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Curie-temperature enhancement of ferromagnetic phases in nanoscale heterogeneous systems

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The dependence of Ni Curie temperature, T_C, on the Ni thickness in Co-Ni and Ag-Ni multilayers is reported. It is shown that T_C increases 60 °C for the Co-Ni samples, as the Ni thickness decreases from 100 to 50 Å. The difference in T_C between Co-Ni and Ag-Ni multilayers increases as the Ni thickness decreases, reaching 75 °C for 25 Å thickness. We propose as a possible explanation that the molecular field of Co layers penetrates into the Ni layer so enhancing T_C. The influence on the coercive field of the Ni transition from ferromagnetic to paramagnetic state is also shown.

It is to be noted that magnetic materials with outstanding technical properties are heterogeneous systems. Softer materials, as Fe rich nanocrystals,[1,2] as well as the harder $3d$-$4f$ intermetallic compounds[3] are characterized by the coexistence of different structural and magnetic phases. The influence of the microstructure on the macroscopic magnetic properties is governed through the degree of coupling between the different magnetic phases. The degree of coupling is described through the ratio between the exchange correlation length, L, and the structural fluctuation length, l. For $L>l$ the magnetization process is a collective process whereas for $L<l$ each phase magnetizes separately.[4] Nanocrystals or, more generally, materials for which l is of the order of nanometers—along one, two or three dimensions—have been shown to be of particular relevance not only for technical purposes but also for basic studies as is the case of magnetic multilayers. As concerns exchange interactions between the different magnetic phases, the more important characteristic of nanostructured samples is the enormous area of the phase boundary which gives rise to an enormous number of magnetic atoms at the interface.[5]

For the sake of simplicity let us restrict our discussion to systems consisting of two different phases, namely A and B phases. Three types of exchange constants can be distinguished, corresponding to (i) atoms in the bulk of phase A, J^A, (ii) atoms in the bulk of phase B, J^B, and (iii) atoms at the interface with exchange constant ranging from J^A to J^B. J is expected to change locally as we move along the perpendicular direction to the interface. As far as exchange interactions are concerned, we can introduce here the concept of exchange interface thickness (EIT), which can be defined as that along which J evolves from J^A to J^B. The characteristics of the exchange matching thickness should be of great interest to understand the magnetic behavior of multiphase magnetic systems[6] as well as to improve understanding of exchange between ferromagnetic layers through paramagnetic spacers.[7] As the exchange interface thickness is expected to be restricted to one or two interatomic distances, its influence on the macroscopic magnetic properties should be noticeable in those samples with outstanding interface area per unit volume.[8] The macroscopic property which is expected to be more affected by the nature of the interface exchange is the coercivity, through the influence on L, but it is worth noting that also the Curie temperature might be influenced.

Soft magnetic Fe-based nanocrystals consist of an ultrafine structure of randomly oriented crystallites, with size l and volume fraction x, which are surrounded by an amorphous integranular matrix. Therefore, the magnetic softness evidences that exchange propagates through the interfaces crystallite-amorphous matrix. Recently Hernando and Kulik[9] and Slawska-Waniewska *et al.*,[10] by measuring thermal dependence of coercivity, concluded that exchange interactions, responsible for the magnetic softness, also act between the grains through the paramagnetic intergranular region, i.e., above T_C^a. We have also observed that when the distance between crystallites is smaller than 6 nm the Curie temperature of the amorphous intergranular region is higher (60 °C) than the corresponding for an amorphous ribbon of the same composition.[11,12] Nevertheless, even though important interface exchange phenomena have been detected in soft nanocrystals there is an essential difficulty—associated with both their complex chemical composition and the lack of knowledge about some structural details of the nanocrystallization process—to interpret them.

In order to inquire into the influence of the interface exchange on the macroscopic properties of samples with nanoscale fluctuations of magnetic properties, the thermal dependence of coercivity as well as the dependence of the Curie temperature of Ni layers with the layer thickness, l_{Ni}, have been studied in Co-Ni and Ag-Ni multilayers. These multilayers present a remarkable advantage with respect to nanocrystalline materials which is the geometrical and chemical simplicity. The thickness dependence of the Ni Curie temperature for Ag-Ni multilayers has been previously determined and shows a decrease with decreasing l_{Ni} as predicted by the mean-field approximation.[13,14]

Co-Ni and Ag-Ni multilayers, consisting of 40 bilayers, were prepared by planar magnetron sputtering technique on (111) Si wafer substrates kept at room temperature. Co and Ni layers were grown in the rf mode whereas the dc mode was used to grow Ag. For all cases the discharge gas was Ar working at a pressure of 5×10^{-3} mbar. Sample thicknesses have been calibrated by low-angle x-ray diffraction.[15] Co and Ag thicknesses were kept constant at 150 Å. This is the typical dimension of crystallites embedded in the amorphous low Curie temperature phase of the Fe-based nanocrystals. The Ni layer thickness, l_{Ni}, varies between 25 and 100 Å.

