Magnetic properties of metallic Co- and Fe-based granular alloys

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We have studied the magnetic properties of Co-Ag and Fe-Ag granular alloys made using vapor-quenching techniques and thermal annealing. Magnetic coercivity ($H_c$) and remanence can be controlled over a large range by varying annealing temperature and particle volume fraction. A large $H_c$ on the order of 2 kG has been obtained in the Co-Ag system. We have investigated magnetic anisotropy, the effect of particle size, and coalescence in these nanostructured materials.

Magnetic granular solids have received considerable attention in the past few years. In these composite materials, ultrafine magnetic particles of a few nanometers in size are embedded in a metallic or insulating matrix by certain synthesis processes. Because of their microstructure and the tunability in materials and geometrical parameters, these materials possess different and sometimes enhanced properties when compared with their bulk counterparts. In particular, a giant magnetic coercivity ($H_c$) has been achieved in Fe-SiO$_2$ granular films, with $H_c$ enhanced by as much as three orders of magnitude over the bulk value. The large $H_c$ and magnetization of the material make it suitable for application in magnetic recording. It has also been discovered that metallic granular alloys, such as Co-Cu, Co-Ag, and Fe-Ag, exhibit giant magnetoresistance effects (GMR) with a magnitude rivaling the best multilayers with GMR. These developments in granular solids call for more systematic studies of their magnetic properties. The understanding of the novel GMR effect also requires the exploration of the underlying magnetic state which strongly correlates with the behavior of GMR. In this work, we present a study on two transition metal granular solids, Co-Ag and Fe-Ag, both of which have been shown to have GMR effect. The main focus here is how the thermal treatment and volume fraction of the magnetic particles affect the magnetic properties.

We have fabricated Co-Ag and Fe-Ag granular films by taking advantage of the immiscibility between Co (or Fe) and Ag in alloy formation. High vacuum sputtering from a cold-pressed composite target yields a phase-separated film with magnetic particles precipitating from the Ag matrix. The particle size of an as-sputtered sample is very small, on the order of 1–2 nm. We have also fabricated samples using codeposition technique and obtained similar physical properties. Thermal annealing is an effective means to enlarge the particle size. We have prepared a series of samples with different thermal annealing as well as varying volume fraction. Phase separation has been confirmed by using a combination of analysis, i.e., transmission electron microscopy (TEM), x-ray diffraction, and magnetic susceptibility measurement. Detailed results will be presented elsewhere. Analysis of phase separation for the Co-Ag system can also be found in Ref. 12.

We used a superconducting quantum interference device (SQUID) magnetometer to measure the magnetic hysteresis curve of our samples. Since we are interested in the ground state properties, most of our measurements were carried out at low temperatures. The saturated magnetization of the magnetic component (Fe or Co) is approximately equal to that of the bulk. In addition to magnetic measurements, we have also performed magnetoresistance and Hall effect measurements. Both Fe-Ag and Co-Ag show GMR effect and extraordinary Hall effect. The Hall resistivity can be described by $\rho_{xy} = \rho_{xy}^0 + R_M$. In this relation, $\rho_{xy}^0$ is due to the ordinary Hall effect and is linear in magnetic field. The second term, due to the extraordinary Hall effect, results from the left-right asymmetry in electron scattering in magnetic systems. Because of its linear relationship with $M$, the field dependence of $\rho_{xy}$ after removing $\rho_{xy}^0$ shows a one-to-one correspondence with the magnetic hysteresis curve. Therefore, when the sample plane is perpendicular to the external magnetic field, we can consistently obtain remanent magnetization and coercivity from either Hall effect or magnetization measurements. It is noted that it is more efficient and economical to measure the Hall effect than the magnetization using a SQUID magnetometer.

Figure 1 shows the magnetization curves at $T=5$ K for two representative as-prepared samples, Co$_{29}$Ag$_{80}$ and Fe$_{29}$Ag$_{80}$, with $H$ perpendicular and parallel to the sample plane (both samples are specified by volume fractions of their components). The initial susceptibility measurement indicates that the superparamagnetic transition temperature is about 20–30 K. Therefore, at 5 K, the magnetic moment vectors of the particles are fixed in random directions. As shown in Fig. 1, the Co$_{29}$Ag$_{80}$ sample has a much larger $H_c$ than the Fe$_{29}$Ag$_{80}$ sample. Most interestingly, the easy axis tends to be out of plane for Co-Ag, whereas it is in plane for Fe-Ag.

