Exchange-induced phase separation in Ni-Cu films

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Abstract
Magneto-structural properties of films of diluted ferromagnetic alloys NiCu1−x in the concentration range 0.7 < x < 1.0 are studied experimentally. Films deposited by magnetron sputtering show partial phase separation, as evidenced by structural analysis and ferromagnetic resonance measurements. The phase diagram of the NiCu1−x bulk system is obtained using numerical theoretical analysis of the electronic structure, taking into account the inter-atomic exchange interactions. The results confirm the experimentally found partial phase separation, explain it as magnetic in origin, and indicate an additional metastable region connected with the ferromagnetic transition in the system.

Keywords: dilute ferromagnets, thin films, phase diagram, ferromagnetic resonance, Curie temperature

1. Introduction

Magnetic multilayered films have been receiving much attention from the research community in the field of spintronics. Recently, a device has been proposed [1] and demonstrated [2,3], in which the magnetic and spin-transport properties are controlled thermo-electrically. At the core of the new design is a tri-layer (F/F/F) of two strong ferromagnets (F) exchange-coupled by a weakly ferromagnetic spacer (f) having the Curie point at/or near room temperature (300 – 500 K). The spacer f, controlling the exchange coupling between the outer layers, can be made of a diluted ferromagnetic alloy, such as NiCu1−x [2,3]. It is desirable that the spacer is compositionally uniform and does not contain multiple phases, which can form as a result of atomic segregation during film deposition or subsequent heat treatment.

Alloys NiCu1−x, in their bulk form are fcc binary substitution alloys (α-phase), with Ni and Cu mutually solvable in any proportion up to the temperature of 627 K, where at x = 0.67, the α phase separates into two, α1 and α2 [4]. According to [4], the phase diagram contains a metastable region with phase separation at the nickel concentration of 0.86 < x < 0.91, which can lead to additional magneto-structural inhomogeneities in the system. The results, obtained in this work, however, are obtained using an empirical model, based on the experimental data. It is desirable to independently simulate the phase equilibria in the system NiCu1−x, first without using experimental information and then compare the results with the experimental findings. Of particular interest is the influence of the magnetic interactions in the system on the potential structural and/or compositional phase separation. The Curie temperature of bulk NiCu1−x alloys depends linearly on the Ni concentration [4].

By varying the Ni content from 0.5 to 1 the Curie temperature is changed from 0 K to 627 K. However, based on neutron scattering data, it was shown that both bulk samples [5,6] and sputtered films of Ni-Cu alloys [7] exhibit partial phase separation and form Ni rich clusters of typical size 5 – 10 Å and magnetic moment 8 – 12 µB. The formation of such Ni clusters and the resulting magnetic inhomogeneity in the material can lead to anomalous magnetic [8] and transport [9] properties.

In this work we investigate the mechanisms behind phase formations in diluted ferromagnetic alloy films of NiCu1−x, and explain using first-principles calculations the enhancing effect of the exchange interaction on phase separation in the ferromagnetic composition range of 0.7 < x < 1.0. We discuss optimum ways to prepare films with enhanced magneto-structural homogeneity.

2. Experimental methods

Films of diluted ferromagnetic NiCu1−x alloys, with 0.7 < x < 0.9 in Ni concentration, 100 nm thick, were deposited at room temperature on thermally oxidized Si substrates using DC magnetron co-sputtering from Cu and Ni targets. Substrates of 150 × 10 mm in size, placed above the Cu and Ni targets, along the line connecting the centers of the targets, were used to produce a continuous and essentially linear compositional gradient along the substrate strip. The base pressure in the deposition chamber was ~ 5 × 10−8 Torr and the Ar pressure used during deposition was 5 mTorr. The deposition rate for Ni and Cu in the center of the substrate was ~ 0.5 Å/sec. Samples for magneto-structural measurements were cut from the substrate strip into short sections with dimensions of 5 × 10 mm. In total, 30 samples of various composition NiCu1−x were produced in the same fabrication cycle under the same conditions. The thickness of the films was determined using a surface profilometer. The composition of the films was determined using

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x-ray dispersion spectroscopy analysis.