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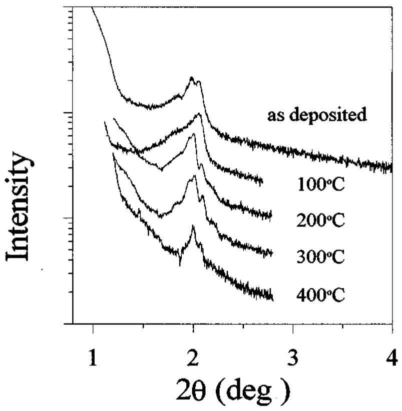

FIG. 1. Low-angle x-ray spectra in a Ni 25 Å–Co 25 Å multilayer, as deposited and after each heat treatment.

Low-angle x-ray diffractions (XRD) have been performed in a D-5000 Siemens Diffractometer. Due to the experimental limitations of this equipment, it is not possible to detect the multilayer periodicity peaks in samples with this rather large periodicity, for which low-angle reflexions would lie into the incident beam. The minimum work angle is around 0.5°, which means that maximum detectable periodicity is around 100 Å. In order to establish the quality of the interface in the multilayered structure, a sample with lower periodicity (25 Å of Co, 25 Å of Ni, 40 bilayers) has been deposited under the same conditions. XRD of as deposited sample, exhibits a neat superlattice periodicity (Fig. 1). The same piece of the sample has been submitted to four consecutive annealings in argon atmosphere (as in magnetic measurements). XRD spectra after each annealing are also displayed in Fig. 1. During heat treatments, the sample was held to a given temperature (which designates the treatment) for 12 min. Warming up and cooling down times were 10 min. Thus, total time in each treatment was approximately 30 min. This XRD observation shows that the interface quality is not too much degraded during high-temperature magnetic measurements. At least, the possible interdiffusion length is much lower than 25 Å.

Magnetization curves and hysteresis loops, which allow the saturation magnetization and coercive field H_c to be determined, were measured by means of a LDJ 9500 VSM, for temperatures ranging from room temperature to 500 °C. Figures 2(a) and 2(b) illustrate H_c as a function of temperature for Co-Ni and Ag-Ni multilayers, with $l_{\mathrm{Ni}}=100$ Å and $l_{\mathrm{Ni}}=50$ Å, respectively. The behavior exhibited by H_c for the Co-Ni multilayers points out, after comparing with the H_c behavior of the Ag-Ni multilayers, that the magnetization reversal process is nucleated in the Ni layers, presumably as a consequence of its lower anisotropy. Between 20 and 200 °C H_c decreases with temperature, as is the case of H_c for Ag-Ni samples up to T_C. This decrease corresponds to the normal thermal dependence of coercivity. However H_c stabilizes and shows a subsequent increase for Co-Ni samples as T approaches T_C. This anomalous thermal dependence, which has also been observed in nanocrystalline materials as in other type of multiphase systems,[16] is originated by the shortening of L produced by the transition from the ferro to the paramagnetic state of the Ni layers. For the Co-Ni sample with $l_{\mathrm{Ni}}=25$ Å, H_c is higher (45 Oe) at room temperature and decreases with a smooth increase at T_C, illustrated by Fig. 2(c). These results indicate that l_{Ni} is too short to reduce effectively H_c, but for the same reason the coupling between the Co layers is less affected by the paramagnetic transition of Ni. The general trend exhibited by the thermal dependence of H_c pointed out that (i) below T_C, exchange interactions through the interfaces lead to L larger than the bilayer thickness and (ii) the Ni transition from the ferro to the paramagnetic state produces hardening as a consequence of the shortening of L.

