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Coercivity behavior in $\text{Gd}(\text{Co}_{1-x}\text{Cu}_x)_5$ system as function of the microstructure evolution

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ABSTRACT

Magnetic measurements, X-ray diffraction and scanning electron microscopy (SEM) experiments were carried out in the as-cast $\text{Gd}(\text{Co}_{1-x}\text{Cu}_x)_5$ samples with different Co/Cu content. Already in the as cast state, this system shows high coercive field for $x=0.3$ and a magnetization driven by nucleation of reversal domain. SEM micrograph and microanalysis show possible spinodal decomposition in the as-cast state, hence regions with different Co/Cu-content are observed, while the Gd-content almost does not change. High resolution X-ray diffraction patterns show a main CaCu_5 -type structure with traces of a secondary phase and distorted peak profiles as function of the Cu content. The evolution of the microstructure is discussed in relation with the Cu incorporation into the CaCu_5 -type structure. The Cu addition avoids the formation of the 2:7 phase within the 1:5 matrix, favoring the formation of a more homogeneous $\text{Gd}(\text{Co,Cu})_5$ phase. The relation between the observed microstructure and the magnetic behavior is also discussed.

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1. Introduction

Rare earth (RE)–transition metals alloys used as permanent magnets have been the focus of systematic research since decades due to the wide range of applications. Of this family, SmCo_5 has been the most studied alloy as a result of its high magnetocrystalline anisotropy, which in turn results in high coercivity values and critical temperature (T_C). In particular, the role of Cu in changing the magnetic behavior of RECo_5 alloys has been the subject of an important number of studies [1–6]. Within this family, Gadolinium alloys with transition elements have also been studied [7–9]. Although GdCo_5 alloy has a high production cost, this has the advantage of exhibiting a higher value of T_C compared with the SmCo_5 compound [4]. Potential applications of GdCo_5 as contactless temperature sensors and thermally controlled actuators has been reported [10] taking advantage of the change of magnetic properties of this ferromagnetic compound as function of the temperature. Further dynamic applications under high magnetic fields can be thought due to its small viscosity effect [11].

GdCo_5 shows also extremely high intrinsic coercivity, but obtaining this alloy as single phase has been a difficult task [12]. Previous studies in single crystals has explained the mechanism of magnetization as driven by nucleation of magnetic domains [13,14]. In the Cu containing GdCo_5 alloy its antiferromagnetic nature is preserved within the limits of solubility [15], additionally Cu improves the homogeneity of the samples. The former studies have been performed on as cast samples, while annealed samples did not show any significant quality improvement.

As cast $\text{Gd}(\text{Co}_{1-x}\text{Cu}_x)_5$ samples show increasing segregation with increasing Cu content, while DebyeSherrer X-ray diffraction experiments exhibit broadened diffraction lines [16]. In this study nothing is said about the possible sources of the observed broadening effects on the diffraction profiles. Studies on single crystal and polycrystalline samples of this system showed improvement of the coercivity with increasing Cu content, reaching its maximum for $x=0.3$ [10,11]. It has been shown that Cu substitutes Co without modifying the CaCu_5 type structure; but the microstructure is affected as indicated by X-ray diffraction studies [11]. The observed microstructure evolution as function of the Cu content could be closely related to the reported broadening of the diffraction profiles.

Measured small viscosity effects could be an indication that the microstructure in the as cast $\text{Gd}(\text{Co,Cu})_5$ system is different to

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that of the as cast $\text{Sm}(\text{Co,Cu})_5$, where structural and compositional disorder favors high coercivity values and large viscosity behavior [17,18]. As far as the authors know, no systematic microstructural study of as cast $\text{Gd}(\text{Co,Cu})_5$ has been carried out. In Ref. [16] only a micrograph for the composition $x=0.5$ (within our compositional range) has been reported.

Although rare earth–transition metal alloys such as the CaCu_5 family are not new to research, basic open questions remains unanswered, sometimes “forgotten” as a result of the advent of new materials which shift the focus to novel systems, while still scientific relevant issues of the older system are still at large. Furthermore, the development of new materials in nanoscale requires a better understanding of the fundamentals of the underlying compounds in their bulk state, in this sense old issue suddenly becomes relevant to the development of the new systems.

