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Mössbauer study of Fe–Co nanowires

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Abstract

Arrays of Fe_{1-x}Co_x (0.0 ≤ x ≤ 0.92) nanowires have been prepared by an electrochemical process, co-depositing Fe and Co atoms into the pores of anodic aluminium; their compositions were determined by atomic absorption spectroscopy. Transmission electron microscope results show that the nanowires are regularly spaced and uniform in shape with lengths of about 7.5 μm and diameters of 20 nm. The x-ray diffraction indicates a texture in the deposited nanowires. For the composition below 82 at.% cobalt, the nanowires had a body-centred-cubic structure with a [110] preferred orientation. For the 92 at.% cobalt sample, the alloy exhibited a mixture of bcc and face-centred-cubic structure. The room temperature ⁵⁷Fe Mössbauer spectra of the arrays of Fe_{1-x}Co_x nanowires have second and fifth absorption lines of the six-line pattern with almost zero intensity, indicating that the internal magnetic field in the nanowires lies along the long axis of the nanowire. The maximum values of the hyperfine field ($B_{\text{hf}} = 36.6 \pm 0.1$ T) and isomer shift (IS = 0.06 ± 0.01 mm s⁻¹) occur for 44 at.% cobalt. The variations of the isomer shift and the linewidths with composition indicate that the Fe_{1-x}Co_x alloy nanowires around the equiatomic composition are in an atomistic disordered state.

1. Introduction

Synthesized one-dimensional magnetic nanowires and their periodic arrays have attracted much attention recently because of their distinctive properties and potential applications. From the point of view of applications, the electrodeposited nanowires/arrays are of interest for magnetoresistive devices of very small size [1] and for high-density recording media [2]. The density in conventional longitudinal recording may be less than 50 Gb in⁻² because of

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the limitations in the thermal stability [3]. However, the arrays of magnetic nanowires may potentially produce areal density in excess of 100 Gb in^{-2} [4]. Furthermore, anodization of aluminium is a much cheaper process for the synthesis of a nm-scale porous structure than most previous methods. Magnetic materials can be deposited into such pores by ac electrodeposition to produce isolated, needle-like magnetic nanowires. Arrays of ferromagnetic Fe [4, 5], Co [4, 6], Ni [7, 8], and Fe–Ni [9] and Co–Ni [10] alloy nanowires have been fabricated and their magnetic properties have been studied systematically.

The Fe–Co alloys are important magnetic materials due to their high saturation magnetization and high Curie temperature, which cannot be matched by any other alloy system. A saturation magnetization up to 2.4 T and a Curie temperature around 950°C are typical for Fe–Co alloys with compositions of 25–50% Co. Bulk Fe–Co alloys in the composition range between about 30 and 70% Co also undergo an order–disorder transition at approximately 730°C and form ordered alloys at room temperature even in rapidly quenched samples. The ordered state displays decreased resistivity, as expected, and decreased ductility compared to the disordered material. Normally the degree of long-range atomic order is determined via specific heat measurements [11] and neutron diffraction [12].

As important magnetic materials, both bulk and nanoparticulate Fe–Co alloys have been studied widely [13–16]. However, Fe–Co nanowires have not been investigated to nearly the same extent as other ferromagnetic alloy-based nanowires. Owing to the special shape of one-dimensional nanowires, many novel properties may be exhibited. In addition, the arrays represent a model system for the study of magnetic reversal and interaction processes in low-dimensional magnetic structures. There is, therefore, much interest in investigating these Fe–Co nanowires.

2. Experimental procedure

Arrays of $\text{Fe}_{1-x}\text{Co}_x$ ($0.0 \leq x \leq 1.0$) nanowires have been prepared by co-electrodepositing Fe and Co into anodic aluminium oxide (AAO) templates. The long axis of the nanowires will then be perpendicular to the AAO film. The preparation of AAO templates was described elsewhere in detail [4, 5]. In the process of preparing AAO templates, Al foils (99.999%) were anodized at $15 V_{\text{dc}}$ for an hour in $1.2 \text{ M H}_2\text{SO}_4$ aqueous solution at 20°C , using the Al foil as the cathode. The Fe and Co atoms were electrodeposited into the AAO templates from an aqueous bath containing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, HBO_3 and ascorbic acid. The compositions of the $\text{Fe}_{1-x}\text{Co}_x$ nanowires were adjusted by varying the $\text{Fe}^{2+}:\text{Co}^{2+}$ -ion ratio in the bath. The pH value of the electrolyte was maintained at about 3.0 throughout. The electrodepositions were all conducted at 200 Hz, 15 V (ac) for 5 min, using graphite as the counter-electrode. The AAO films filled with nanowires were removed from the Al substrates using HgCl_2 aqueous solution. Nanowires were liberated from the AAO film by dissolving the alumina layer with aqueous NaOH.

