FMR evidence of finite-size effects in CoCu granular alloys

B. R. Pujada,[1,*] E. H. C. P. Sinnecker,[1] A. M. Rossi,[1] C. A. Ramos,[2] and A. P. Guimarães[1]
[1]*Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, Rio de Janeiro 22290-180, Brazil*
[2]*Centro Atómico Bariloche and Instituto Balseiro, 8400 San Carlos de Bariloche, Rio Negro, Argentina*
(Received 16 April 2002; revised manuscript received 3 September 2002; published 6 January 2003)

Granular CoCu ribbons, as cast and heat treated, were studied by means of the *X*-band ferromagnetic resonance (FMR) as a function of temperature, in the range from 10 K to 250 K. The FMR spectra were fitted as a sum of absorption and dispersion functions. The effective anisotropy constant K_{eff} and average grain diameter of the magnetic grains were obtained from a model derived for identical independent particles with effective uniaxial anisotropy. K_{eff} is enhanced in comparison to values for the bulk materials, and also shows a decrease with increasing mean grain diameter. The asymmetry parameter for the FMR line shows both temperature and grain-size dependence. In addition, zero-field cooled and field cooled magnetization measurements at higher fields show irreversibility for smaller grains. These results indicate an important role of the finite grain size in the magnetic behavior of the granular alloys.

DOI: 10.1103/PhysRevB.67.024402 PACS number(s): 75.75.+a, 73.22.−f, 76.50.+g

I. INTRODUCTION

Magnetically structured granular systems composed of magnetic grains of a ferromagnetic metal embedded in a nonmagnetic matrix have been a source of scientific interest due to the different properties in comparison with their bulk counterpart.[1] Nanostructured systems exhibit many promising technological applications in new high-density recording media, ferrofluids, magnetic sensors and reading heads. The latter make use of the giant magnetoresistance effect, an effect arising from the spin-dependent scattering of electrons from magnetic moments in magnetic multilayers and granular solids.[2–4]

In order to understand the physical properties of the granular systems, a series of theoretical and experimental studies have been made in recent years.[5–7] Factors such as the shape, size, and spatial distribution of the nanoparticles, crystalline structure, interactions between ferromagnetic grains, etc., affect the properties of these materials. Surface and size effects in small magnetic particles have recently gained increasing attention since they can also modify the magnetic properties of the granular systems.[8] Kodama *et al.*[9] and Martínez *et al.*[10] observed in their studies of $NiFe_2O_4$ and γ-Fe_2O_3 nanoparticles, respectively, anomalous magnetic behaviors at low temperatures, particularly a high-field irreversibility in the zero-field cooled and field cooled (ZFC-FC) magnetization measurements. Their results were related to the existence of a ferromagnetic core surrounded by canted spins of multiple stable configurations on the particle surfaces (spin-glass-like surface layer). Bødker *et al.*,[11] in their study of α-Fe particles using Mössbauer spectroscopy, proved that the effective anisotropy energy density of a whole particle increases with decreasing particle diameter. This result was interpreted in terms of an increased contribution from the surface anisotropy analogously to what occurs in ultrathin films.[12–16]

In this context, ferromagnetic resonance (FMR) has proved to be an extremely sensitive spectroscopic technique for the local study of magnetic properties and internal structure of a variety of systems.[17–22] De Biasi and Devezas[18] described expressions for the temperature dependence of the magnetic anisotropy assuming superparamagnetic grains with similar shape, size, and anisotropy constant *K*. This temperature dependence was obtained through considerations on the thermal fluctuations of the magnetic moments. Some experimental studies in systems of magnetic nanoparticles at different temperatures show that the line shape of the FMR spectra remains symmetric in the whole range of temperatures.[19,20] In this case, a correlation between the resonance field and linewidths is observed, and the magnetic properties of the system can be established. However, when the line shape of the FMR spectra is asymmetric, the changes of symmetry with temperature can also reflect differences in the magnetic behavior of the system.[23–25]

We have recently[17] reported FMR spectra of Co_xCu_{100-x} alloy samples, where a thermal treatment creates a distribution of grains of cobalt with a mean diameter that depends on the Co concentration and annealing temperature. The results also show deviations from the independent superparamagnetic character for the samples treated at high annealing temperatures.