Following the magnetic measurements reported in Ref. [11], in this contribution microstructural and crystallographic study of $\text{Gd}(\text{Co}_{1-x}\text{Cu}_x)_5$ samples with $x=0-0.5$ are related to the reported magnetic behavior. The goal is to describe the microstructure evolution in relation with the Cu addition and to establish a correlation between the observed magnetic behavior and the microstructure evolution.

Studies were carried out by high resolution X-ray diffraction (XRD), scanning electron microscopy (SEM). XRD will give information on the crystal structure and the microstructure of the material, while SEM provides information on the local variations of the microstructure.

2. Samples and experimental setup

Samples of the composition $\text{Gd}(\text{Co}_{1-x}\text{Cu}_x)_5$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5) were prepared by arc melting in a controlled atmosphere using raw material with purity of at least 99.9 wt.%. Samples reduced to powder were taken for X-ray diffraction experiments. They were conducted on beamline XRD at the LNLS, Synchrotron facility in Campinas, Brazil. The Bragg-Brentano optical system consisted of a bending magnet light source, a double-crystal Si (111) monochromator and a Ge (111) crystal analyzer, the specimen was mounted in a 10 mm diameter rotating sample holder, the radiation energy was 7001.1 eV which corresponds to a wavelength of 1.77093 Å. The powder diffraction data was collected at room temperature, with a step of 0.01° and a time count of 1 s. Lattice parameters were calculated by a least-square refinement using Si as external standard.

From the samples several disk were cut and polished. The observations were carried out in a SEM equipped with a Si energy dispersive microanalysis system (JEOL JSM-6490LV). Observations were made using the backscattered electron signal. Magnetic measurements were made using a vibrating sample magnetometer (VSM OXFORD Instrument) with an applied field up to 1.6 T at room temperature. The hysteresis loops measurements were performed on polycrystalline bulk samples of spherical shape with dimensions of 2 mm. The correction for the demagnetization factor for this geometry was taken into account.

3. Results and discussion

It is well known that GdCo_5 single crystals are characterized by domain nucleation and propagation [13]. However, such behavior should not be extended straightforward to polycrystalline $\text{Gd}(\text{Co}_{1-x}\text{Cu}_x)_5$ as result of the evolved microstructure. As shown from the initial magnetization curves in Fig. 1 (for clarity, only compositions $x=0, 0.3$ and 0.5 have been shown) the magnetization rises quickly already for low applied field, which could be

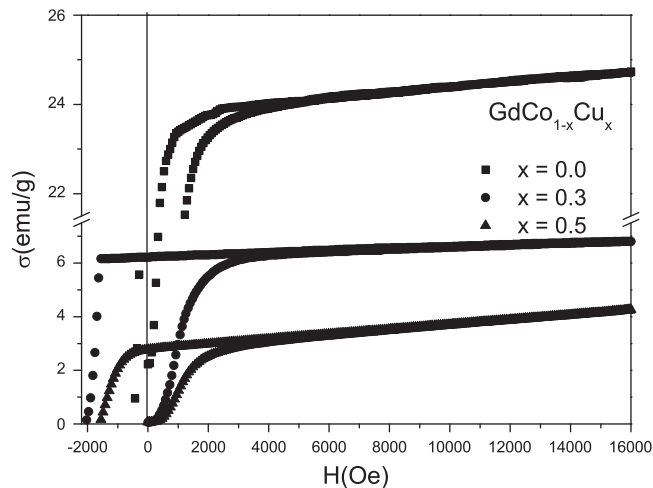


Fig. 1. The magnetic initial magnetization curve for the as-cast $\text{Gd}(\text{Co}_{1-x}\text{Cu}_x)_5$ samples with $x=0, 0.3$ and 0.5 measured in the VSM.

related with the absence of effective pinning sites. On the other hand, viscosity measurements performed on the same set of samples [11] have shown almost non-dependence of the coercivity (H_c) on dH/dt . Attending to these results, it seems that the mechanism of magnetization in the studied polycrystalline samples does not change its nature upon Cu addition, being of nucleation of magnetic domains followed by coherent rotation of the magnetization in the studied compositional range. The observed behavior suggests that the addition of Cu in the Gd-system does not induces an structural disorder like in the Sm-system.