Structural characterization was performed by means of x-ray diffraction (XRD) using a Rigaku D/Max-2400 diffractometer with $\text{Cu K}\alpha$ radiation. The atomic percentages of Fe and Co in the nanowires were determined by atomic absorption spectroscopy (AAS). The nanowires were also examined by transmission electron microscopy (TEM) using a JEOL 2000 \times microscope operating between 75 and 100 kV. The Mössbauer spectra were collected at room temperature using a constant-acceleration spectrometer with a ^{57}Co in Rh source. All of the spectra were computer fitted with a Lorentzian sextet using a least-squares method. The isomer shifts determined are relative to $\alpha\text{-Fe}$ at RT.

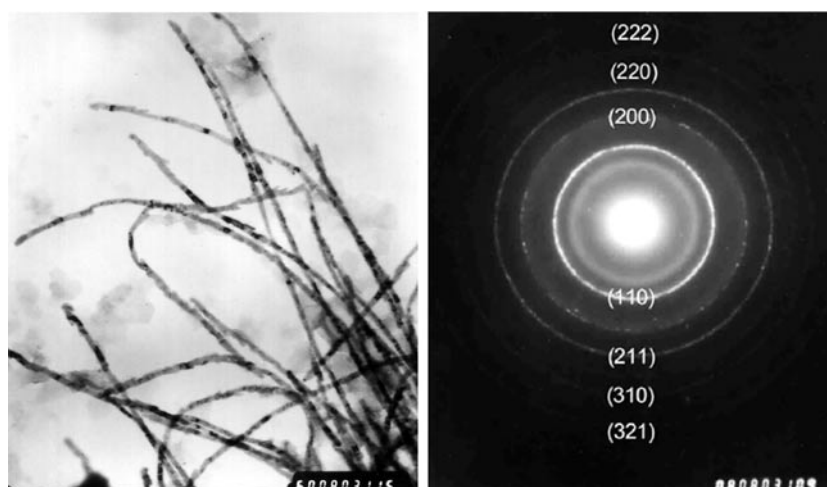


Figure 1. A TEM image of $\text{Fe}_{0.56}\text{Co}_{0.44}$ nanowires and the corresponding electron-diffraction pattern.

3. Results and discussion

Using the electrochemical method described above, arrays of $\text{Fe}_{1-x}\text{Co}_x$ nanowires were prepared with composition ranging from $x = 0.0$ to 0.92 . Figure 1 shows the TEM bright-field image of the $\text{Fe}_{0.56}\text{Co}_{0.44}$ nanowires and the corresponding electron-diffraction pattern. It can be seen that the nanowires are regularly spaced and uniform in shape, about 20 nm in diameter and $7.5\ \mu\text{m}$ in length. The electron-diffraction pattern indicates that the nanowires have a bcc structure. All of the AAO templates were prepared under the same conditions and all of the samples were deposited for an equal time. The diameter of the nanowires depends on the pore size in the AAO film and the length mainly depends on the time of electrodeposition. This leads to nanowires with different compositions being approximately the same size.

Due to the difference in depositional velocity, the concentration of Fe or Co in the nanowires does not equal the concentration of Fe^{2+} or Co^{2+} in the electrolyte. Figure 2 shows the alloy composition of the $\text{Fe}_{1-x}\text{Co}_x$ nanowires (expressed as an atomic fraction) as obtained by AAS versus the ionic fraction of Co^{2+} in the electrolyte. The sum of the Fe^{2+} and Co^{2+} ionic fractions in the solution is set to unity. Because Co is less electronegative than Fe, the depositional velocity of Co is slightly higher than that of Fe. Thus, the concentration of Co in the nanowires is slightly higher than the concentrations of Co^{2+} in the corresponding solution, which is consistent with the results obtained on deposited Fe–Co films [17].