In this work, we present the systematic study of the temperature dependence of the FMR spectra for melt-spun Co_xCu_{100-x} granular alloys with different nanostructures induced by annealing.

II. EXPERIMENT

The Co_xCu_{100-x} ($x=5$ and 10) alloy samples were prepared by melt spinning on a Cu-Zr wheel in a He atmosphere. The samples used in the experiments were ribbons, either as cast or annealed in quartz tubes during 1 h under argon atmosphere, at temperatures $T_A=450$, 500, 550, and 600 °C. For simplicity, for the as-cast sample, it was considered that $T_A=30$ °C.

FMR measurements of the Co_xCu_{100-x} alloys as a function of temperature were recorded at the *X* band (9.45 GHz), with a Bruker ESP 300E spectrometer provided with an ER 4102ST rectangular cavity using a helium gas-flow cryostat ER 4118 CF (Oxford) and a temperature controller model

ICT4 (Oxford). Measurements were carried out from 10 K to 250 K using 2 mW of microwave power and modulation amplitude of 1 G. The samples were mounted on the tip of a goniometer and the magnetic field was applied parallel and perpendicular to the ribbon plane by rotating the sample. The microwave magnetic field was maintained within the plane of the sample. Because of the asymmetry of the FMR line, the FMR spectra were fitted as a mixture of absorption and dispersion functions.[17] From these fits, the resonance fields H_r, linewidths ΔH, and the ratio of absorption and dispersion functions in the FMR line η were obtained.

Magnetization measurements were performed using the standard ZFC-FC procedures in the range of 4.2–300 K with applied fields of 90 kOe, in a quantum design PPMS magnetometer.

III. FMR LINEWIDTH IN SMALL PARTICLES

For an ensemble of identical independent magnetic particles with the same anisotropy constant K and magnetization M_s, de Biasi and Devezas[18] developed a model that takes into account the effects of temperature on the crystalline anisotropy, and which was applied to the interpretation of FMR spectra. Using this approach, information on the structure and magnetism of the granular system can, therefore, be obtained. In the case of axial symmetry, the effective anisotropy of the superparamagnetic particles has been shown[18] to be

$$H_A^{SP}=H_A\frac{1-(3/x)L(x)}{L(x)}, \tag{1}$$

where $x=\mu H/k_BT$, and $H_A=K/M_s$ is the anisotropy field of the particle. M_s is the particle saturation magnetization, and $L(x)$ is the Langevin function defined by

$$L(x)=L\left(\frac{\mu H}{k_BT}\right)=\coth\left(\frac{\mu H}{k_BT}\right)-\frac{k_BT}{\mu H}, \tag{2}$$

where $\mu=vM_s$, v the mean particle volume, and H is the applied magnetic field.

For our study, we assume that the effective magnetic anisotropy H_{eff} of the magnetic grains has uniaxial symmetry, i.e., the sum of the contributions of the intrinsic magnetocrystalline anisotropy, shape anisotropy, and stress- and surface-induced anisotropy shows a uniaxial character. Since the line broadening is caused by the random distribution of local effective anisotropy fields,[26] we can take the linewidth as proportional to the effective uniaxial anisotropy, and therefore,

$$\Delta H=\Delta H_o+\sigma H_{eff}\frac{1-(3/x)L(x)}{L(x)}, \tag{3}$$

where ΔH_o is the linewidth at high temperatures and σ is a proportionality constant.

From the fitting of the curve of ΔH vs $1/T$, it is possible to obtain the average size of the magnetic particles and the term proportional to the effective uniaxial anisotropy σH_{eff} of the magnetic grains. In this simplified model, the description is applicable to an average magnetic particle size.

