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Evidence of a high-spin ferromagnetic state in fcc-structured Fe–Ag (Au) alloys synthesized by ion beam manipulation

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Abstract

Based on the design of interfacial free energy in Fe–Ag (Au) multilayered films, metastable Fe₄₀Ag₆₀ and Fe₄₀Au₆₀ alloys were synthesized by ion beam manipulation in the Fe–Ag and Fe–Au systems. The synthesized alloys were identified to crystallize in a large fcc structure with a lattice constant of 0.38–0.39 nm and the associated magnetic moments per Fe atom were measured to be around 2.10–2.30 μ_B . The above experimental observations, together with some theoretical analysis, confirm the existence of a high-spin ferromagnetic state in the fcc-structured Fe-containing alloys.

The physical nature of the magnetic properties of 3d ferromagnetic metals (Fe, Co, Ni) has been a long standing research objective of general interest, because of its vital importance for the basic understanding of the structure of matter as well as for the practical application in high technology. In recent years, the magnetic behaviours of these metals in the nonequilibrium (namely metastable) structures have attracted much interest, and the previous theoretical investigations have indicated that a ferromagnetic state could also be retained in fcc and bcc Co as well as in bcc and hcp Ni, yet the associated magnetic moments per Co/Ni atom did not show considerable change from the equilibrium values [1]. For the metastable fcc Fe, first principles calculations based on various methods have been carried out, since the mid-1980s, to study its magnetic ordering [1–6], and a similar conclusion has been reached that the metastable fcc Fe with a large lattice constant preferred to be in a high-spin ferromagnetic (HS-FM) state [2–4, 6]. Recently, Kong *et al* found that when the lattice constant of the metastable fcc Fe was greater than 0.36 nm the magnetic moment per Fe atom (abbreviated

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as μFe hereafter) could be $2.52 \mu_{\text{B}}$ or even higher, which is significantly greater than that of the equilibrium bcc Fe ($2.21 \mu_{\text{B}}$) [6]. Such a large magnetic moment is certainly of great interest in terms of basic understanding as well as of potential application. In fact, the HS-FM state of fcc Fe has been predicted for more than a decade, yet from a philosophic point view the HS-FM state can only be considered as a real state after obtaining a sound experimental confirmation, which is in a way of the same importance as the theoretical prediction. In this regard, experimental studies have been conducted, and the results obtained so far did suggest that the metastable fcc Fe could feature various magnetic behaviours; however, in some cases, the reported results seemed to be in controversy or even contradict each other. For example, for fcc Fe precipitates in a Cu matrix, neutron scattering analysis at low temperature suggested an antiferromagnetic (AFM) configuration [7] or AFM modulated with a spiral spin-density wave component [8], whereas both Mössbauer [9] and susceptibility [10] measurements suggested a ferromagnetic ordering. Similar disparity exists in the experimental study of fcc-Fe thin film epitaxially grown on Cu(100) substrates [11–13]. In short, up to now, although the richness of magnetic orderings of the metastable fcc Fe has been observed in experiments, the predicted HS-FM state has not been soundly confirmed.

The present authors propose, in this paper, a relatively neat approach to pursue further experimental study concerning the magnetic ordering of fcc Fe. The main idea is to locate the Fe atoms in a large fcc lattice of a host metal to form fcc-structured Fe-containing alloys, while not forming any intermetallic compound. The best candidates are Ag and Au. First, Ag and Au are both of fcc structure with large lattice constants of 0.409 and 0.408 nm, respectively. Second, the Fe–Ag and Fe–Au systems both feature positive heats of formation (+42 and +12 kJ mol^{-1} , respectively) [14] and therefore can hardly form any intermetallic compound. Accordingly, here we adopt a far-from-equilibrium scheme, i.e. ion beam manipulation (IBM), which was recently developed by Li *et al* for synthesizing highly energetic metastable alloys or artificial solid-state microstructures in the binary metal systems [15]. Compared with the traditional ion beam mixing [16], the new scheme mainly deals with systems featuring positive heats of formation, and the major driving force for alloying should be from the interfacial free energy, which is in positive proportion to the layer number of the multilayered films. In designing the initial multilayered samples, the thickness of the individual layer was frequently down to 2–3 nm from the traditional 7–8 nm, resulting in more layers at a fixed total thickness.