The XRD patterns of the AAO films filled with the $\text{Fe}_{1-x}\text{Co}_x$ nanowires are shown in figure 3. The XRD patterns clearly indicate a texture in the deposited AAO films. All $\text{Fe}_{1-x}\text{Co}_x$ nanowires with $x \leq 0.82$ have a bcc structure with a [110] preferred orientation. However, $\text{Fe}_{1-x}\text{Co}_x$ nanowires with a small amount of Fe ($x = 0.92$) exhibit a mixture of body-centred-cubic (bcc) and face-centred-cubic (fcc) structure with a [111] preferred orientation. In addition, an $\alpha \rightarrow \gamma$ phase transition in the $\text{Fe}_{1-x}\text{Co}_x$ nanowires occurs between $x = 0.82$ and 0.92 , whereas the $\alpha \rightarrow \gamma$ phase transition in bulk $\text{Fe}_{1-x}\text{Co}_x$ alloys takes place at a composition of 73% Co. Clearly, the phase boundary for the $\alpha \rightarrow \gamma$ phase transition shifts to higher Co concentration in the Fe–Co nanowires. The XRD results also show that the lattices of the $\text{Fe}_{1-x}\text{Co}_x$ nanowires are slightly enlarged in comparison with those of bulk $\text{Fe}_{1-x}\text{Co}_x$ alloys.

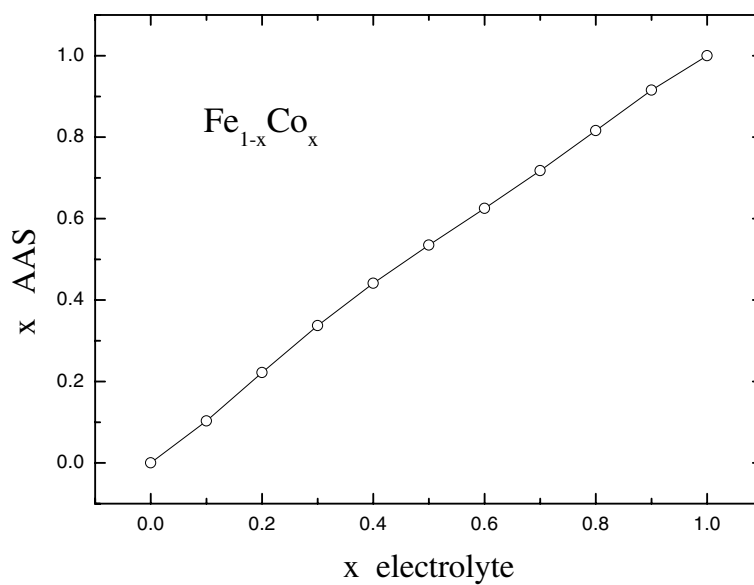


Figure 2. A plot of the concentration of Co (atomic fraction) as obtained by AAS against the ionic fraction of Co²⁺ in the electrolyte.

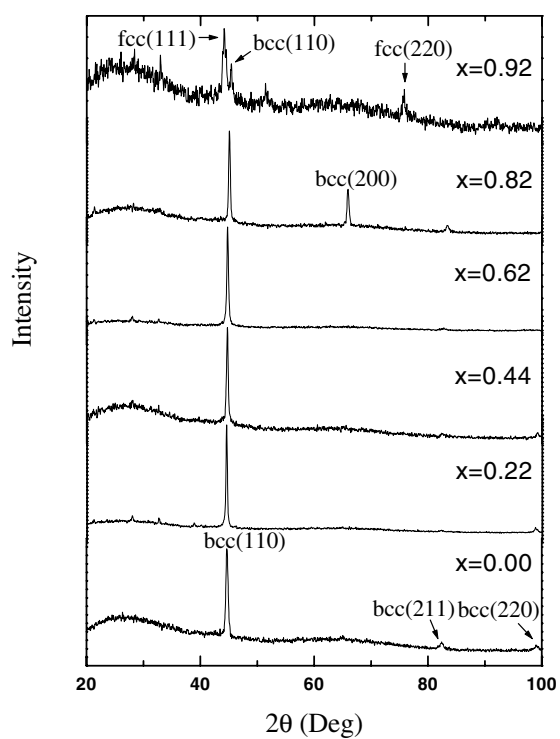


Figure 3. XRD patterns of AAO films filled with Fe_{1-x}Co_x nanowires, obtained using Cu K α radiation.