IV. EXPERIMENTAL RESULTS

All the samples were characterized by the FMR spectra as a function of temperature, for both parallel and perpendicular

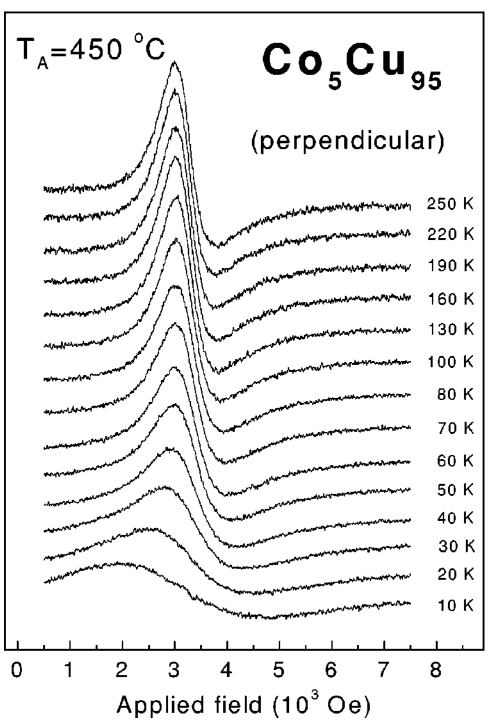

FIG. 1. The FMR spectra of Co_5Cu_{95} annealed at 450 °C and measured perpendicular to the ribbon plane as a function of temperature.

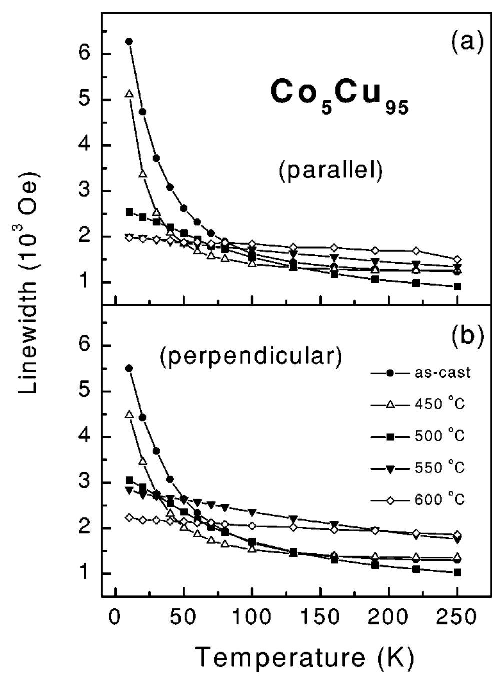

FIG. 2. The FMR linewidths from spectra for Co_5Cu_{95} samples with magnetic field (a) parallel and (b) perpendicular to the ribbon plane. The solid lines are a guide for the eyes.

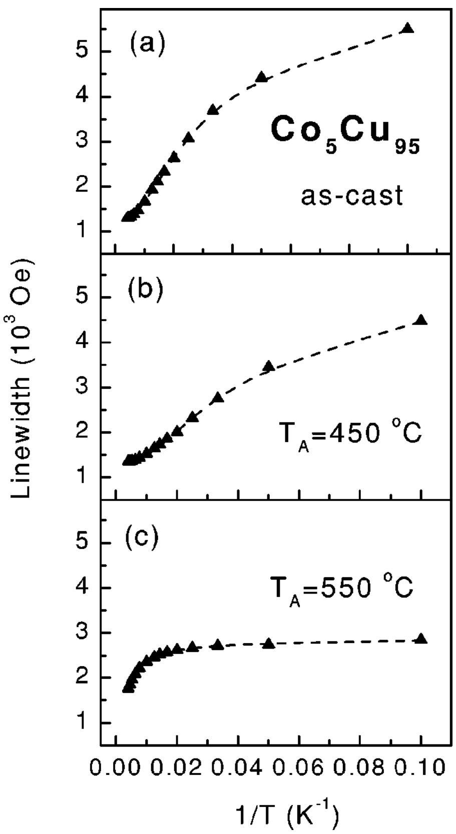

FIG. 3. Experimental FMR linewidth (filled triangles) versus inverse temperature for Co_5Cu_{95} samples. The dashed lines are computer fits using Eq. (3) for samples (a) as cast, (b) $T_A=450\,°C$, and (c) $T_A=550\,°C$.

configurations of the external applied magnetic field relative to the plane of the ribbon. Figure 1 illustrates the experimental spectra in the perpendicular configuration recorded at different temperatures for Co_5Cu_{95} heat treated at 450 °C. To allow a comparison between the different results, all the FMR spectra have been normalized to the same area. The first analysis of Fig. 1 shows a broadening of the FMR lines upon cooling. The behavior of the resonance field shows a trend towards lower fields with decreasing temperature. A more rigorous analysis of the behavior of the resonance fields and linewidths with the temperature can be performed through the computer fitting of the FMR spectra.