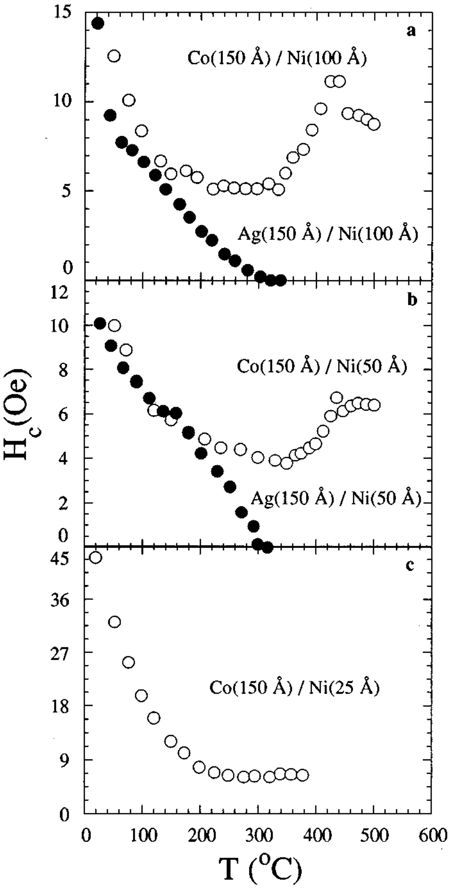

FIG. 2. Thermal dependence of coercivity of Ag-Ni and Co-Ni multilayers for different Ni thicknesses, 100 Å (a), 50 Å (b), and 25 Å (c). The full dots correspond to the Ag-Ni samples.

The dependence of saturation magnetization on temperature in Co-Ni multilayers is shown in Fig. 3 for l_{Ni} 50 and 100 Å. The maximum measuring temperature is far below the Curie temperature of Co (1087 °C). T_C was approximately obtained from the thermal dependence of the magnetization, as the intersection of the steepest tangent to the magnetization curve with the extrapolation at lower temperatures of the magnetization curve of Co layers, as indicated in Fig. 3. It can be clearly seen that T_C increases 60 °C as l_{Ni} decreases from 100 to 50 Å. The dependence of T_C on l_{Ni} is illustrated in Fig. 4 for the two types of multilayers. It is worth noting that the differences between the experimental points corresponding to Co-Ni and Ag-Ni multilayers are much larger than the experimental error associated with the

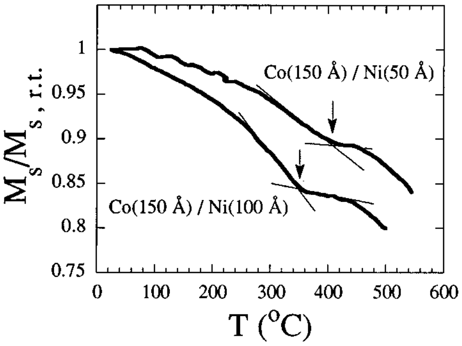

FIG. 3. Thermal dependence of saturation magnetization normalized to its room-temperature value, for Co-Ni multilayers 50 and 100 Å in the Ni thickness. It is also shown the estimated T_C in both samples.

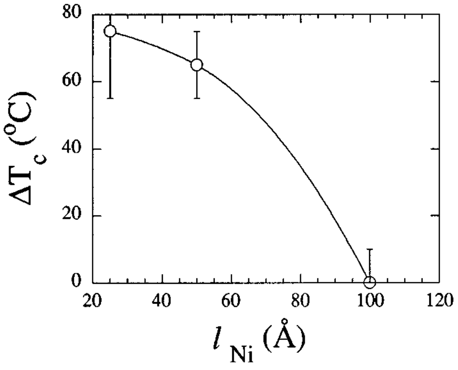

FIG. 5. Dependence on l_{Ni} of the difference between T_C in Co-Ni and in Ag-Ni samples (ΔT_C).

approximated method used for determining T_C, which has also been indicated by means of the error bars. The behavior exhibited by T_C in Ag-Ni samples is in good agreement with the results previously reported for Au-Ni and Ag-Ni multilayers.[13,14] Figure 5 illustrates the difference between the T_C values corresponding to Co-Ni and Ag-Ni multilayers, ΔT_C, as a function of l_{Ni}. According to this figure, it is clear that, for any l_{Ni} lower than 100 Å, T_C strongly depends on the magnetic nature of the adjacent layers. When those layers are ferromagnetic, as is the case of Co, T_C is well above the corresponding T_C observed for paramagnetic adjacent layers, as is the case of Ag. In Fig. 6, the M_{Ni}/M_{Co} ratio is plotted against l_{Ni}, where M_{Ni} and M_{Co} are, respectively, the Ni and Co magnetizations in the multilayer, at room temperature. They have been obtained from the drop of the multilayer magnetization when the temperature reaches T_C. In all cases M has been considered as the multilayer magnetization at T_C, supposing that it remains approximately constant within this temperature range. The value of M_{Ni} which is expected to be independent of l_{Ni}, approximately 30% of the cobalt magnetization, shows a drastic increase with decreasing l_{Ni} as illustrated by the figure.