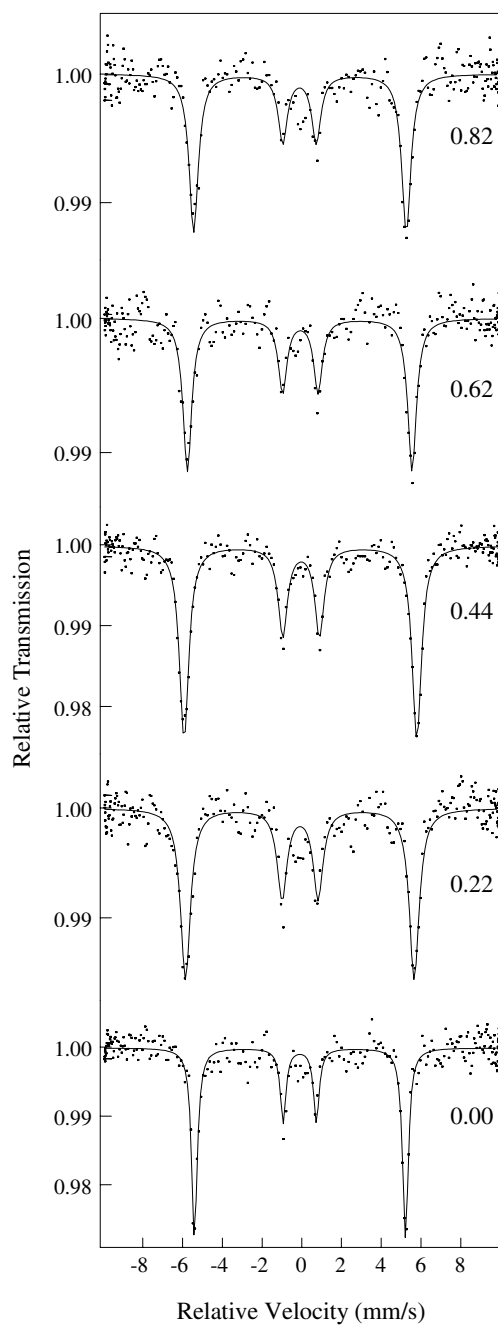


Figure 4. Room temperature ^{57}Fe Mössbauer spectra of arrays of $\text{Fe}_{1-x}\text{Co}_x$ nanowires within supporting AAO films. The γ -ray beam is perpendicular to the AAO films.

Room temperature ^{57}Fe Mössbauer spectra were taken for the arrays of the $\text{Fe}_{1-x}\text{Co}_x$ nanowires within the supporting AAO films, with the γ -ray beam perpendicular to the AAO film. Figure 4 shows a number of such Mössbauer spectra. It can be seen that for each sample the second and fifth absorption peaks in the sextet have almost disappeared, which indicates

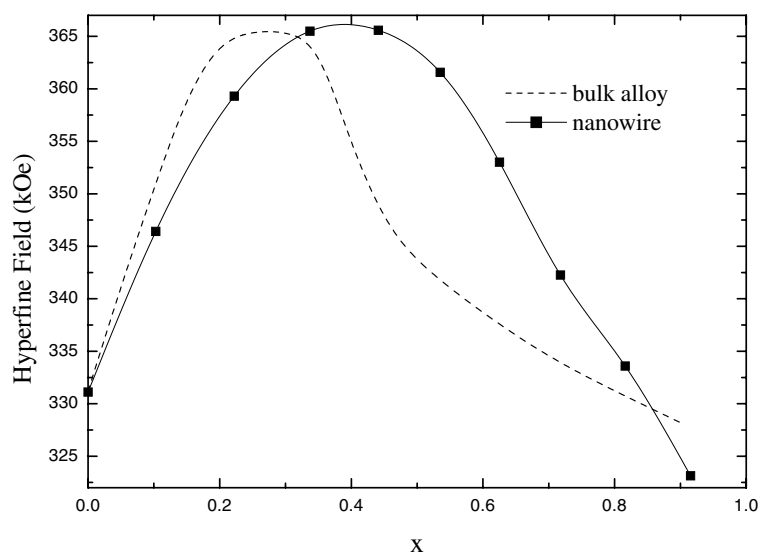


Figure 5. Hyperfine field of the $\text{Fe}_{1-x}\text{Co}_x$ AAO films as a function of composition, along with earlier results for bulk alloys.