The behavior of the temperature dependence of the linewidth obtained from the fits is summarized in Fig. 2 for Co_5Cu_{95} alloy samples. It is clear that for samples as cast and annealed at 450 °C, a more marked increase in the linewidth at temperatures lower than 60 K is observed in both parallel [Fig. 2(a)] and perpendicular [Fig. 2(b)] configurations, in comparison to the samples treated at higher temperature. A similar behavior was observed for $Co_{10}Cu_{90}$. For the samples annealed at 500, 550, and 600 °C, for both $x=5$ and 10, the linewidths show only a monotonic increase upon cooling, and their values at the lowest temperatures are smaller in comparison to the ones treated at lower temperatures.

Because the temperature dependence of the linewidth is related to the effective magnetic anisotropy and size of the grain, computer fits of the linewidth as a function of the inverse of the temperature were performed using Eq. (3), for all the samples. The results for the case of perpendicular linewidth ($\Delta H_\perp$) are shown in Fig. 3 for Co_5Cu_{95} samples, as cast and treated at 450 and 550 °C. The dashed lines are the computer fits; a good agreement between the model and the experimental points is observed.

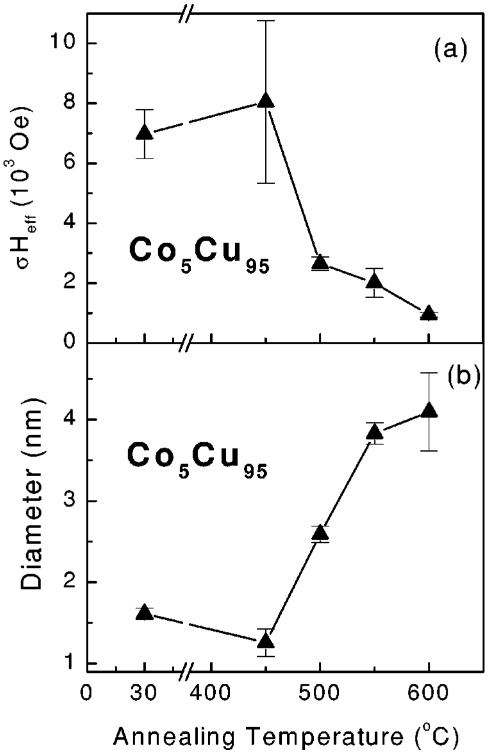

FIG. 4. Evolution of (a) σH_{eff} and (b) mean diameter D as a function of the annealing temperature for Co_5Cu_{95} samples. The solid lines are a guide for the eyes.

The parameters σH_{eff} and mean diameter shown in Fig. 4 for Co_5Cu_{95} samples are the averages of those obtained in parallel and perpendicular configurations. Figure 4(a) shows the evolution of the quantity proportional to the effective uniaxial anisotropy (σH_{eff}) with the annealing temperature. Figure 4(b) presents the results obtained for the mean particle diameter, as a function of temperature, for all the Co_5Cu_{95} samples. These results show an increase in the grain diameter with annealing temperature from 1.3 nm to 4.1 nm. For $Co_{10}Cu_{90}$ samples, the increase was from 1.5 nm to 6 nm; the incertainties vary from about 0.1 nm to 0.5 nm.

