. The spectrum of sample A shows a slight asymmetry, which can be well described by a second doublet with IS=0($\pm$0.01) mm/s and Q=0.33($\pm$0.01) mm/s, as shown in Fig. 1. It is worth mentioning that subspectra with Q=0.6–0.8 mm/s, reported for codeposited[4,15] alloys, cannot be observed in our spectra. Preliminary results show that a coevaporated sample with Fe content and preparation conditions[7] similar to those of sample A exhibit a spectrum similar to that of sample A. This way we think that the appearance of further components, as observed in Refs. 4 and 15, is not related to the actual deposition sequence, but to other experimental details of the sample preparation.

The spectra measured at 4.2 K in zero and in different applied fields are shown in Fig. 2. For both samples, the spectra exhibit broad but definitely structured lines, which allow a separation into two components, as shown in the figure. A similar spectrum was observed[10] in the case of an ultrathin Fe layer on Ag. There is a strong correlation between the isomer shift and the hyperfine field values, resulting in an apparent asymmetry of the overall spectra. The presence of a significant quadrupole distribution is obvious from the opposite asymmetry of the 1-6 and 2-5 line pairs of the broad sextets. Application of an external field at 4.2 K does not influence the shape of the distributions, and the measured spectra correspond to a ferromagnetic behavior. In accordance with the saturating bulk magnetization,[7] the intensity of the second and fifth lines goes to zero above 3 T at 4.2 K, i.e., the magnetic moments are aligned along the applied field. (Small deviations can be observed due to a slight
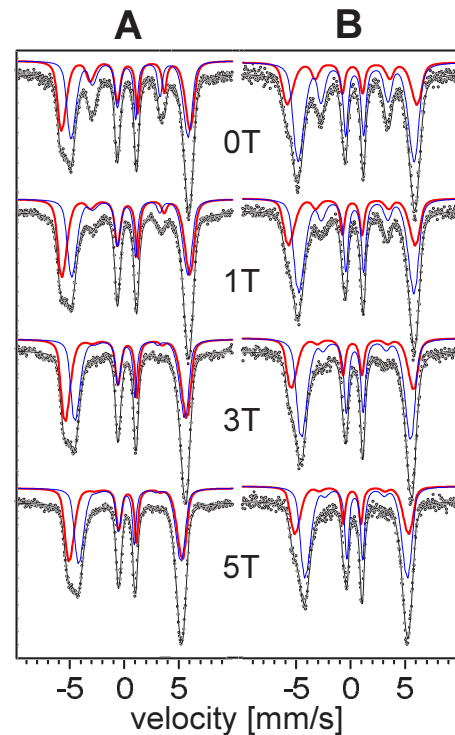

FIG. 2. (Color online) Spectra measured at 4.2 K in different external fields for samples A and B. The fitted high (red, thick) and low field (blue, thin) subspectra are also indicated.

misalignment and waviness of the samples being removed from the substrate.) Since the hyperfine field is aligned opposite to the magnetization, the saturation of $B^{+}=B_{obs}+B_{ext}$, i.e., the sum of the measured HF and the external field, also indicates the ferromagnetic alignment of the magnetic moments along the applied field. The average values of B^{+} for the full HF distribution and the two subcomponents are shown in Fig. 3(a) for the two samples. The observed saturation proves that the significant differences found in the 4.2 K spectra of the two samples are not due to relaxation effects or to the presence of magnetically different sites, but reflect differences of the HF of Fe atoms sitting in different neighborhoods.

Differences of the Fe neighborhoods originate from a different grain structure of the samples. Decrease of the grain size increases the relative number of the surface atoms, i.e., the surface over volume ratio. This effect is complemented by the possibility that in the large-size tail of the grain-size distribution, the crystal structure changes to bcc. Finally, it cannot be excluded that the grains contain a few at % Ag, and the relative amount of intermixed Ag increases with decreasing grain size.