The results plotted in Figs. 4, 5, and 6 point out that, when the Co-Ni exchange interface thickness is not negligible in comparing to l_{Ni}, T_C is affected by the presence of the Co layers. This effect can be described by assuming an enhancement of the average molecular field in Ni layers. Such enhancement would depend on the EIT. Two factors may contribute to EIT: (i) structure of the interface; roughness and interdiffusion lead to a compositional gradient through the perpendicular direction of the ideal interface. Therefore a distribution of local Curie temperature associated with structural EIT should be expected. (ii) Electron-electron interactions through the interface; it is known that exchange interactions propagate through paramagnetic spacers via electron polarization, even for ideal interfaces.[7] Details of this interaction are conditioned by band matching at the interface, existence of bound states, and in general by electronic configurations.[7,17]

In a rough approximation, when a magnetic material reaches its T_C, the thermal agitation energy is high enough to overcome the ferromagnetic ordering energy. This can be established by means of the immediate relation $\mu_B B_{mol} = kT_C$, where μ_B is the Bohr magneton, B_{mol} the molecular field and k the Boltzman constant. After considering that in Ni, ΔT_C reaches 75 °C for $l_{Ni} = 25$ Å, we found that the contact with the Co layers is equivalent to an increase of the average molecular field, ΔB_{mol}, of the order of

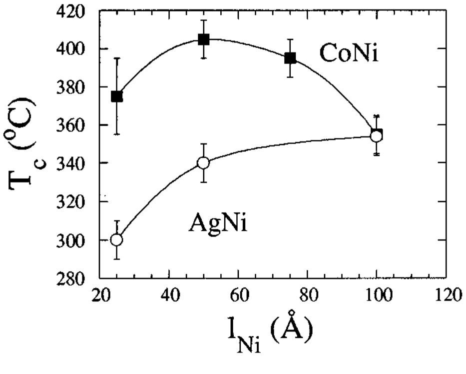

FIG. 4. Dependence of T_C on l_{Ni} for Co-Ni and Ag-Ni multilayers. The Co and Ag thickness remains constant in all the smaples and equal to 150 Å.

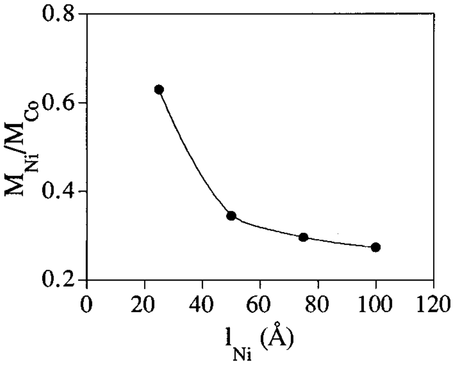

FIG. 6. Dependence of M_{Ni}/M_{Co} on l_{Ni} for Co-Ni multilayers. The value of M_{Ni} is approximately 30% of the cobalt magnetization, however it shows a drastic increase with decreasing l_{Ni}.

100 T. Taking into account the Ni-Co miscibility, such increase could be explained by the gradient of Curie temperatures associated with the possible gradient of Co-Ni compositions at the interface. At the interface T_C would range from the Co Curie temperature to the Ni one, following an almost linear law.[18] But it can also be explained by assuming a molecular-field penetration, originated by electron-spin polarization, with an exponential decay into the Ni layers. As the molecular field in Co at 300 °C is of the order of 1000 T an average of 100 T and Ni can be obtained if the exponential decay is of one atomic distance. Further experiments should be performed in order to elucidate the relative contribution of these two factors to EIT.

The experiments reported in this work support the idea that the exchange interface thickness becomes a relevant parameter for magnetic structures with nanoscale fluctuations as is the case of nanocrystalline materials and multilayers. In particular it has been shown that the Curie temperature of thin magnetic layers is not only dependent on its thickness but also on the magnetic nature of the neighbor layers.

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