The anisotropy in Co-Ag is most likely caused by the crystalline and shape anisotropies of the Co particles. The maximum $H_c$ which could result from crystalline or strain anisotropy is about 2900 (Oe) or 600 G respectively. The large perpendicular $H_c$ value of about 2 kG seen in Fig. 1 can be accounted for by magneto crystalline anisotropy. The perpendicular $H_c$ in Co-Ag is larger than the parallel $H_c$. To account for the observed perpendicular $H_c$, it is reasonable to conjecture that the Co particles are slightly elongated along the growth direction. Another possible source of anisotropy is from the interface between the magnetic particles and the surrounding Ag matrix. Because of the
small size of the particles, interfacial effect could play an important role. Nevertheless, without the proposed growth texture, it is difficult to imagine how the interface anisotropy could cause the observed perpendicular anisotropy under the influence of the large demagnetization field of the thin film.

The \( H_c \) for the Fe-Ag system is of the magnitude of 300 G. While it is considerably larger than that of a polycrystalline Fe film (a few tens of G), it is much below the limit of crystalline (540 G) and strain (600 G) anisotropy for single-domain particles.\(^\text{14}\) The shape anisotropy in Fe can provide a maximum \( H_c \) of 10.7 kG,\(^\text{14}\) although experimentally such a large \( H_c \) in single-domain Fe particles has never been discovered. In Fe-SiO\(_2\) granular films, a maximum \( H_c \) value of about 3 kG has been observed,\(^\text{1}\) where the Fe particle size is about 50 Å. We have obtained the particle sizes in our Fe\(_{20}\)Ag\(_{80}\) samples using both TEM and analysis of superparamagnetic behavior.\(^\text{11}\) The Fe\(_{20}\)Ag\(_{80}\) sample used for Fig. 1 has an average particle size of 22 Å. Thermal annealing at 300 °C enlarges the particle size to 51 Å, but the \( H_c \) was found to decrease to about 200 G. The comparison between Fe-Ag and Fe-SiO\(_2\) granular systems shows convincingly that particle-matrix interface could be one of the important factors in the magnetic anisotropy of Fe-based systems.

Among the magnetic parameters of a ferromagnetic solid, the ground state magnetization is basically an intrinsic parameter, whereas \( H_c \) and remanence \( M_r/M_s \) are primarily extrinsic parameters. They are sensitive to disorder, stress, and particle morphology. Thermal treatment is an effective means to induce phase separation, to enlarge particle size, and to reduce crystalline disorder and stress in granular materials. In Fig. 2, we present the results of annealing on \( H_c \) for Co\(_{20}\)Ag\(_{80}\) and Fe\(_{20}\)Ag\(_{80}\). Also included in Fig. 2 is an annealing temperature \( (T_\text{A}) \) dependence of \( M_r/M_s \) for Fe\(_{20}\)Ag\(_{80}\). Thermal annealing was done in high vacuum \((1 \times 10^{-7} \text{ Torr})\) at a chosen \( T_\text{A} \) for 15 min, followed by natural cooling. From the TEM micrograph, it was found that the Co particle size increases from about 20 to 130 Å as \( T_\text{A} \) reaches 605 °C. X-ray diffraction revealed that the Co particles have fcc structure and are [111] textured.\(^\text{8}\)

As shown in Fig. 2, \( H_c \) for Co\(_{20}\)Ag\(_{80}\) drops by a large amount once \( T_\text{A} \) exceeds 250 °C. This variation of \( H_c \) has been verified more than once. Such a drop in \( H_c \) is desirable because it tends to reduce the saturation field and hysteresis in GMR effect, which was indeed observed.\(^\text{8}\) There are a few possible causes for this drop. First of all, it is not due to the enlarged particle size which may induce multidomain formation and reduce \( H_c \). Within our \( T_\text{A} \) range, the Co particle size is always below the critical single-domain particle size.\(^\text{14}\) Most likely, as the particle size grows, the original growth texture diminishes, which reduces the particle shape anisotropy. Another possible cause is that annealing makes phase separation more complete and tends to reduce crystalline disorder and stress. Both effects will reduce pinning force for magnetization, and, therefore, lower \( H_c \).
The variation of $H_c$ with $T_A$ for Fe$_{20}$Ag$_{80}$ resembles the behavior in Co$_{20}$Ag$_{80}$, in that we see a similar drop in $H_c$ near 250 °C. However, beyond 250 °C, $H_c$ increases as Fe particles become larger. The remanence has a similar dip near 250 °C. Particle size analysis shows that the Fe particle size steadily increases from 21 Å in the as-sputtered sample to 71 Å at the maximum $T_A$ of 400 °C. All are considered as single-domain particles.\textsuperscript{14}