The GdCo_5 sample has the higher magnetization for a given applied field, decreasing for the same applied field with increasing Cu content. Although saturation is not reached, the relative behavior of the H_c as function of Cu content can be followed, reaching its maximum value for $x=0.3$, as also reported previously [11]. Two main differences compared with the as cast system $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5$ were found. The maximum value of coercivity is reached for $x=0.3$ compared to $x=0.5$ for $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5$. In the Sm sample the demagnetization mechanism is pinning driven for as cast samples even for low Cu content [17].

Fig. 2 shows the electron backscattering micrograph and the X-ray microanalysis spectrum corresponding to the $x=0$ and 0.1 samples. Two zones are well distinguished, the gray region has a composition $\text{GdCo}_{5 \pm x}$ close to the nominal one (Table 1); the lighter regions within the 1:5 matrix, has a higher Gd content corresponding to a composition $\text{Gd}_2\text{Co}_{7 \pm x}$ close to a 2:7 phase (hexagonal Ce_2Ni_7 type structure, SG $P6_3/mmc$). A detailed analysis of both micrographs shows that the volume fraction of the Gd-rich phase decreases after Cu has been added to the composition. An estimation of the percent contribution of gray and light regions in the micrographs has been made after imaging processing, giving a $V_{1:5}/V_{2:7}$ ratio of approximately 5 for the undoped sample and 19 for $x=0.1$.

For $x=0.2$ the 2:7 phase has completely disappeared (Fig. 3a). Yet, starting at $x=0.2$ and above, a segregation of two well distinguished regions can be observed with different Co/Cu ratio. In Fig. 3, a contrast between two zones with almost the same composition is well distinguished. The dark matrix has a composition of $\text{Gd}(\text{Co}_{0.66}\text{Cu}_{0.13})_{5.1}$, while the light region has a composition of $\text{Gd}(\text{Co}_{0.55}\text{Cu}_{0.24})_{4.4}$; with a slightly larger Cu content (Table 1). The sample with $x=0.3$ exhibits the same behavior. The Gd content seems to increase slightly in those regions with smaller Co/Cu ratio, but it does not change the structure of the CaCu_5 -type phase. The volume fraction of the rich Cu phase

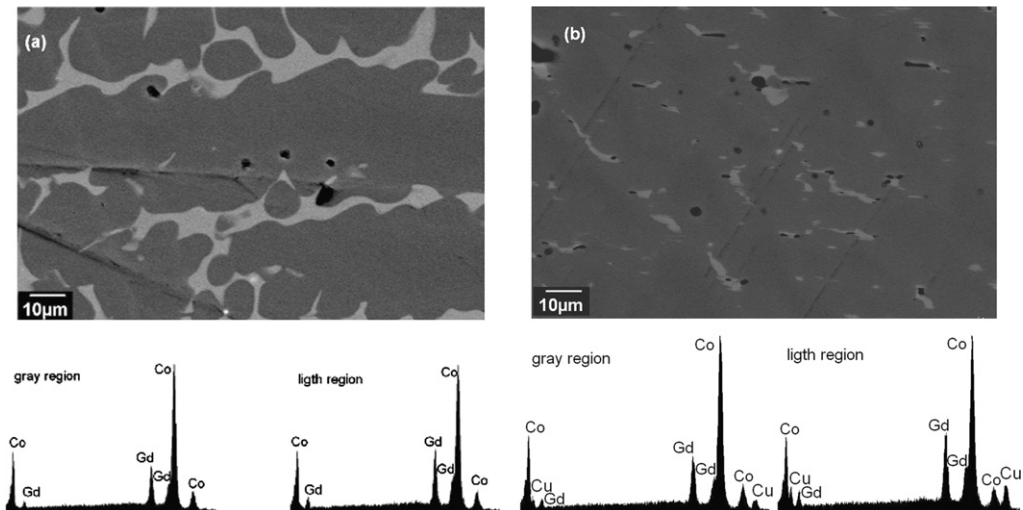


Fig. 2. Backscattering micrographs and the X-ray microanalysis spectrum of the samples $x=0$ (a) and 0.1 (b). In both cases the gray region shows a composition close to the nominal one, while lighter regions within the 1:5 matrix exhibits a composition close to a 2:7 phase (Table 1). The volume fraction of the phase 2:7 decreases after Cu addition.