Ferromagnetic resonance (FMR) was used to determine the effective magnetization of the Ni$_x$Cu$_{1-x}$ films ($M_{eff}$) and their Curie temperature ($T_c$). FMR measurements were performed at 9.45 GHz using a Bruker ELEXSYS-E500 spectrometer equipped with a goniometer for angle-dependent measurements and a variable temperature cryostat. The effective magnetization was obtained from the resonance fields using the Kittel formulae [10]:

\[
\frac{\omega}{\gamma} = \frac{H_\perp - 4\pi M_{eff}}{H_\parallel + 4\pi M_{eff}},
\]

(1)

where $H_\perp$ and $H_\parallel$ are the measured perpendicular and in-plane FMR resonance fields, respectively, $\omega$ – frequency, and $\gamma$ – the gyromagnetic ratio.

The Curie temperature of the films was determined from the FMR data as temperature at which either $M_{eff}$ or the FMR signal vanished. The degree of magneto-structural non-uniformity in the films was estimated from the width of the FMR peaks (magnetic non-uniformity leads to broader FMR peaks).

Mechanical stress arising from mismatches in the lattice parameters of the substrate and the films can lead to perpendicular to the plane magnetic anisotropy in the films through magnetostriction. This magnetostrictive contribution to $M_{eff}$ can be estimated using [11]:

\[
4\pi M_{eff} = 4\pi M_s - H'^\perp_
\]

(2)

Here $M_s$ is the saturation magnetization of the film, $H'^\perp$ = $-2\lambda\sigma/\lambda$ – magnetostriction-induced perpendicular-anisotropy field, $\lambda$ – magnetostrictive constant, $\sigma$ – mechanical stress in the film. It follows from (2) that for a strong magnetostrictive contribution and/or small saturation magnetization, the effective magnetization can become negative, which corresponds to its perpendicular-to-the-plane orientation in the absence of external fields [10].

3. Experimental results and discussion

Figure 1 shows the temperature dependence of the FMR resonance fields for Ni$_x$Cu$_{1-x}$ films with different Ni content. For Ni$_{0.71}$Cu$_{0.29}$ and Ni$_{0.77}$Cu$_{0.23}$ films, $H_\perp < H_\parallel$ in a broad temperature range, which indicates an out-of-plane magnetization orientation for these compositions. For films with higher concentrations of Ni ($x = 0.82$ – 0.92), $H_\perp > H_\parallel$ and the magnetization is in-plane at zero field.

The temperature dependence of the effective magnetization obtained using (1) and the measured resonance fields (see Fig. 1) are shown in Fig. 2. For all compositions, the effective magnetization first increases with increasing temperature from 150 K to ~ 320 K and subsequently decreases above $T > 320$ K. This indicates a significant magnetostrictive contribution to the anisotropy. For low Ni concentrations, Ni$_{0.71}$Cu$_{0.29}$ and Ni$_{0.77}$Cu$_{0.23}$, $M_{eff}$ is negative, while for Ni$_{0.82}$Cu$_{0.18}$, Ni$_{0.85}$Cu$_{0.15}$, Ni$_{0.87}$Cu$_{0.13}$, Ni$_{0.89}$Cu$_{0.11}$ and Ni$_{0.92}$Cu$_{0.08}$ $M_{eff} > 0$. Thus, in films with low Ni concentrations and therefore low saturation magnetization, magnetostriction results in perpendicular magnetic anisotropy.