In the present study, three Fe–Ag compositions, i.e. $\text{Fe}_{20}\text{Ag}_{80}$, $\text{Fe}_{30}\text{Ag}_{70}$ and $\text{Fe}_{40}\text{Ag}_{60}$, were selected to cover a relatively broad composition range, aiming to form an Fe–Ag fcc solid solution containing as much Fe as possible, and 200 keV xenon ions were employed to perform the IBM experiments. The total thickness of the Fe–Ag samples was then designed to be around 45 nm matching the range of the irradiation ions, according to the well documented TRIM program [17]. The initial multilayered samples are in a high enough energy state according to Miedema's theory [14]. Take the $\text{Fe}_{40}\text{Ag}_{60}$ sample as an example; the multilayered films consisted of nine Fe and ten Ag layers, respectively, and the initial free energy of the multilayered films was 46.0 kJ mol^{-1} , which was much higher than that of the expected metastable fcc-structured $\text{Fe}_{40}\text{Ag}_{60}$ supersaturated solid solution (calculated to be 21.5 kJ mol^{-1}). The Fe–Ag multilayered films were prepared by alternately depositing pure Ag and Fe onto newly cleaved NaCl single crystals in an ultra-high vacuum electron-beam evaporation system. The as-deposited films were then irradiated in an implanter by 200 keV xenon ions with a fine current density ($<1 \mu\text{A cm}^{-2}$) at room temperature to various doses ranging from 5×10^{14} to 7×10^{15} ions cm^{-2} . Transmission electron microscopy (TEM) and selected area diffraction (SAD) were employed to characterize the structural change in the multilayered films. The energy-disperse spectrum (EDS) was used to determine the real compositions of the samples. The alternating gradient magnetometer (AGM) was employed

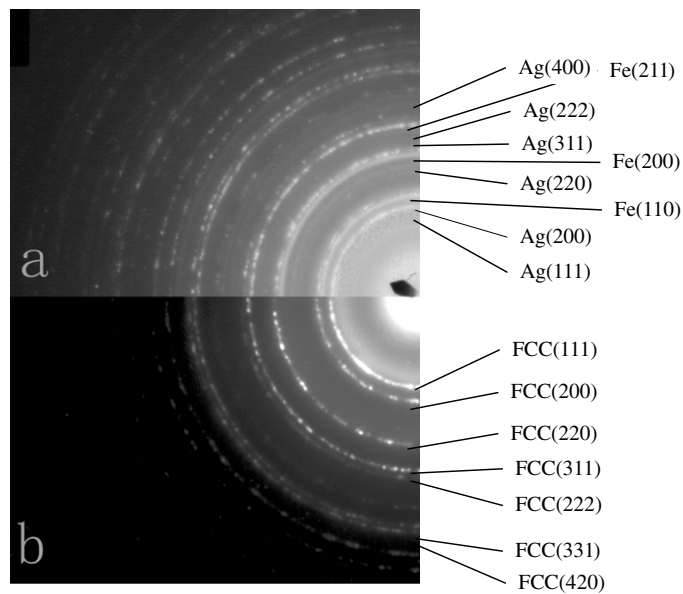


Figure 1. The SAD patterns of the $\text{Fe}_{40}\text{Ag}_{60}$ multilayered films: (a) in the as-deposited state and (b) after irradiation to a dose of $2 \times 10^{15} \text{Xe}^+ \text{cm}^{-2}$.

to measure the magnetic properties of the samples. The AGM had a resolution of $2 \mu\text{emu}$ in an applied magnetic field up to 5 kOe; the measuring error can therefore be ignored. After the magnetic measurement, the samples were completely dissolved into 10 ml solution of an $\text{HNO}_3 + \text{HCl}$ mixture to determine the Fe content by the PLASMA-SPEC-I inductive coupled plasma atomic emission spectrum (ICP). The measuring error of ICP was about 5%. Then, the μFe was deduced from the obtained data from the AGM and ICP measurements [18], and combining the errors involved in the AGM and ICP measurements the total error for the deduced μFe was therefore around 5%.