Table 1
X-ray microanalysis results for the studied samples.

Gd(Co _{1-x} Cu _x) ₅ (x)	Microanalysis
0.0	GdCo _{5±x} gray regions Gd ₂ Co _{7±x} light regions
0.1	GdCo _{5±x} gray regions Gd ₂ Co _{7±x} light regions
0.2	Gd(Co _{0.66} Cu _{0.13}) _{5.1} dark regions Gd(Co _{0.55} Cu _{0.24}) _{4.8} light regions
0.3	Gd(Co _{0.64} Cu _{0.15}) _{5.3} dark regions Gd(Co _{0.40} Cu _{0.39}) _{4.2} light regions
0.4	Gd(Co _{0.55} Cu _{0.24}) _{4.9} dark regions Gd(Co _{0.25} Cu _{0.54}) _{4.1} light regions Range of composition of the diffuse pattern
0.5	Gd(Co _{0.53} Cu _{0.26}) _{4.9} Gd(Co _{0.27} Cu _{0.52}) _{4.8}

increases with Cu content. Again, an estimation of the percent contribution of the volume fraction of the Cu-rich phase has been made for $x=0.2$ and 0.3 after imaging processing, giving a $V_{1:5}^{dark}/V_{2:7}^{light}$ ratio of 18 and 10 respectively.

Observing the SEM micrograph for $x=0.4$, its microstructure can be described again by two compositionally different regions (Fig. 4a). However, light regions with a Co/Cu of 0.46 appear to be diluted in the dark matrix with a larger Co/Cu ratio of 2.3. The Co rich area has given a composition of Gd(Co_{0.55}Cu_{0.24})_{4.9}, while the small light regions show a composition of Gd(Co_{0.25}Cu_{0.54})_{4.1} (Table 1), both far from the nominal Co/Cu : 1.5 ratio but preserving the 1:5 structure. A careful inspection to the micrograph of Fig. 4a shows that a diffuse pattern of light and dark areas begins to emerge. The composition of these diffuse areas is between the light and dark regions. In the case of the sample with $x=0.5$ (Fig. 4b), where the light regions have completely disappeared, a diffuse pattern of light and dark areas is more clearly observed. The X-ray microanalysis spectrum of this sample varies in the composition range reported in Table 1. An increase of Cu favors a diffusion of the constituents resulting in a more homogeneous sample. An $V_{1:5}^{dark}/V_{1:5}^{light}$ ratio estimation for these last two compositions were not possible due to the occurrence of the diffuse areas.

The high resolution XRD studies proved that all samples crystallized in the CaCu₅ type structure, with space group P6/mmm. For the

$x=0$ composition, additional peaks were found, these additional peaks could be indexed as a rhombohedral crystal structure with space group R3m, corresponding to a Gd₂Co₇ phase. This is in perfect agreement with the SEM observations on this sample. For the sample $x=0.1$, where small fractions of the 2:7 phase are still locally observable, no diffraction peaks of this phase have been detected due to its small volume fraction. The 2:7 phase disappears with increasing Cu content which is also in correspondence with the SEM results. Some low intensity additional peaks that appears for the composition $x=0.3$ and 0.5 were identified as gadolinium oxide phase, which is also observed as very small bright white spots in the micrographs.

Fig. 5 shows the peak profile behavior for reflections (200) and (002) as a function of Cu content, and they were chosen as representative of all the other maximum of the diffraction patterns (peaks of the 2:7 phase for $x=0$ are marked with arrows). The shift of the peaks to lower angles results from the increase of the unit cell parameters due to the Cu incorporation in the crystal structure. The calculated lattice parameters (Fig. 6) show a nearly linear increase of both a and c parameters with increasing Cu content following the Vegard's law. It should be noted that for each sample two pairs of values of lattice parameters have been calculated taking into account the broadened and asymmetric shape of the diffraction maxima. The reflections (200) and (002) were fitted with two Voigt functions with agreement factors R_p and R_{wp} below 10% for all samples. The criterion for selecting two functions is based on the results of SEM, where areas of different Co/Cu ratio and in correspondence with different average lattice parameters values has been observed. The diffraction peaks appear as splitted for low Cu content, merging in a single broadened peak for higher Cu content. The former is also in correspondence with the SEM observations, where a more homogeneous microstructure is observed.