The asymmetry parameter η is a measure of the ratio of absorption to dispersion in the FMR line. Figure 5 shows the temperature dependence of the asymmetry parameter η, obtained by fitting the FMR spectra, for Co_5Cu_{95} samples as cast and annealed at 450 and 500 °C. It should be noted that as the measuring temperature is lowered, the parameter η decreases for samples as cast and treated at 450 °C. Similar behavior was observed for $Co_{10}Cu_{90}$ treated at 450 °C. In contrast, for Co_5Cu_{95} samples annealed at 500 and 550 °C, the behavior of the η parameter with the temperature of measurement undergoes a drastic change, increasing at lower temperatures of measurement. For higher annealing tempera-

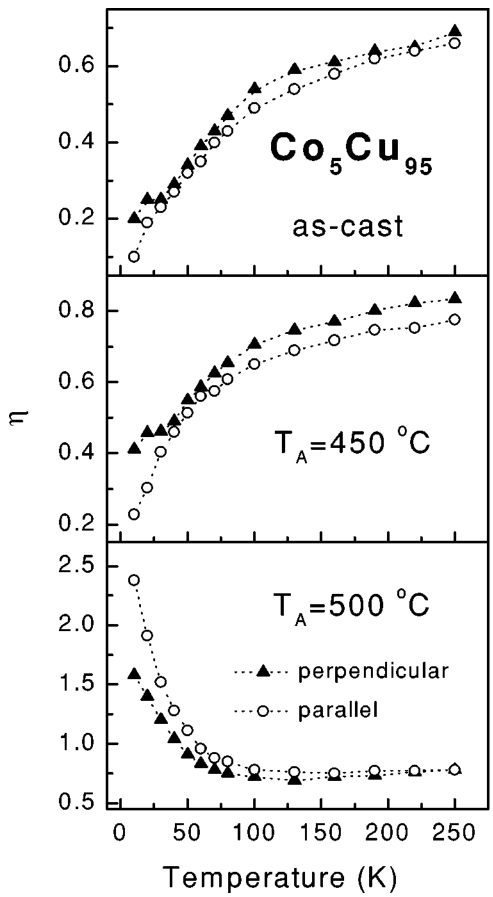

FIG. 5. Variation of the asymmetry parameter of the FMR line shape (η) for as-cast and annealed Co_5Cu_{95} samples as a function of temperature in both parallel and perpendicular configuration. The solid lines are a guide for the eyes.

tures, η is approximately constant with the temperature of measurement.

Figure 6 shows the high-field (90 kOe) ZFC-FC magnetization measurements for Co_5Cu_{95} alloy, as cast and heat treated at 500 °C (inset). A clear irreversibility was found below 60 K for the as-cast sample, which practically disappears after annealing.

V. DISCUSSION AND CONCLUSIONS

The FMR spectra of Co_5Cu_{95} as cast and annealed up to 600 °C show the presence of a single peak in the whole range of temperatures as shown in Fig. 1 for 450 °C. The $Co_{10}Cu_{90}$ as-cast sample was not considered in these studies because there are evidences of a size distribution with at least two peaks. This arises from our FMR spectra, which show two resonance lines, and from NMR measurements.[5]

The mean diameter of the magnetic grains and its evolution with the annealing temperature, shown in Fig. 4(b) for Co_5Cu_{95}, is essentially the same as obtained in our previous work,[17] where this parameter was determined from the angular variation of the FMR spectra at room temperature, giving further confidence on the reliability of the present method.

From Fig. 4(a), it is observed that for Co_5Cu_{95} samples as

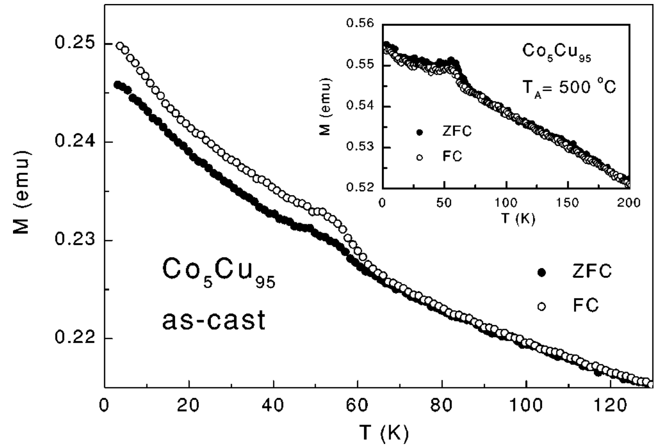

FIG. 6. The ZFC-FC magnetization measurements (90 kOe) at low temperatures for as-cast Co_5Cu_{95}, showing the high-field irreversibility. In the inset, the curves for the sample annealed at $T_A = 500\,°C$.

