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HYSTERETIC MAGNETISATION CURVES IN THE GRANULAR $Cu_{100-X}Co_X$ SYSTEM

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Abstract—The magnetic hysteresis properties of granular $Cu_{100-x}Co_x$ alloys (x = 5 to 20) containing nanometric Co particles, prepared under different quenching conditions and submitted to various anneals, have been measured at room temperature. Major loops (vertex field 1×10^4 Oe) and minor loops (vertex field between 1×10^2 and 9×10^3 Oe) were measured by vibrating-sample magnetometry. The features of major loops were analysed in terms of sample composition and structural state; the dependence of remanence and coercivity of minor loops on vertex field has been analysed in detail. A novel graphical representation method, particularly suitable for describing the details of the narrow hysteresis loops observed in granular systems has been proposed and checked. *©1999 Acta Metallurgica Inc.*

Introduction

Granular magnetic systems, where nanometer-sized, nearly-superparamagnetic particles of a ferromagnetic metal are dispersed in a non-magnetic metal, were first developed in view of applications in magnetic recording owing to their isotropic giant magnetoresistance (GMR) [1]. The $Cu_{100-x}Co_x$ system has been thoroughly investigated, because it can be easily obtained in ribbon form over a wide composition range ($0 < x \leq 20$) by planar flow casting on a massive rotating wheel. A variety of granular structures characterised by rather different average values of the particle sizes can be easily obtained by varying Co content, the quenching parameters and/or by annealing the as-cast material [2,3]. The sizes of superparamagnetic Co particles are typically distributed in the interval 2–8 nm; typical interparticle distances are in the same range [3]. In this way, it is possible not only to optimize the GMR response [3], but also to produce granular materials with different magnetic properties. Generally speaking, all magnetisation curves of $Cu_{100-x}Co_x$ alloys exhibit room-temperature magnetisation curves which are characterised by definite, if small hysteretic effects, with values of coercivity H_c ranging between 50 and 350 Oe and reduced remanence M_r/M_s ranging between 0.05 and 0.2 (M_S is the saturation magnetisation) [4]. These small values of both M_r/M_s and H_c lead one to consider hysteretic effects as truly minor and quite negligible, so that no efforts aimed to elucidate their nature were produced. Consequently, the hysteretic properties of magnetisation curves of granular $Cu_{100-x}Co_x$

systems were never experimentally analysed in full detail, although Monte-Carlo algorithms were sometimes exploited to simulate the magnetisation dynamics of these granular systems [5–8].

Recently, however, a new interest in this area has emerged, owing to the discovery of the fact that magnetic hysteresis in granular systems may be explained in a non-trivial way. In fact, the hysteretic behaviour of a granular magnetic system could be related either to the presence of a fraction of blocked particles (i.e., particles whose size exceeds the critical size for superparamagnetism at the measurement temperature), or to the existence of interactions among superparamagnetic particles.

The hypothesis of a distribution of particle sizes with a tail towards sizes larger than the critical one for the onset of superparamagnetism leads quite naturally to the emergence of hysteretic properties. Such a rather naive view (the whole magnetisation curve appears as a mere superposition of superparamagnetic and ferromagnetic contributions [9]) is substantiated, in some cases, by direct observation [10,11]. However, this view implies completely neglecting any magnetic interaction among particles, a rather crude hypothesis indeed, in systems where the interparticle distance may be as short as a few nanometers [4]. Recently, a mean-field model relating the magnetic hysteresis in granular systems to the effect of long-ranged interactions among localized magnetic moments has been proposed [12]. In this model, the hysteretic behaviour is accounted for by introducing a field-dependent memory function $\delta(H)$ in the argument of the Langevin function describing the anhysteretic magnetisation [12]. As a consequence, the measured hysteresis loops are viewed as originating from magnetic interactions among nearly-superparamagnetic Co particles rather than from blocked-particle contributions. The model has however been applied so far to the analysis of the remanence-coercivity relationship only.