High anisotropy field is one prerequisite for developing high coercivity. The 1:5 stoichiometry ensures the highest anisotropic field value in RECo₅ systems. Compositions around this phase, such as 2:7 and 2:17 (including the disordered phase 1:7), show values with lower anisotropy field [19,20]. One reason for the low coercivity values measured for the samples $x=0.0$ and 0.1 [11] is due to the presence of the 2:7 phase within the 1:5 matrix, being the former of lower anisotropy. 2:7 acting as pinning center must be discarded, as the size of such regions is much larger than the domain wall size [9]. Also, off-stoichiometry regions GdCo_{5±x} with low anisotropy field values can act as nucleation centers effectively lowering the coercivity

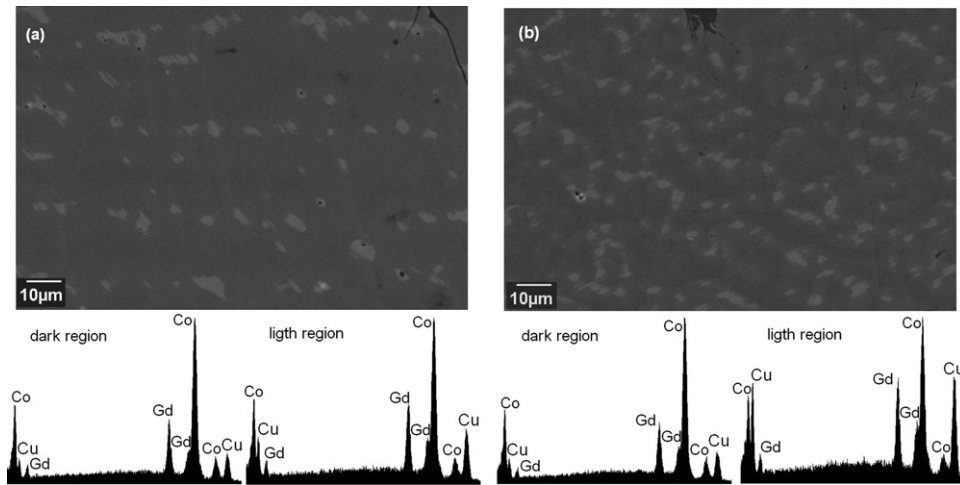


Fig. 3. Backscattering micrographs of the samples $x=0.2$ (a) and 0.3 (b). In both cases the dark and light regions show a composition close to the nominal one (Table 1). The microprobe spectrum in the lower part corresponds to the dark region with smaller Cu/Co ratio than lighter region. The volume fraction of the Cu rich phase increases after Cu addition.