![Figure 1: FMR resonance fields for Ni$_x$Cu$_{1-x}$ films versus temperature.](image1)

![Figure 2: Temperature dependence of the effective magnetization of Ni$_x$Cu$_{1-x}$ films with different Ni content $x$. Dashed line is the approximation for $x = 0.92$.](image2)
films with strong magnetostriction and out-of-plane magnetization, it was more appropriate to determine the $T_c$ directly from the temperature dependence of the respective amplitudes of the FMR signal (Fig. 3). $T_c$ in this case was determined as the temperature at which the FMR signal amplitude approached zero (Fig. 3).

$T_c$ as a function of concentration in Ni$_x$Cu$_{1-x}$ films, determined from the FMR data as described above, is shown in Fig. 4. The figure also shows the phase diagram and $T_c$ for the same system in the bulk form [4]. The phase diagram also shows the lines of the binodal, spinodal, as well as the metastable regions, the existence of which was predicted in [4]. Fig. 4 shows that in the vicinity of the metastable equilibria (lines $ab$–$ab'$), the concentration dependence of the $T_c$ for bulk [4] and film materials (this work) are significantly different. In films, the behaviour of $T_c(x)$ is significantly non-linear, while in the bulk it is practically linear.

The non-linear $T_c$ vs. $x$ in films indicates that magnetic and structural inhomogeneities increase with increasing Cu content, specifically in the concentration range $0.7 < x < 0.9$. The fact that $T_c$ in films is always higher than in the bulk (Fig. 4) suggests that in sputter deposited films regions or clusters rich in Ni compared to the nominal composition of the film are formed. The $T_c$ of such Ni-rich regions is higher than the $T_c$ for the nominal composition.

Additional information about the non-uniformities in the films can be obtained from the analysis of the FMR line width. Fig. 5 shows the half width of the FMR lines for Ni$_x$Cu$_{1-x}$ films, for various temperatures between 200 and 380 K. Judging from the relatively narrow line widths (Fig. 5), the films can be considered rather uniform magnetically, at least within the ferromagnetic exchange length of ~10 nm. It is also seen from the data that the degree of non-uniformity depends on the concentration in Ni$_x$Cu$_{1-x}$ films. Thus, at small Cu concentrations, $0.89 < x < 1.0$, the alloy has a narrow FMR line indicating relatively good magneto-structural uniformity. For higher Cu concentrations, $0.70 < x < 0.89$, the FMR line broadens, which indicates a higher magnetic non-uniformity. This, combined with the observed enhanced $T_c$ from Ni clustering, indicates that in this interesting concentration range near the metastable phase of the phase diagram the films can become structurally non-uniform, possibly consisting from multiple compositional phases. Below we examine theoretically the microscopic mechanism of phase separation in the system, taking into account the interatomic magnetic interactions.

4. Calculation of phase equilibria in Ni$_x$Cu$_{1-x}$ system

There are no direct experimental confirmations that magnetic interactions in Ni$_x$Cu$_{1-x}$ could be responsible for additional phase equilibria in the system. Temperatures required for reaching equilibrium conditions are difficult to attain experimentally, if at all possible. Nevertheless, it was predicted [4] that in Ni$_x$Cu$_{1-x}$ alloys with $0.86 < x < 0.91$ a metastable miscibility gap should exist due to magnetic interactions. For describing the magnetic contribution to the free energy, the authors of [4]
used a model proposed by Chuang. The model contains an empirical expression for the heat capacity of a ferromagnetic alloy, with adjustable parameters obtained from the experiment. In order to obtain a deeper insight into whether such miscibility gap could indeed exist and be due to magnetic interactions, it is highly desirable to first construct a solid state phase diagram of Ni$_x$Cu$_{1-x}$ system using experiment-independent first-principle calculations of interatomic interactions, and then compare the results with the experiment.

The total free energy of the structures were calculated within the density functional theory (DFT) using the FLAPW method (Wien2k package). The calculations were performed taking into account spin polarization, and the GGA exchange correlation potential was taken to be of the form of \[16\]. The MT-radii for Cu and Ni were equal to 2.2 a.u., the electron density was calculated using 500 k-points in the first Brillouin zone. Structural relaxation was performed for the lattice parameters and the atomic positions. The atomic positions were iterated until the forces on the nuclei became smaller than 1 mRy/a.u.