The quadrupole doublet of sample B above T_B (Fig. 1) is surprisingly symmetric and indicates that all the Fe atoms sit in noncubic environments. The observed value of the quadrupole splitting (0.42 mm/s) would be rather unusual in a metallic system, with cubic symmetry even in the case of the presence of a significant amount of impurities. The supposition of a noncubic fct structure can be a more plausible explanation, and the TEM results[6] have not excluded this pos-
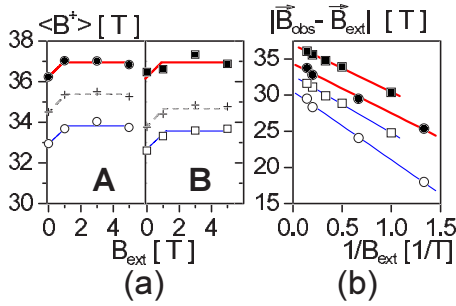
FIG. 3. (Color online) (a) The average $B^+ = B_{obs} + B_{ext}$ values at 4.2 K as a function of the external field, B_{ext}, for the whole HF distribution (crosses) and for the low and the high field components. The lines are guides for the eye. (b) Determination of the Fe grain size from the high and low field components of the Mössbauer spectra measured at 150 K on sample A and at 50 K on sample B. (See text for explanation.) The symbols indicating the two samples (circles for A and squares for B) and the two components (open symbols for the low field and full symbols for the high field) agree in (a) and (b).

sibility. Strain induced tetragonal distortion can also be an explanation of the observed close to perpendicular alignment of the magnetic moments. The component with smaller Q and IS values (see Fig. 1) probably indicates the presence of larger grains with a relaxed or a bcc structure in the case of sample A. The distribution of the IS values is also significant, and the 4.2 K spectra obviously show that it is correlated with the HF distribution. The average IS values of the high/low field components [0.08(4)/0.22(4) mm/s for sample A and 0.02(4)/0.30(4) mm/s for sample B] indicate that Fe atoms contributing to the low field component have more Ag neighbors than those which contribute to the high field part of the spectra.

Theoretical calculations[16,17] indicated an increase of the magnetic moments but a decrease of the ground state hyperfine fields at the Fe/Ag interface, both in the case of fcc clusters[16] and epitaxial bcc layers.[17] Hyperfine fields larger than the bulk value were predicted for Fe atoms inside small fcc clusters.[16] Since such a component was also found[3,18] experimentally in epitaxial bcc layers, it can also be probably attributed to atoms inside grains with a bcc structure but with an increased lattice parameter. These results suggest that the HF rather depends on the number of Ag neighbors than on the structure; therefore, the decrease of the high field component from 47% to 30% ratio (see Fig. 2) and the resultant decrease of the average HF value [see Fig. 3(a)] are mainly attributed to a decrease of the grain size. We apply a simple model to estimate the grain size: the ratio of the low field component is supposed to be proportional to the ratio of interface atoms of spherical grains and the small possible intermixing between Ag and Fe is neglected. The 1.8 and 1.2 nm grain sizes calculated from the SQUID measurements[7] for the two samples are in perfect agreement with the values obtained from the 53% and 70% values of the grain boundary fraction if we suppose 0.2 nm (i.e., about one atomic layer) grain boundary width.

Applying an external field in the superparamagnetic state above T_B results in the reappearance of the magnetic split-
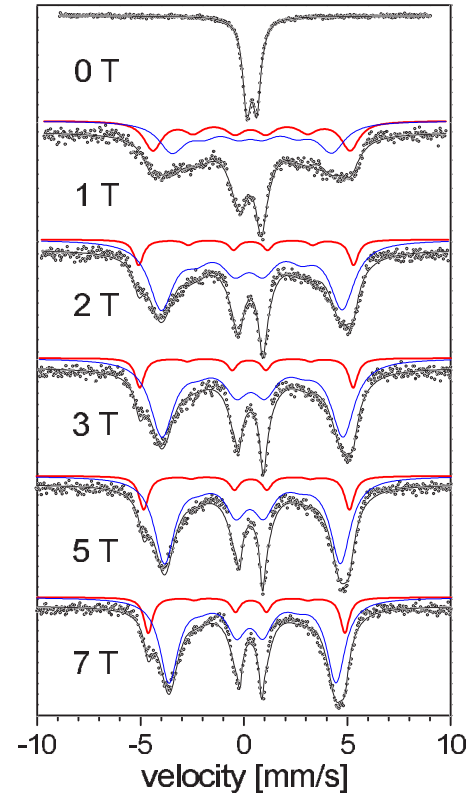