that the direction of the internal field is parallel to the nanowires. However, the AAO films of Fe–Co nanowires do not exhibit macro-magnetism, which suggests that the internal field of each individual nanowire is randomly orientated either parallel or anti-parallel to the nanowire axis. Because of the special shape of each individual nanowire, a strong shape anisotropy exists in them, which results in the preferred orientation of the internal field. However, the preferred orientation is not [100], the easy axis of the bulk bcc Fe–Co alloy, but rather [110]. This means that the shape anisotropy is far stronger than the magnetocrystalline anisotropy in the nanowires. Since the internal field is perpendicular to the principal AAO film surface, the arrays of Fe–Co nanowires are highly promising candidates for application as perpendicular recording media.

The variation of the hyperfine field of the $\text{Fe}_{1-x}\text{Co}_x$ AAO films versus the composition is shown in figure 5, along with earlier results for bulk Fe–Co alloys [14]. It can be seen that the variation of this field in the Fe–Co nanowires is generally similar to that in bulk alloys, that is, it initially increases, reaches a maximum value and then decreases. However, the compositions where the maximum value of B_{hf} appear are different in the bulk and the nanowires. In the latter, the maximum value of $B_{\text{hf}} = 36.6 \pm 0.1$ T occurs at 44% Co, while for bulk alloys, it occurs at 25% Co with B_{hf} equal to the maximum B_{hf} in the nanowires. For $x \leq 0.34$, the B_{hf} -values of the $\text{Fe}_{1-x}\text{Co}_x$ nanowires are thus lower than the B_{hf} -values of bulk alloys. For $0.34 \leq x \leq 0.82$, the B_{hf} -values of the $\text{Fe}_{1-x}\text{Co}_x$ nanowires are correspondingly larger than the B_{hf} -values of bulk alloys.

The maximum value of the half-widths (FWHM) of the outermost absorption peaks occurs around 54% Co where the $\text{FWHM} = 0.65 \pm 0.02$ mm s⁻¹ (figure 6). The minimum value of FWHM occurs at $x = 0.0$ where the $\text{FWHM} = 0.35 \pm 0.02$ mm s⁻¹. Fe–Co alloys with near-equiatomic composition can exhibit both atomic order and atomic disorder. From the viewpoint of simple statistics, the Fe site disorder would be a maximum at the equiatomic composition and conversely the Fe site atomic order would be minimum. Therefore, the Mössbauer spectrum of $\text{Fe}_{0.5}\text{Co}_{0.5}$ has the largest linewidth in the Fe–Co series, as expected. For the case of complete atomic order, $\text{Fe}_{0.5}\text{Co}_{0.5}$ would possess the α' -CsCl structure, and there would be only one kind of Fe site. The linewidth would be equal to that of pure iron, and

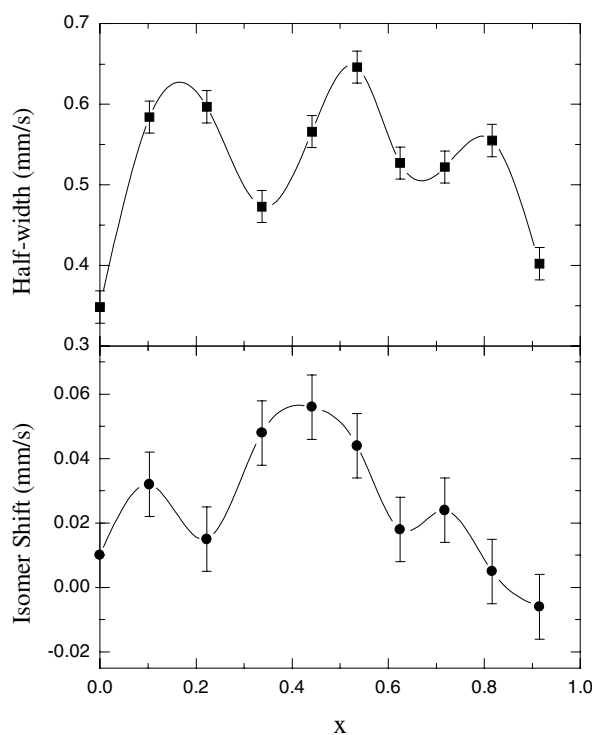


Figure 6. Half-width and isomer shift (relative to pure iron) of $\text{Fe}_{1-x}\text{Co}_x$ nanowires as functions of composition.