cast and annealed at 450 °C, the values for the term proportional to the effective anisotropy field (σH_{eff}) derived from the computer fits to Eq. (3) are larger than those for the samples annealed at 500 °C and above. The values of σH_{eff} can be better studied if plotted as a function of the mean diameter D of the magnetic grains. Such behavior (not shown here) exhibits a reduction of the effective anisotropy field with the mean diameter of the grains. A similar behavior of σH_{eff} with D was observed for annealed $Co_{10}Cu_{90}$ samples.

In order to understand the microscopic origin of this complex behavior, the effective anisotropy constant K_{eff} should be estimated. In analogy to polycrystalline systems,[27] the proportionality factor in Eq. (3) is chosen as 5/3. Assuming that the saturation magnetization of the cobalt grains in Co_xCu_{100-x} samples is the same for bulk cobalt ($M_s = 1430$ Oe), we can obtain the effective anisotropy constant. The calculated values of K_{eff} are presented in Fig. 7 as a function of the inverse of the diameter for all the Co_xCu_{100-x} samples, and an increase of K_{eff} with decreasing grain diameter is observed.

It is known that in dilute CoCu alloys, the cobalt grains adopt an fcc structure.[5–7] Assuming that the magnetocrystalline anisotropy is dominant in bulk fcc Co, K_{eff} (fcc Co) can be estimated[30] as $\approx 6.5\times 10^4$ J/m^3. In our samples, the values obtained for K_{eff} are larger than this value. These results indicate that for very small particles, the contributions of other terms to the effective anisotropy are more important than the crystalline anisotropy.

Similar values for K_{eff}, with the same dependence on the mean diameter found in Fig. 7, have been reported by other authors in the study of supported magnetic nanoparticles.[28–30] Their results were related to the surface anisotropy of the particles. Bødker *et al.*[11] proposed a phenomenological expression for the effective anisotropy constant of spherical particles with mean diameter D:

$$K_{eff} = K_{int} + \frac{6}{D} K_s, \tag{4}$$

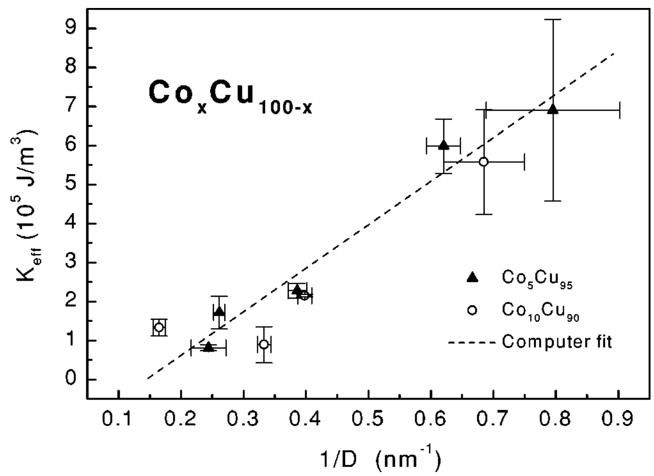

FIG. 7. Effective anisotropy constant as a function of the reciprocal mean diameter for the Co_5Cu_{95} and $Co_{10}Cu_{90}$ alloys. The dashed line is a computer fit to Eq. (4) for the Co_5Cu_{95} samples.

where K_{int} and K_s are the intrinsic and the surface anisotropy constant, respectively. Equation (4) shows a linear variation of K_{eff} with the inverse of the particle diameter. The values obtained from the fit in Fig. 7 with the use of Eq. (4), for Co_5Cu_{95}, are $K_s=(0.18\pm0.02)\times10^{-3}$ J/m^2 and $K_{int}=(-1.61\pm0.62)\times10^5$ J/m^3. The calculated value of K_s is comparable to that found in the literature.[16,30]