In the light of the increased interest towards this subject, a detailed study of the hysteretic behaviour of granular $Cu_{100-x}Co_x$ systems seems to be particularly useful, in order to provide a sound, reliable experimental basis to the existing models of hysteresis (either based on magnetic interactions or on particle-size distribution). In this work, such an experimental study is performed at room temperature on rapidly solidified $Cu_{100-x}Co_x$ alloys (x = 5, 10, 15, 20), and a novel representation of hysteresis curves is proposed in order to evidence the peculiar hysteretic properties of these materials.

Experimental

Continuous ribbons of $Cu_{100-x}Co_x$ (x = 5, 10, 15 and 20 at %) were obtained by planar flow casting in He atmosphere on a CuZr wheel. The quenching parameters were controlled during the rapid solidification process to produce samples with a comparable quenching rate; on the other hand, several $Cu_{90}Co_{10}$ and $Cu_{95}Co_5$ alloys were also rapidly quenched under peripheral wheel velocities ranging in the interval 12–22 m/s in order to study the effect on the magnetic properties of different Co-particle segregation in the as-quenched metallic matrix. All other process parameters (e.g., ejection pressure and crucible-to-wheel distance) were kept constant. Different ribbon strips of all the studied compositions were submitted to dc Joule-heating in vacuum, in order to induce the precipitation of Co particles. Dc Joule-heating is a well-known, simple, reliable technique of fast annealing, where the heat released to a metallic sample by a constant electrical current is exploited to rapidly increase the sample temperature [13].

Magnetisation curves were obtained at room temperature on both as-quenched and annealed ribbon strips. The magnetic moment was measured up to 10 kOe using a vibrating-sample magnetometer VSM (LDJ, model 9500). Major symmetric hysteresis loops were obtained starting from the demagnetized state and cycling up to a maximum applied field $H_v = \pm 10$ kOe with a field step of $\pm$ 100 Oe. Minor symmetric loops were measured with $|H_v|$ ranging in the interval 100 Oe - 9 kOe, and suitably decreasing the field step in order to keep the number of experimental points approximately constant. In addition, the corresponding anhysteretic magnetisation curves were determined starting from the

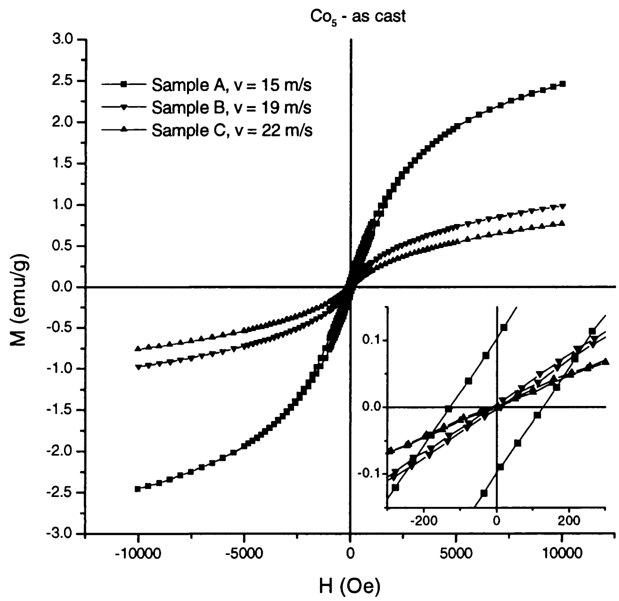

Figure 1. Room-temperature major hysteresis loops of $Cu_{95}Co_{05}$ as-cast ribbons produced with different wheel velocity.

demagnetised state and gradually increasing the applied field in either direction up to H_v = 10 kOe. In this case, the field was again set to zero after each measurement.