would exhibit a minimum at this composition. Previous experimental results on bulk Fe–Co alloys with atomic disorder are consistent with such a picture [18]. From the above discussion and the experimental linewidth data, $\text{Fe}_{1-x}\text{Co}_x$ nanowires with near-equiatomic composition appear atomically disordered. The degree of atomic order can be qualitative judged from the magnitude of the linewidth. In previous work, it has been rather difficult to obtain disordered alloys at room temperature, if thermal treatment has been carried out on the samples. In the electrochemical process of preparing nanowires, thermal treatment is not used and the nanowires have atomic disorder. Thus the electrochemical method is an easy way to prepare the nanowires and films that have atomic disorder. Several samples with near-equiatomic composition were heat treated and subsequently annealed. It was found that the hyperfine field and linewidth of these samples decreased, indicating that an ordered state had formed.

The concentration dependence of the isomer shift is also shown in figure 6. The maximum value of $\text{IS} = 0.06 \pm 0.01 \text{ mm s}^{-1}$ occurs at 44% Co, the composition at which B_{hf} is also largest. The IS decreases from a maximum value at 44% Co to a minimum value ($\text{IS} = -0.01 \pm 0.01 \text{ mm s}^{-1}$) at 92% Co. Such behaviour is similar to that found in disordered bulk Fe–Co alloys [18], while for ordered bulk Fe–Co alloys, a minimum IS appears at the equiatomic composition [18]. Thus the relationship between composition and the isomer shift of $\text{Fe}_{1-x}\text{Co}_x$ nanowires is also consistent with $\text{Fe}_{1-x}\text{Co}_x$ nanowires around the equiatomic composition being atomically disordered. The isomer shift depends itself on the electronic charge density in the vicinity of iron nuclei. In d-group metals, such as iron–cobalt, the density of 4s and 3d electrons are the two main factors affecting the charge density near the iron nuclei. By increasing the cobalt concentration, the lattice parameter decreases [13], which results in an increase of the volume density of both 4s and 3d electrons. Since Co has one more 3d electrons

than Fe, an increase in cobalt concentration results in a significantly higher charge density for 3d electrons. The increase of 4s electron density is known to cause a negative change in the IS, while an increase in 3d electron density causes a positive change. The two effects are opposite and the concentration dependence of IS obviously results from a competition between the two.

4. Conclusions

Arrays of $\text{Fe}_{1-x}\text{Co}_x$ ($0.0 \leq x \leq 0.92$) nanowires have been successfully prepared by using an electrochemical method. The alloy composition of the nanowires was determined by AAS, which shows that the depositional velocity of Co is slightly higher than that of Fe. XRD also indicates a texture in the deposited nanowires. For $x \leq 0.82$, the $\text{Fe}_{1-x}\text{Co}_x$ nanowires have a bcc structure with a [110] preferred orientation. For the sample with $x = 0.92$, the nanowires exhibit a mixture of both bcc and fcc structures. The room temperature ^{57}Fe Mössbauer spectra of $\text{Fe}_{1-x}\text{Co}_x$ AAO films show that the second and fifth absorption peaks almost vanish, indicating that the internal magnetic field in the nanowires orients along the length of the nanowire, suggesting that a strong shape anisotropy exists in arrays of such nanowires. The maximum values of the hyperfine field and the isomer shift occur at 44% Co (where $B_{\text{hf}} = 36.6 \pm 0.1$ T and $\text{IS} = 0.06 \pm 0.01$ mm s $^{-1}$), different from the corresponding composition in bulk alloys. The nature of the order–disorder transition has also been examined by using the Mössbauer parameters. The variations of the IS and the linewidths with composition show that the Fe–Co nanowires near the equiatomic composition are atomically disordered.

Acknowledgments

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