Figure 1(a) is a typical SAD pattern from the as-deposited $\text{Fe}_{40}\text{Ag}_{60}$ sample, and it clearly shows the coexistence of the polycrystalline bcc Fe and fcc Ag, indicating that no intermetallic compound was formed. After irradiation to adequate doses, a unique fcc phase was indeed formed in all the Fe–Ag multilayered films studied in the present study according to the SAD patterns. We concentrate on presenting and discussing the $\text{Fe}_{40}\text{Ag}_{60}$ case, which contained the largest Fe content among the studied samples. After irradiation, TEM bright-field examination over the entire sample showed that a new and homogenous Fe–Ag phase is formed. Figure 1(b) is the SAD pattern of the $\text{Fe}_{40}\text{Ag}_{60}$ sample after irradiation to a dose of $2 \times 10^{15} \text{Xe}^+ \text{cm}^{-2}$, showing the formation of a unique fcc-structured phase. The lattice constant was identified from the SAD pattern to be 0.39 nm, and the real composition was determined by EDS analysis to be $\text{Fe}_{37}\text{Ag}_{63}$, quite close to the designed composition of $\text{Fe}_{40}\text{Ag}_{60}$.

Figure 2 shows the magnetization curves for the as-deposited $\text{Fe}_{40}\text{Ag}_{60}$ multilayered sample and the synthesized fcc-structured $\text{Fe}_{40}\text{Ag}_{60}$ alloy, respectively. In the measurements, the applied magnetic field was parallel to the films. Table 1 lists the obtained data from AGM and ICP measurements together with the deduced μFe . From table 1, one sees that in the as-deposited $\text{Fe}_{40}\text{Ag}_{60}$ sample μFe was measured to be about $1.35 \pm 0.11 \mu_{\text{B}}$, which is lower than the ideal value of $2.21 \mu_{\text{B}}$. Such a deviation might result from some possible influencing factors, such as deformation/defects in the thin films, since the magnetic properties

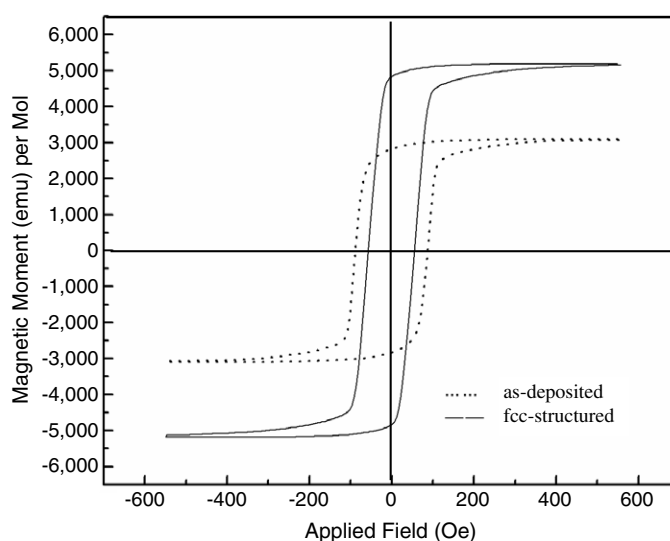


Figure 2. Magnetization curves obtained at room temperature (a) for the as-deposited $\text{Fe}_{40}\text{Ag}_{60}$ multilayered sample, and (b) for the synthesized fcc-structured $\text{Fe}_{40}\text{Ag}_{60}$ alloy film (the applied magnetic field was parallel to the sample).