In systems of metallic particles with regularly distributed nanoparticles of spherical shape and a very narrow size distribution, the dependence of K_{eff} with $1/D$ is linear even for larger particles.[11,28–30] However, in granular alloys, the increase in the mean size of the grains is accompanied by the appearance of stress, deformation of the grains, formation of clusters, and also variation of the saturation magnetization M_s.[17] The influence of these factors would require a more complex function for K_{eff} than that represented in Eq. (4). The results shown in Fig. 7 indicate that the negative value of K_{int} obtained by extrapolation to infinite D may result from the simplified form of Eq. (4). It should be remarked that the values of K_{eff} obtained from different samples fall on the same straight line. This is a surprising result in granular alloys, and indicates that the origin of the magnetic behavior in these samples is a manifestation of the same phenomenon as observed in supported magnetic particles and also in ultrathin films.

In addition, the experimental results in Fig. 6 indicate that the irreversibility found in the smaller grains and which is associated with the presence of cobalt moments that are not aligned even at such a high field, practically disappears for the larger grains. This irreversibility was also observed on small particle systems and attributed to atoms located on the grain surface.[9,10]

It is known that in magnetic particles without chemical bonding at the surface, the atoms located on the surface of the grains present an electronic structure different from that found in the core.[8] This is mostly due to the reduced number of nearest neighbors which leads to an exchange coupling that is weaker than that within the core. Furthermore, the 3d electrons of the atoms situated on the surface of the grain are more localized and have a larger orbital magnetic moment.[28–30] The net effect is the appearance of a surface magnetic anisotropy of uniaxial type, and normal to the surface of the particle. When the particles are very small, the surface-to-volume ratio of the grains increases and an enhancement of the uniaxial surface magnetic anisotropy is expected.

The results in Fig. 5 of η versus temperature reflect a strong dependence of the parameter with the average size of the magnetic grains. For the smaller grains, with a mean diameter less than 1.6 nm, η decreases when the temperature of measurement is lowered. In the other case, for grains larger that 2.6 nm, η increases at lower temperatures of measurement. These results could indicate that the surface effects on the smaller grains increases the dispersive component in the FMR line at low temperatures, and that for larger grains, the absorptive component in the FMR line, increases at low temperatures.

In conclusion, we have studied the FMR spectra of granular CoCu alloys at different temperatures, and derived the anisotropy constant (K_{eff}). We have found that the values of K_{eff} obtained with different samples fall on the same straight line, increasing for smaller diameters. We have observed ZFC-FC irreversibility in the samples with smaller particles. These results give experimental evidence for the surface disorder on the particles and finite-size effects in CoCu alloys and that eventually they become less relevant as the particle size increases.

ACKNOWLEDGMENTS

This work was supported by the Brazilian agencies FAPERJ and CNPq; the authors thank P. Tiberto, P. Allia, and F. Vinai (IEN Galileo Ferraris, Torino, Italy) for kindly supplying the samples used in this study. E.H.C.P.S. thanks the PROFIX program from CNPq. C.A.R. acknowledges partial support of the ANCYT, Grant No. PICT99 No 36340 (Argentina) and of the CLAF.

*Corresponding author. Email address: brpu@cbpf.br

[1] *Studies of Magnetic Properties of Fine Particles and their Relevance to Materials Science*, edited by J. L. Dormann and D. Fiorani (North-Holland, Amsterdam, 1992).
[2] M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazeles, Phys. Rev. Lett. **61**, 2472 (1988).
[3] A.E. Berkowitz, J.R. Mitchell, M.J. Carey, A.P. Young, S. Zhang, F.E. Spada, F.T. Parker, A. Hutten, and G. Thomas, Phys. Rev. Lett. **68**, 3745 (1992).
[4] J.Q. Xiao, J.S. Jiang, and C.L. Chien, Phys. Rev. Lett. **68**, 3749 (1992).
[5] P. Panissod, M. Malinowska, E. Jedryka, M. Wojcik, S. Nadolski, M. Knobel, and J.E. Schmidt, Phys. Rev. B **63**, 014408 (2000).
[6] P. Allia, M. Coisson, P. Tiberto, F. Vinai, M. Knobel, M.A. Novak, and W.C. Nunes, Phys. Rev. B **64**, 144420 (2001).