The accuracy of the total energy was approximately 1 meV. The calculated values of the interatomic interactions (in meV) were: \( v_{ij} = [-16.37, 32.55, -7.72, -2.52] \), \( J_{ij} = [-6.78, -18.27] \). The calculation of the phase equilibria was performed within the mean-field approximation for the Hamiltonian of \[3\]. All Ni atoms were taken to have the same value of magnetic moment \( m = (0,0,m) \). \( m \) is obtained as \[17\] \( m = L(H/k_B T) \), with \( H = -\sum_{ij} J_{ij} m c \) being the effective magnetic field, \( k_B \) – Boltzmann constant, \( T \) – absolute temperature, \( L(x) \) – Langevin function. The free energy is given by the expression:

\[
F = \frac{1}{2} \left( \sum_{ij} v_{ij} c_i c_j \right) + k_B T \left( c \ln c + (1-c) \ln(1-c) \right) + \frac{1}{2} \sum_{ij} J_{ij} c_i c_j \left( 1 + x (\text{atomic fraction Ni}) \right) - Hmc - k_B T c \text{ ln} \left( \frac{\sinh(H/k_B T)}{H/k_B T} \right).
\]

Phase equilibria were calculated using the standard “common tangent” method. The obtained phase diagram of the solid Ni$_{x}$Cu$_{1-x}$ is shown in Fig. 6. The lines shown are the binodal, spinodal, metastable equilibria, and the Curie temperature \( T_c \) of the alloy versus composition. The Curie temperature below the binodal line corresponds to a homogeneous solid solution. Metastable equilibria \( b''d' - bd \) and \( bc - b'c' \) are shown as dashed lines.

The phase diagram contains a stable miscibility gap (lines \( ab - ab' \)) due to magnetic transformations in the alloy. A similar miscibility gap exists in the Fe-Ni system (phases \( \gamma_1, \gamma_2 \))

For describing the Ni$_x$Cu$_{1-x}$ alloy we use a model Hamiltonian taking into account the Ni-Ni exchange interactions. The Hamiltonian is similar to the one used in \[14\] for describing Fe$_x$Ni$_{1-x}$ alloys. The approach relies on a lattice model, with each site \( i \) of the fcc lattice being occupied either by an atom of Ni \( (c_i = 1) \) or Cu \( (c_i = 0) \). The atomic fraction of Ni \( (x) \) will be taken as \( c \). The magnetic interactions between the Ni atoms in the system are described by the classical isotropic Heisenberg model. Since the local magnetic moment of Cu atoms is negligible, the magnetic interactions of Cu-Ni are omitted. Thus, the model Hamiltonian of the system is:

\[
E = \frac{1}{2} \sum_{ij} v_{ij} c_i c_j + \frac{1}{2} \sum_{ij} J_{ij} c_i c_j s_i s_j,
\]

where \( v_{ij} \) are the mixing potentials responsible for “chemical” interactions between the atoms, \( J_{ij} \) – magnetic exchange constants for Ni-Ni interactions (independent of concentration \( c \)), \( s_i \) – vector of unit length along the direction of the Ni local magnetic moment. Values of unknowns \( v_{ij} \) for first 4 coordination shells and \( J_{ij} \) for 2 shells were obtained as solutions of a system of equations \[4\] for a set of ordered superstructures representing the Ni$_{x}$Cu$_{1-x}$ alloys. The structures have various distributions of nickel atoms and different magnetic ordering. Since the most interesting region of the phase diagram is at high concentrations of Ni, 5 superstructures of composition CuNi$_7$ (32 atoms per unit cell, ferromagnetic ordering) and 3 structures of pure Ni with ferromagnetic and antiferromagnetic ordering were selected.
The presence of this miscibility gap in Ni$_x$Cu$_{1-x}$ system results in additional equilibria of phases with close compositions but different magnetic properties and, importantly, different Curie temperatures. The presence of different phases in the alloy should broaden the magnetic transition, which is indeed observed in our Ni$_x$Cu$_{1-x}$ films.

