Magnetic properties of Fe$_{2-x}$Al$_x$CoO$_4$ (0 ≤ x ≤ 1) nanoparticles

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Abstract.

Nanocrystalline particles of the Fe$_{2-x}$Al$_x$CoO$_4$ (0 ≤ x ≤ 1) ferrites with cubic spinel structure have been synthesized by the sol-gel method. Size of the particles decreases from 39 nm to 6 nm as the Al content x increases. In the present work magnetic hysteresis curves and ZFC-FC curves have been studied. The magnetization of the Fe$_2$CoO$_4$ nanoparticles is lower than the magnetization of the bulk sample due to the surface and finite size effects. Saturation magnetization and remanent magnetization decrease as the x increases because of substitution of magnetic Fe ions with non-magnetic Al ions and possibly due to the spin canting and changes in ferrimagnetic structure. Coercive field changes with x in a complex way. Anisotropy barrier is lowered by reducing the size of the particle, but it can be increased by changing the distribution of Fe and Al ions in the spinel structure. The observed splitting between ZFC-FC curves in a rather high field indicates the presence of particles with the large anisotropy barrier for all samples.

1. Introduction

Magnetic nanoparticles exhibit some novel properties compared to the bulk, which make them promising material for technological applications in high-density magnetic recording [1], magnetic fluids, contrast enhancement in magnetic resonance imaging, magnetically guided drug delivery [2] etc. Nanometer sized particles of spinel ferrites offer excellent opportunity to study relationship between magnetic properties and their chemical composition and structure. Furthermore, it is possible to tune magnetic properties of spinel ferrites by means of chemical manipulations. Besides chemical composition, also size and shape of the particle determine their magnetic properties. As the size of the particle reduces, surface to volume ratio increases, which affects magnetic properties because surface layer generally has disordered spin structure which reduces magnetization and induces magnetic anisotropy.

In this work magnetic properties of the aluminium substituted cobalt ferrite Fe$_{2-x}$Al$_x$CoO$_4$ (0 ≤ x ≤ 1) nanoparticles have been studied. Influence of the chemical composition, cation distribution and size of the particles on magnetic properties of the Fe$_{2-x}$Al$_x$CoO$_4$ nanoparticles is discussed.
2. Experimental
The powder of nanoparticles was dispersed and fixed in paraffine within measuring ampoule in order to avoid rotation of the particles. Magnetization measurements were performed using the commercial SQUID magnetometer MPMS5 (Quantum Design). Magnetic hysteresis loops $M(H)$ were measured in the magnetic field range $\pm 5$ T at temperatures 10 K and 290 K. Temperature dependence of magnetization was measured in applied magnetic field 0.5 T to obtain zero field cooled (ZFC) and field cooled (FC) curves. At first, the sample was cooled from room temperature down to 10 K in zero applied field. Then the magnetic field was applied and magnetization was measured upon warming the sample. This gave ZFC curve. After that, the sample was cooled again, but now in applied field. The magnetization was measured during the increase of temperature, which gave FC curve.

3. Results and discussion
Nanocrystalline particles of the Fe$_{2-x}$Al$_x$CoO$_4$ ($0 \leq x \leq 1$) ferrites have been synthesized by the sol-gel method and their structure and morphology have been studied previously [3]. Prepared samples crystallize in cubic spinel structure. Size of the particles was found to decrease from 39 nm to 6 nm as the Al content $x$ was increased. Lattice parameter was also decreased as $x$ increased due to the substitution of larger Fe ion with smaller Al ion. Magnetic hysteresis loops of the Fe$_{2-x}$Al$_x$CoO$_4$ nanoparticles measured at 10 K and 290 K are shown in Figures 1 and 2, respectively. At maximal applied field of 5 T the saturation was increased due to the substitution of larger Fe ion with smaller Al ion. Values of the remanent magnetization $M_r$ and coercive field $H_c$ obtained from measured magnetic hysteresis loops are given in Table 1.

![Figure 1](image1.png)

**Figure 1.** Magnetic hysteresis loops of Fe$_{2-x}$Al$_x$CoO$_4$ nanoparticles measured at 10 K.

![Figure 2](image2.png)

**Figure 2.** Magnetic hysteresis loops of Fe$_{2-x}$Al$_x$CoO$_4$ nanoparticles measured at 290 K.

The basic magnetic properties of the spinel ferrites depend on the kind of metal cations and their distribution among the tetrahedral A sites and octahedral B sites in the spinel structure. The structure of cobalt ferrite CoFe$_2$O$_4$ is almost inverse in which most of the Co ions occupy octahedral positions. Accordingly, magnetic moment per formula unit of CoFe$_2$O$_4$ is mainly determined by the magnetic moment of the Co ions [4]. Upon substitution of the Fe ions with Al ions changes in the cation distribution take place, which affect the value of the magnetic moment per formula unit. It was found that Fe ions migrate from the octahedral B sites to the tetrahedral A sites as the concentration of the Al ions increases so that Fe and Al ions occupy both A and B sites in the spinel structure of CoFe$_{2-x}$Al$_x$O$_4$. Therefore, magnetic moment per
formula unit decreases as the Al content \( x \) increases due to the substitution of the magnetic Fe ion with non-magnetic Al ion and changes in cation distribution [4, 5]. From the Figures 1 and 2 it can be observed that the magnetization of CoFe\(_{2-x}\)Al\(_x\)O\(_4\) nanoparticles decreases as the Al content \( x \) increases, which is in accordance with the results given in reference [4].