Properties of Major and Minor Hysteresis Loops

The major hysteresis loops of selected as-quenched ribbons of composition $Cu_{95}Co_{05}$ (Sample A: v = 15 m/s; B: v = 19 m/s; C: v = 22 m/s) produced with different wheel velocity v are reported in Fig. 1. In the inset, the region close to the coercive field value is highlighted. All curves display both superparamagnetic and ferromagnetic features. The small area of measured loops and the unsaturating behaviour of the curves indicate a superparamagnetic behaviour. On the other hand, the ferromagnetic behaviour is evidenced by the non-zero values of remanence and coercivity (vanishingly small in the $Cu_{95}Co_5$ samples prepared with high quenching rate). These curves clearly indicate that the starting material is not an ideal solid solution of Co in Cu. The segregation of more Co particles improves the ferromagnetic character; in fact, both H_c and M_r/M_s are observed to increase with decreasing wheel velocity in both compositions; similarly, high-field magnetisation increases with decreasing wheel velocity.

The hysteresis loops of selected samples submitted to different Joule-Heating treatments are reported in Figs. 2 and 3 for $Cu_{95}Co_{05}$ (Sample B) and $Cu_{90}Co_{10}$ (Sample F). In both cases, the reported curves refer to three measurements, performed: i) on as-cast materials, ii) on samples displaying the highest GMR values at H = 20 kOe, iii) on samples annealed under an electrical current value higher than the one corresponding to the maximum GMR. The high-field magnetisation and coercive field H_c are observed to increase in annealed samples with respect to the as-cast ones, indicating either an increased fraction of precipitated Co or a larger mean size of Co clusters [3]. The differences among samples produced with different quenching rates tend to reduce after annealing. Although the hysteresis loops substantially maintain their superparamagnetic features (no tendency towards saturation, and contained

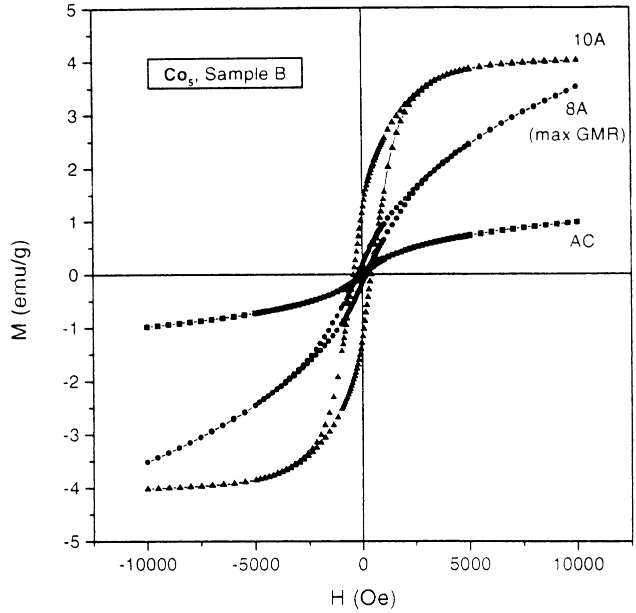

Figure 2. Room-temperature major hysteresis loops of selected $Cu_{95}Co_{05}$ samples (as-cast and annealed condition; see text).

loop area), samples treated with electrical current values higher than the ones corresponding to the maximum GMR display a relevant enhancement of ferromagnetic characters.

Minor hysteresis loops have been measured for all studied compositions (either in as-cast or annealed samples). A first analysis of the minor loops may be performed by plotting H_c and M_R as a function of

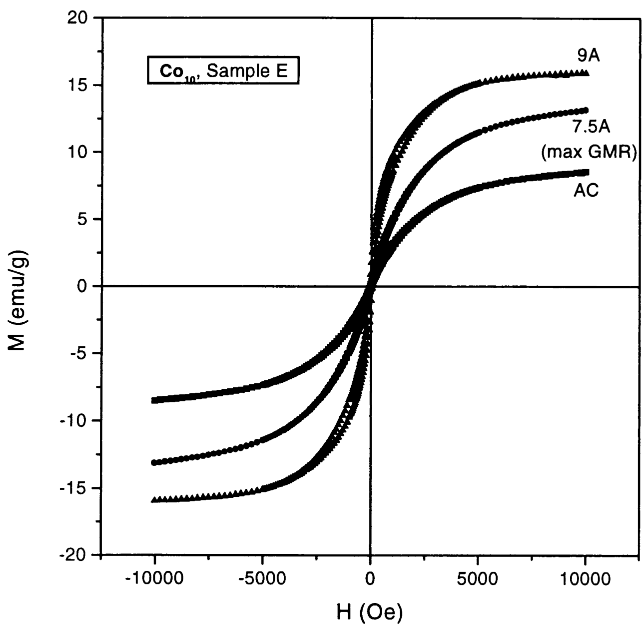

Figure 3. Same as in Fig. 2 for selected $Cu_{90}Co_{10}$ samples.