The above results reveal that thermal annealing has the universal effect of increasing particle size, however, its role on $H_c$ is not straightforward, but is material dependent in metallic granular solids. At present, the cause for these diverse observations is not clear. However, it is important to remember that there are many sources at play for $H_c$, almost all are affected by varying degrees by thermal annealing.

Earlier studies have shown that thermal annealing substantially enhances $H_c$ of various Fe\textsuperscript{2,4} and Co-based\textsuperscript{3,4} granular solids. This is in sharp contrast with the behaviors of our Fe-Ag and Co-Ag systems, where moderate annealing decreases $H_c$. The difference is due to the fact that the earlier studies were performed at room temperature, whereas ours are at low temperature. At $T = 300$ K, thermal relaxation reduces $H_c$ severely for moderately annealed samples where the magnetic particles are small in size. In fact, any super-paramagnetic sample has zero hysteresis. For samples annealed at high temperatures, and therefore, having large particle size, thermal agitation is less important, and $H_c$ appears higher. In order to eliminate the effect of thermal relaxation, measurements need to be done at low temperatures.

Next we turn our attention to the effect of particle volume fraction ($x$) on magnetic properties. Here, $x$ was determined from the composition and the bulk density of each component. Figure 3 shows $H_c$ and $M_r/M_s$ as functions of $x$ for the Fe$_x$Ag$_{100-x}$ as-sputtered system. In the low $x$ region ($x<0.2$), $H_c$ remains relatively constant. Starting at $x=0.2$, $H_c$ gradually decreases, approaching the bulk value of polycrystalline Fe. $M_r/M_s$, on the other hand, increases smoothly with $x$ in the whole $x$ range studied. The evolution of $H_c$ and $M_r/M_s$ with $x$ is the result of the transition from an assembly of almost independent particles to a network of connected particles. As $x$ increases, there is an increasing coalescence of magnetic particles. In fact, above the percolation threshold $x_c$, cluster network of infinite extension is formed. Beyond this limit, the granular solid becomes increasingly bulk-like, and bulk polycrystalline Fe film is characterized by low $H_c$ and large remanence.

For a random three-dimensional system, the percolation threshold $x_c$ is near 0.2. In our granular material, $H_c$ starts to decrease at almost the same $x$. We have also measured the GMR effect ($\Delta \rho/\rho$) as a function of $x$.\textsuperscript{10} $\Delta \rho/\rho$ exhibits a peak at $x=0.2$, coinciding with the peak of $H_c$. This is because both GMR and $H_c$ are sensitive to multidomain or cluster formation in a granular solid.

In summary, ground state magnetic properties have been measured for Co-Ag and Fe-Ag granular alloys which exhibit GMR. The Co-Ag films have a perpendicular magnetic anisotropy, whereas the easy axis of the magnetization of the Fe-Ag films is in-plane. The large $H_c$ and perpendicular anisotropy in Co-Ag are attributed to the crystalline anisotropy and the elongation of Co particles in the growth direction. Thermal annealing affects $H_c$ profoundly in both systems. This cannot be explained by the monotonical increase of magnetic particle size. Other mechanisms such as phase separation, effect of disorder, and evolution of particle shape need to be considered. It is also found that coalescence of particles reduces $H_c$.

We are grateful to Dr. C. L. Chien for providing some Co-Ag samples. We also thank Dr. P. Xiong for helpful discussion and technical assistance. This work was supported by National Science Foundation Grant No. DMR-9258306. G. X. wishes to thank the A. P. Sloan Foundation for a fellowship.

\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig3.png}
\caption{Coercivity $H_c$ (upper panel) and remanence $M_r/M_s$ (lower panel) for Fe$_x$Ag$_{100-x}$ alloys as functions of volume fraction $x$. $T=3$ K.}
\end{figure}