Possibly due to our Ni atomic magnetic moments taken to be independent of composition, the obtained theoretical $T_c$ versus composition (Fig. 5) deviates from the measured one (Fig. 4). It should also be mentioned, that in contrast to the results of [4], our calculations show that the additional miscibility gap is stable.

Thus, our ab-initio numerical theoretical analysis, not relying on experimental data, shows additional phase equilibria in the Ni$_x$Cu$_{1-x}$ system at high concentrations of Ni. These additional equilibria are due to the ferromagnetic interactions in the system.

Using the expression for the free energy of Eq. (4) it is possible to obtain the general condition for the existence of an additional miscibility gap. For this, it is convenient to introduce the following quantities: $V_0 = \sum v_{ij}$, $J_0 = \sum J_{ij}$. The lines of the spinodal and magnetic transformations intersect at point $a$ (Fig. 5), which gives two conditions: $\partial^2 F/\partial^2 c = 0$, $T = T_c$.

The expressions for the spontaneous magnetization near $T_c$, $T < T_c$: $m = \sqrt{3} \sqrt{(T_c - T)/T_c}$, and that for the Curie temperature $T_c = -J_0/c/3k$, yield the following equation for the concentration at point $a$:

$$\frac{\partial^2 F}{\partial^2 c} = V_0 - \frac{1}{3(1-c_a)} J_0 + \frac{5}{6} J_0 = 0.$$  

Thus:

$$c_a = \frac{6 + 3J_0/V_0}{6 + 5J_0/V_0}.$$  

Condition $0 < c_a < 1$ yields for the interaction parameters: $J_0/V_0 > 0$. This in turn gives the concentration range for the miscibility gap: $3/5 < c_a < 1$. To sum up, for binary alloys with decomposition ($V_0 < 0$) and with one element being ferromagnetic ($J_0 < 0$), there must exist an additional miscibility gap due to the inter-atomic magnetic interactions.

The obtained phase diagram indicates that the magnetic and structural properties of the samples should strongly depend on the temperature of fabrication (substrate temperature for films). Specifically, quenching the material on to substrates is expected to be beneficial for the uniformity of the films. Here, a uniform mixing of the two elements in the magnetron plasma flux is frozen in on the substrate before the magnetic atoms have time to interact by exchange. If annealed at a sufficiently high temperature and then cooled slowly, the exchange interaction in the film is expected to result in atomic diffusion as to favor Ni-clustering and therefore partial phase separation into a Ni-rich and Cu-rich phases, as discussed above.

5. Conclusions

Diluted ferromagnetic alloy films Ni$_x$Cu$_{1-x}$ obtained by magnetron sputtering exhibit partial phase separation into Ni-rich and Cu-rich phases. The phase separation is more pronounced for higher Cu dilution and leads to a broadening of the ferro-paramagnetic phase transition in the system. This process is modeled using ab-initio calculations, taking into account the magnetic interactions in the system. Our analysis shows that the phase separation in the concentration range of interest is due to the Ni-Ni exchange interaction, which favors clustering of Ni and thereby compositional gradients in the alloy. This can additionally lead to a significantly non-linear dependence of the Curie temperature on the alloy concentration. Our analysis further suggests that the general nature of the observed phase separation in Ni-Cu, namely the exchange-induced magnetic atom clustering in an otherwise perfectly solvable two-component system, should be found in other diluted alloys of magnetic-nonmagnetic or strongly magnetic-weakly magnetic elements and likewise lead to magneto-structural inhomogeneities there.

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