Table 1. Magnetic properties of the $\text{Fe}_{40}\text{Ag}_{60}$ and $\text{Fe}_{40}\text{Au}_{60}$ multilayered films and the respectively alloys synthesized by ion beam manipulation.

Sample		Concentration of Fe ^a (g m^{-3})	Magnetic moment ^b (10^{-6} A m^2)	μFe (μB) ^c
$\text{Fe}_{40}\text{Ag}_{60}$	As-deposited	0.20	0.271	1.35 ± 0.11
	fcc alloy	0.30	0.691	2.30 ± 0.15
$\text{Fe}_{40}\text{Au}_{60}$	As-deposited	0.10	0.139	1.39 ± 0.11
	fcc alloy	0.31	0.652	2.10 ± 0.15

^a Concentration of Fe in the 10 ml solution.

^b Saturated magnetic moment of the sample.

^c $\mu\text{B} = 9.273 \times 10^{-24} \text{ A m}^2$.

are sensitive to the detailed structural characteristics in the films [19]. In fact, such deviation is frequently observed in thin solid films and therefore the measured magnetic moment per Fe atom in the as-deposited Fe–Ag sample is in a way a reference for the present experimental condition. In fact, such deviation is frequently observed in thin solid films and therefore the measured μFe atom in the as-deposited Fe–Ag sample is in a way a reference for the present experimental condition. An important finding from table 1 is that for the irradiated sample, in which a unique fcc-structured phase was formed, μFe is deduced to be $2.30 \pm 0.15 \mu\text{B}$, which is significantly greater than the measured value in the as-deposited sample, suggesting a significant enhancement of μFe in the synthesized Fe-containing fcc-structured alloy.

The first-principles calculations predict that the Fe atoms will show a high-spin ferromagnetic state when they arrange themselves in a fcc lattice with a constant beyond 0.36 nm. Here in the present experimental study, the significant enhancement of the magnetic moment for the Fe atoms is just related to the structure transformation; i.e., when the Fe atoms are arranged in a bcc lattice μFe is only about $1.35 \mu\text{B}$, while arranged in a large fcc lattice μFe increased to $2.30 \mu\text{B}$. Considering the significant enhancement together with the

structure transformation, we conclude that the above results provide experimental evidence for the predicted HSFM state of Fe. One may argue that there is a deficiency of about $0.2 \mu_B$ between the experimentally measured μ_{Fe} ($2.30 \mu_B$) and theoretically predicted $2.52 \mu_B$ [6]. In fact, this is inevitably caused by the temperature. According to the investigations on the fcc-Fe/Cu(Au) alloys [20], the Curie temperature (T_c) of these alloys were estimated to be about 500–600 K. In the present study, the magnetic moment was measured at room temperature, which is about $T_c/2$, and the measured moment should be somewhat lower than that predicted for 0 K, i.e. the so-called zero Kelvin moment. In addition, the difference between the film and the ideal crystal could also cause some variation.

Similar IBM experiments were also conducted for the Fe–Au system, and a unique fcc-structured $Fe_{40}Au_{60}$ alloy with a lattice constant of 0.38 nm was also obtained. For the synthesized $Fe_{40}Au_{60}$ alloy, the magnetic moment per Fe atom was measured to be around $2.10 \pm 0.15 \mu_B$, also listed in table 1, confirming again the HS-FM state of Fe.

In summary, we have shown the possibility/feasibility of synthesizing metastable fcc-structured Fe–Ag and Fe–Au alloys with a large lattice constant ranging from 0.38 to 0.39 nm by far-from-equilibrium IBM, and the magnetic moments per Fe atom in the synthesized alloys were measured to be in a range of 2.10 – $2.30 \mu_B$, which could be considered as evidence confirming the existence of an HS-FM state of Fe.

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