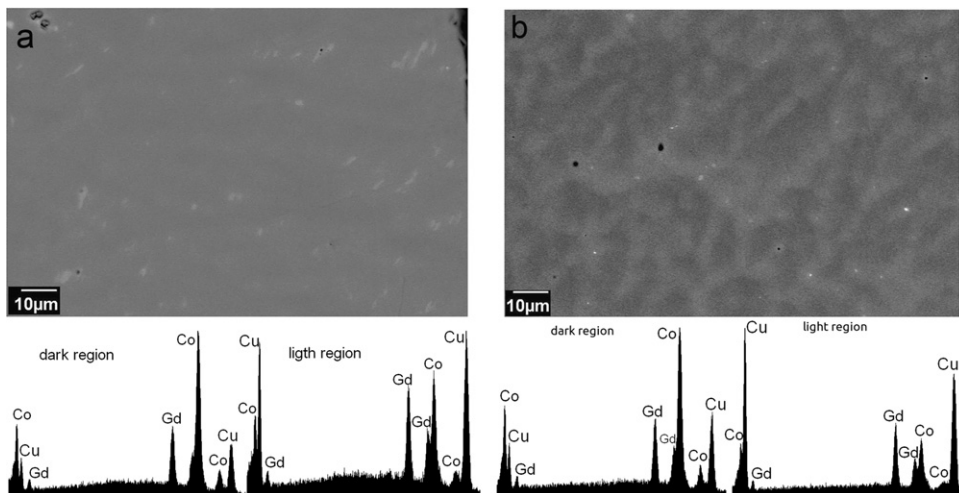


Fig. 4. Backscattering micrographs of the samples $x=0.4$ (a), where the light regions have almost disappeared and of the sample $x=0.5$ (b) showing a diffuse pattern of light and dark areas. The X-ray microanalysis spectrum of the samples are shown in Table 1.

value. The H_c values in these two compositions are affected primarily by the presence of the secondary phase and off-stoichiometry regions.

Cu addition drives the compound towards a more homogeneous $\text{Gd}(\text{Co,Cu})_5$ phase, hence the 2:7 phase is not reported in the Gd–Cu phase diagram. This alone could explain the higher coercivity value as more homogeneous, higher anisotropic phase is achieved. We observed in the $x=0.2$, 0.3 samples the formation of $\text{Gd}(\text{Co,Cu})_{5 \pm x}$ regions, with different Co/Cu ratios. This means that Cu does not homogeneously diffuse in the GdCo_5 matrix, but instead segregates in well defined isolated islands. The size of the islands is too large for being effective pinning sites. The estimated wall domain width for $\text{Gd}(\text{Co,Cu})_5$ ranges between 11 and 20 nm [9] much smaller than the observed island sizes. For $x=0.4$ and 0.5 , the regions of different Co/Cu content starts to merge and a more diluted microstructure (higher homogeneity) is achieved. The decrease of H_c could be associated with the lowering of the anisotropy in the higher Cu content samples (Table 1).

The coercivity will also depend on other factors. Low anisotropy field regions (domain wall pinning sites), e.g. in $\text{Sm}(\text{Co,Cu})_5$, are associated with regions with local crystal defects. It is known

that $\text{RE}(\text{Co,Cu})_5$ structures can be disordered, hence defects can come from various sources. One of the sources was described by Allen et al. [21], which considers the appearance of sessile dislocations resulting from the solution of RE atoms into the CaCu_5 structure, which in turns could shift the composition towards a Gd rich region of the pseudo-binary phase diagram leading to the 2:7 phase. However, for $\text{Gd}(\text{Co,Cu})_5$ this kind of defect is not favored because the Gd_2Cu_7 phase does not exist. The former is confirmed after the SEM and diffraction results presented in this paper.

The substitution of Gd atoms in the “1a” crystallographic position of the CaCu_5 structure either by Co or by Cu dumbbells would shift the structure toward a $\text{Gd}_2\text{Co}_{17}$ phase (not observed in SEM and XRD patterns). However, before reaching the 2:17 phase, this randomly compositional substitution leads into the occurrence of the disordered $\text{Gd}(\text{Co,Cu})_7$ phase (GdCo_7 is known to exist), which could favors the formation of low anisotropy regions locally [22]. This kind of disorder can contribute to the observed decrease of H_c with increasing Cu content as well but it was not observed by X-ray diffraction experiments.