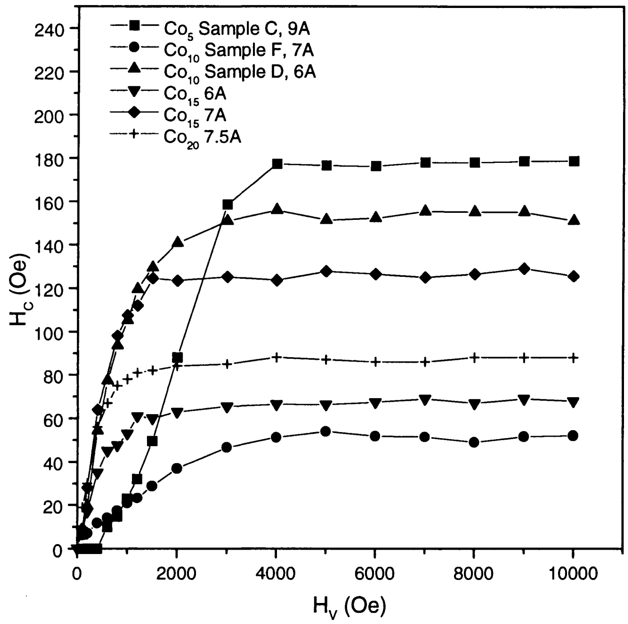

Figure 4. Minor loops: coercive field behaviour as a function of the amplitude of the vertex field for selected $Cu_{100-x}Co_x$ samples.

the vertex field H_v, as shown in Figs. 4 and 5, respectively. In all systems, the coercivity is seen to increase with increasing H_v up to a constant value reached at a vertex field H_v^* which turns out to be of the order of 3×10^3 Oe for $Cu_{95}Co_5$/$Cu_{90}Co_{10}$ alloys and of the order 1×10^3 Oe for $Cu_{85}Co_{15}$/ $Cu_{80}Co_{20}$ alloys. The same behavior is observed in Fig. 5, where the remanence is reported as a function of H_v. These results indicate that increasing the vertex field H_v beyond H_v^* neither H_c nor M_R are further modified. In other words, the value of applied field where the two loop branches are observed to merge no longer increases when $H_v > H_v^*$. It should be finally noted that the $Cu_{95}Co_5$ sample (sample A, Joule heated at I = 9 A and t = 60 s) displays no hysteresis for loops measured at low field values ($H_v < 600$ Oe).

A first analysis of the hysteretic character of the magnetization curves may be performed reporting for each sample the reduced magnetic remanence M_R/M_S along with the coercivity H_c, both measured at room temperature on minor and major hysteresis loops. Such an analysis has been performed at room temperature (i.e., well above the blocking temperature of superparamagnetic particles) on more than forty samples of all studied compositions, submitted to various anneals. The results were published in Ref. [12], where it has been shown that, although no definite relation exists between reduced remanence and coercivity measured in different samples, the M_R/M_S values are always very close to the ratio $\frac{1}{3}(\mu_o H_c/kT)$, where μ_o is the average magnetic moments of Co particles. Such a behaviour is observed not only in major loops, but also in minor loops, obtained by conveniently reducing the vertex-field value [12].