FIG. 4. (Color online) Spectra measured at 50 K in different external fields for sample B. The fitted high (red, thick) and low field (blue, thin) subspectra are also indicated.

ting, as can be seen in Fig. 4 for sample B. An elaborate description[19] of the relaxation line shapes is not amenable in the presence of a quadrupole splitting, but the positions of the appearing two magnetic components can be followed by fitting two broad sextetts to the spectra, as shown in Fig. 4. The magnetic moment of the superparamagnetic clusters can be determined from the hyperfine fields induced by the external field in the framework of a collective excitation model.[13,20] In external fields large enough that $\mu B_{ext}/kT \gg 1$, the approximation

$$|\vec{B}_{obs} - \vec{B}_{ext}| \cong B_{hf}\left(1 - \frac{kT}{\mu B_{ext}}\right)$$

can be used, where B_{obs}, B_{hf}, and B_{ext} are the observed HF, the saturation HF, and the external magnetic field; μ is the cluster moment, and k and T are Boltzmann's constant and the temperature, respectively. A plot of $|\vec{B}_{obs} - \vec{B}_{ext}|$ as a function of $1/B_{ext}$ gives a straight line with slope $B_{hf}kT/\mu$ and intercept B_{hf}. This plot is shown in Fig. 3(b) for the two fitted magnetically split subspectra (indicated in Fig. 4 for sample B) at 150 and 50 K for samples A and B, respectively. When the spectra are fitted with a hyperfine field distribution, the average values do not show a linear dependence on this plot. Fitting the whole spectrum with a distribution of sextets means to include an average over the fast relaxing broadened components that can produce a large variation as a function of the applied field. Fits of the high field subspectra yield

B_{hf}=34.3(3) and 37.0(1) T and μ=1121(70) and 420(12) μ_B, while that of the low field components yield B_{hf} =30.5(3) and 32.7(1) T and μ=720(35) and 307(6) μ_B for A and B, respectively. The B_{hf} values agree well with those calculated for the 4.2 K spectra [see Fig. 3(a)] in the case of sample B, but slightly smaller for sample A due to the much higher measuring temperature. The cluster moments calculated from the low field subspectra are smaller than those calculated from the high field components. This behavior should be related to the presence of a distribution of the grain size and it is consistent with the supposition that the Fe atoms at the interface have hyperfine fields smaller than the ones inside the grains. The small grains, having a large surface fraction, give a larger contribution to the small field component than the large grains having small surface fraction. Both μ values are significantly larger than the values determined from the SQUID measurements. The evaluation based on the description of the sharp features of the spectra obviously overestimates the grain size because it does not take into account those small grains that do not exhibit well-resolved peaks in the applied field range. We note, however, that if we calculate the grain diameters supposing spherical particles and $2.2\mu_B$ magnetic moment, 2.2/1.9 and 1.6/1.4 nm values are obtained from the high/low field components in contrast to the 1.8 and 1.2 nm values calculated from the SQUID results. The difference hardly exceeds the accuracy of determining an average size by x-ray diffraction or electron microscopy methods.

In conclusion, two well-resolved components have been observed in the low temperature Mössbauer spectra of small superparamagnetic Fe clusters in Ag. The relative fraction of the two components varies in accordance with the grain size determined from the dynamic properties if, in a simple model, they are associated with Fe atoms at the surface and in the volume of the grains. Since the hyperfine field distribution is determined by the local neighborhoods of the Fe atoms and is not affected by possible dipole or exchange interactions among the clusters, it undoubtedly proves that the thickness of the Ag spacer influences the size of the clusters formed in the discontinuous Fe layers.

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