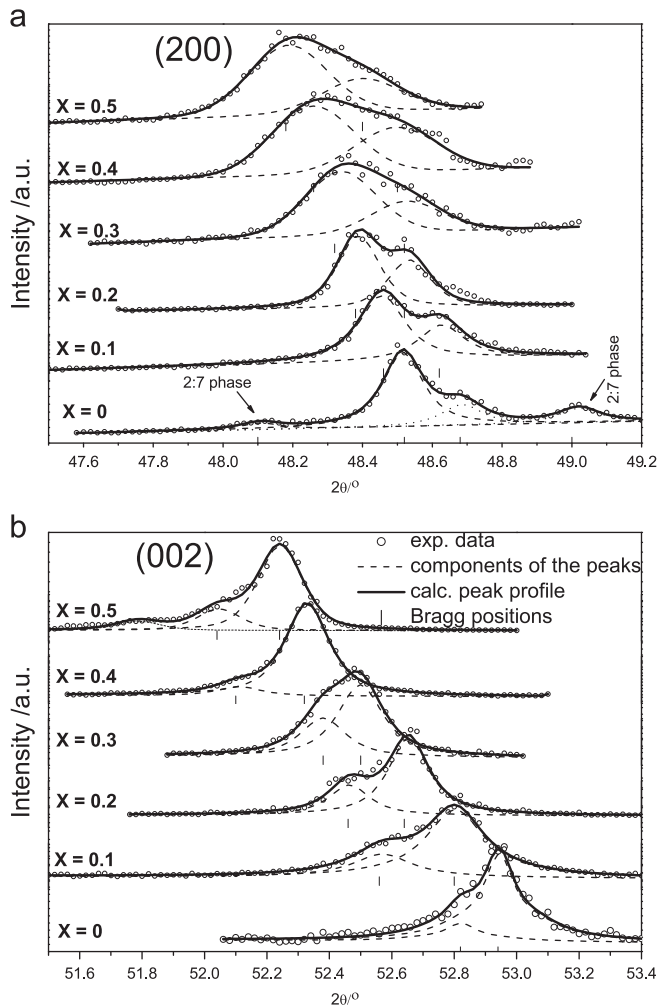


Fig. 5. Peak profile evolution with Cu content for the (a) (200) and (b) (002) reflections. Experimental data are represented with open circles, the components of the peaks with dashed lines, the calculated peak profiles from the components with solid lines and the calculated Bragg positions with vertical bars.

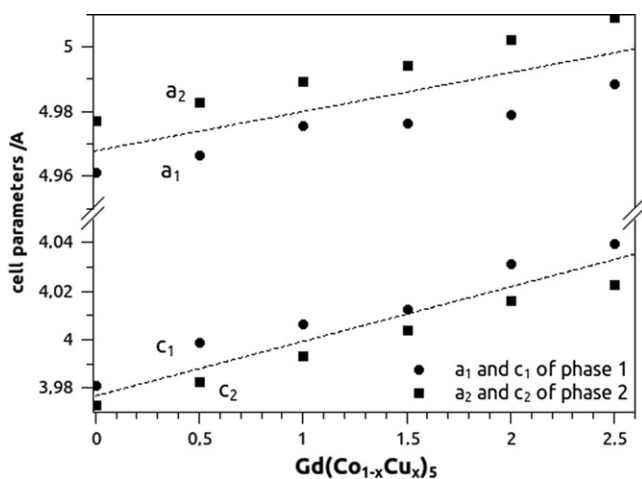


Fig. 6. Lattice parameter variation with Cu content. Unit cell parameters have been represented for each phase together with the corresponding average values (dash lines). In all cases a linear behavior with non-significant departure from Vegard's law is observed.

The defects resulting from locally compositional disorder have been observed in the as cast $\text{Sm}(\text{Co}_{0.5}\text{Cu}_{0.5})_5$ alloy, favoring higher H_c values in the studied compositional range [17,23]. In our case

for $x=0.3$, where the higher H_c value is observed, the microstructure is completely different. It has been concluded that the observed magnetic behavior is connected primarily to compositional variations between different regions of the studied samples as function of Cu content as shown in the microstructural analysis and not due to the described local structural defects.

4. Conclusions

The mechanism of magnetization in the studied as cast samples were attributed to nucleation of magnetic domains followed by coherent rotation of the magnetization in the studied compositional range. The addition of Cu has a well defined microstructural effect, it avoids the formation of the 2:7 phase within the 1:5 matrix, which favors the formation of a more homogeneous $\text{Gd}(\text{Co,Cu})_5$ phase. High H_c values in the as cast $\text{Gd}(\text{Co,Cu})_5$ system are reached with a microstructure exhibiting a spinodal decomposition with different Co/Cu ratios. Low anisotropy field regions due to local crystal defects like in $\text{Sm}(\text{Co,Cu})_5$, which are responsible for large H_c values, are not observed in the present study. The former suggests a difference between the microstructure of the compounds $\text{Sm}(\text{Co,Cu})_5$ and $\text{Gd}(\text{Co,Cu})_5$.

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