[7] E.H.C.P. Sinnecker, I.S. Oliveira, P. Tiberto, and A.P. Guimarães, J. Magn. Magn. Mater. **218**, L132 (2000).
[8] X. Batlle and A. Labarta, J. Phys. D **35**, R15 (2002).
[9] R.H. Kodama, A.E. Berkowitz, E.J. McNiff, Jr., and S. Foner, Phys. Rev. Lett. **77**, 394 (1996).
[10] B. Martínez, X. Obradors, Ll. Balcells, A. Rouanet, and C. Monty, Phys. Rev. Lett. **80**, 181 (1998).
[11] F. Bødker, S. Mørup, and S. Linderoth, Phys. Rev. Lett. **72**, 282 (1994).
[12] P. Bruno, Phys. Rev. B **39**, 865 (1989).
[13] R.J. Hicken and G.T. Rado, Phys. Rev. B **46**, 11 688 (1992).
[14] B.N. Engel, M.H. Wiedmann, R.A. Van Leeuwen, and C.M. Falco, Phys. Rev. B **48**, 9894 (1993).
[15] G.M. Pastor, J. Dorantes-Dávila, S. Pick, and H. Dreyssé, Phys. Rev. Lett. **75**, 326 (1995).
[16] D. Weller, J. Stöhr, R. Nakajima, A. Carl, M.G. Samant, C. Chappert, R. Megy, P. Beauvillain, P. Veillet, and G.A. Held, Phys. Rev. Lett. **75**, 3752 (1995).
[17] B.R. Pujada, E.H.C.P. Sinnecker, A.M. Rossi, and A.P. Guimarães, Phys. Rev. B **64**, 184419 (2001).
[18] R.S. de Biasi and T.C. Devezas, J. Appl. Phys. **49**, 2466 (1978).
[19] K. Nagata and A. Ishihara, J. Magn. Magn. Mater. **104-107**, 1571 (1992).
[20] R.D. Sánchez, M.A. López-Quintela, J. Rivas, A. González-Penedo, A.J. García-Bastida, C.A. Ramos, R.D. Zyaler, and S. Ribeiro Guevara, J. Phys.: Condens. Matter **11**, 5643 (1999).
[21] H.K. Lachowicz, A. Sienkiewicz, P. Gierlowski, and A.S. Waniewska, J. Appl. Phys. **88**, 368 (2000).
[22] Yu A. Koksharov, S.P. Gubin, I.D. Kosobudsky, G.Y. Yurkov, D.A. Pankratov, L.A. Ponomarenko, M.G. Mikheev, M. Beltran, Y. Khodorkovsky, and A.M. Tishin, Phys. Rev. B **63**, 012407 (2000).
[23] H. Kodera, J. Phys. Soc. Jpn. **28**, 89 (1970).
[24] R. Gupta, J.P. Joshi, S.V. Bhat, A.K. Sood, and C.N.R. Rao, J. Phys.: Condens. Matter **12**, 6919 (2000).
[25] J.P. Joshi, R. Gupta, A.K. Sood, S.V. Bhat, A.R. Raju, and C.N.R. Rao, Phys. Rev. B **65**, 024410 (2001).
[26] E. Schlömann, Phys. Rev. **182**, 632 (1969).
[27] E. Schlömann and J.R. Zeener, J. Appl. Phys. **29**, 341 (1958).
[28] D.A. Dimitrov and G.M. Wysin, Phys. Rev. B **50**, 3077 (1994).
[29] M. Respaud, J.M. Broto, H. Rakoto, A.R. Fert, L. Thomas, B. Barbara, M. Verelst, E. Snoeck, P. Lecante, A. Mosset, J. Osuna, T.O. Ely, C. Amiens, and B. Chaudret, Phys. Rev. B **57**, 2925 (1998).
[30] F. Luis, J.M. Torres, L.M. García, J. Bartolomé, J. Stankiewicz, F. Petroff, F. Fettar, J.L. Maurice, and A. Vaurès, Phys. Rev. B **65**, 094409 (2002).