| Sample          | \(M_r\) (10 K) [emu/g] | \(M_r\) (290 K) [emu/g] | \(\mu_0 H_c\) (10 K) [T] | \(\mu_0 H_c\) (290 K) [T] |
|-----------------|-------------------------|--------------------------|--------------------------|--------------------------|
| Fe\(_2\)CoO\(_4\) | 45.4                    | 26.9                     | 0.6474                   | 0.1228                   |
| Fe\(_{1.8}\)Al\(_{0.2}\)CoO\(_4\) | 48.8                    | 24.0                     | 0.8330                   | 0.0919                   |
| Fe\(_{1.6}\)Al\(_{0.4}\)CoO\(_4\) | 37.6                    | 19.6                     | 1.0600                   | 0.1113                   |
| Fe\(_{1.4}\)Al\(_{0.6}\)CoO\(_4\) | 32.8                    | 17.2                     | 1.0234                   | 0.1067                   |
| Fe\(_{1.2}\)Al\(_{0.8}\)CoO\(_4\) | 14.4                    | 5.1                      | 1.3338                   | 0.0806                   |
| FeAlCoO\(_4\)    | 24.5                    | 12.2                     | 1.2010                   | 0.1307                   |

The value of the magnetization of the Fe\(_2\)CoO\(_4\) nanoparticles in applied field 5 T at 290 K (when the saturation was almost achieved) was measured to be 63.4 emu/g which is lower than the value of 80 emu/g corresponding to the saturation magnetization of the bulk sample at room temperature [6]. Reduction of magnetization in nanometer sized particles compared to bulk material can be explained within a model of a particle which consists of a core with normal spin arrangement and a surface layer with non-collinear spin arrangement [7, 8]. Smaller particles have larger surface to volume ratio and therefore reduction of magnetization is more pronounced. Some authors suggest that the canting of surface spins, caused by broken exchange bonds, is responsible for lowering of magnetization of spinel ferrite nanoparticles [9, 10, 11]. Besides canting of surface spins, it was also proposed that the core spins exhibit canted spin structure due to the large magnetocrystalline anisotropy induced by the changes in the cation distribution [12].

Thus, observed lowering of magnetization of the CoFe\(_{2-x}\)Al\(_x\)O\(_4\) nanoparticles with the increase of Al content can be understood taking into account changes in the cation composition and distribution in the spinel structure as well as surface and finite size effects in nanometer sized particles. Reduction of particle size and magnetization with the increase of Al content was also observed previously in Al doped nickel ferrite nanoparticles [13].

From the Figures 1 and 2 it can be observed that hysteresis loops are narrower at higher temperature, as expected for the system of superparamagnetic particles. Measured value of the coercive field of the Fe\(_2\)CoO\(_4\) nanoparticles at room temperature \(\mu_0 H = 0.1228\) T is in accordance with the value reported in [14]. The value of the coercive field is lower at higher temperature and changes with Al content \( x \) in a complex way. Generally, the coercive field decreases as the size of the particle decreases due to the lower anisotropy barrier in smaller particles. As the Al content increases, changes in the cation distribution in the spinel structure can induce rather large magnetocrystalline anisotropy which results in higher coercive field. Thus, the change in the coercive field upon increase of the Al content \( x \) is a result of two effects: lowering of anisotropy barriers as the size of the particles reduces and enhanced magnetocrystalline anisotropy induced by the different cation distributions.

The measurements of the temperature dependence of magnetization \(M(T)\) in applied magnetic field of 0.5 T for all samples are shown in Figure 3. The values of FC magnetization are consistent with the values obtained from the hysteresis loops measured at 290 K. The splitting
of the ZFC and FC curves, observed for all samples, is a result of the blocking of the magnetic moment of nanoparticles in the sample and indicates superparamagnetic behaviour of the studied systems. In the Figure 3 the splitting between ZFC and FC curves at temperatures $\geq 250$ K can be registered. This could be expected considering that hysteresis loops measured at 290 K are irreversible up to 0.5 T at least.

Figure 3. The dependence of magnetization $M$ on temperature $T$ of the CoFe$_{2-x}$Al$_x$O$_4$ nanoparticles measured after cooling in zero field (ZFC, open symbols) and after cooling in applied magnetic field (FC, full symbols).

4. Conclusion

Magnetic properties of the Fe$_{2-x}$Al$_x$CoO$_4$ ($0 \leq x \leq 1$) nanoparticles have been studied. It was observed that the magnetization of the nanoparticles reduces as the Al content $x$ increases due to the changes in cation distribution and non-collinear spin structure of the surface layer of the particles. Coercive field also changes with the Al content $x$, which was explained in terms of lower anisotropy barriers in smaller particles and induced magnetocrystalline anisotropy by the different cation distribution. More quantitative description of the measured systems will be subject of further investigations.

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