It should be noted that usually the M_S value cannot be determined from the largely unsaturating experimental magnetisation curves, and is obtained by fitting the anhysteretic curve with the superposition of two Langevin functions characterized by different values of the magnetic moment (see next Section for further comments). Such a fit [$M = M_S \Sigma_i p_i L(\mu_i H/kT)$] allows one to obtain the value of the average magnetic moment μ_o. This standard analysis, already discussed in detail in Ref. [4], was

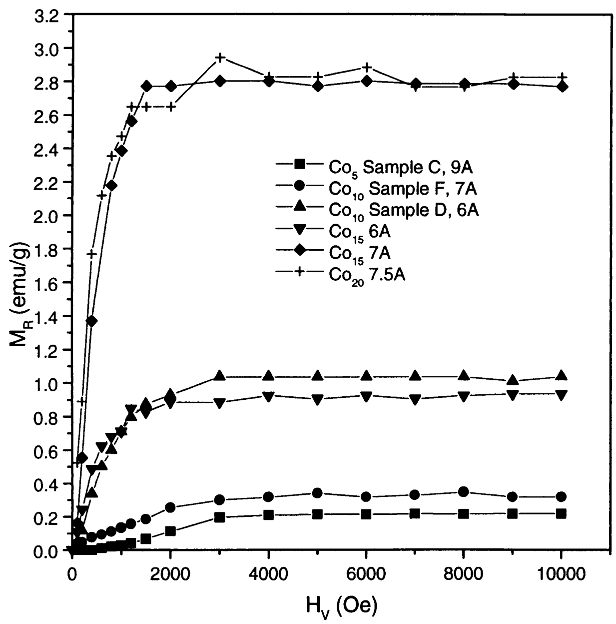

Figure 5. Minor loops: magnetic remanence behaviour as a function of the amplitude of the vertex field for selected $Cu_{100-x}Co_x$ samples.

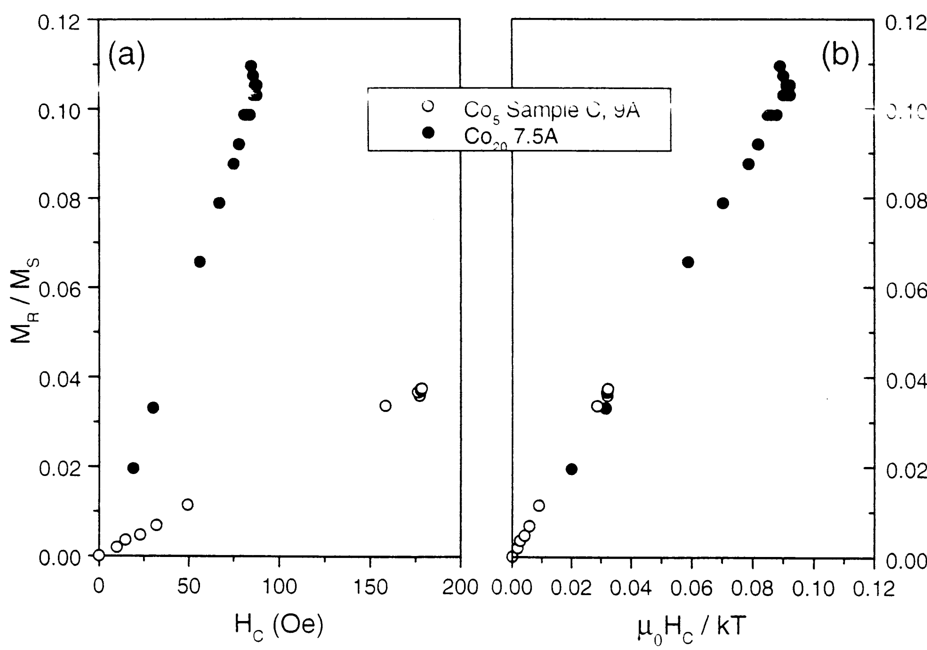

Figure 6. (a): M_R/M_s vs H_c and (b): M_R/M_s vs $\mu_o H_c/kT$ for Joule heated $Cu_{95}Co_{05}$ (open circles; I = 9A) and $Cu_{80}Co_{20}$ ribbons (full circles; I = 7.5A).

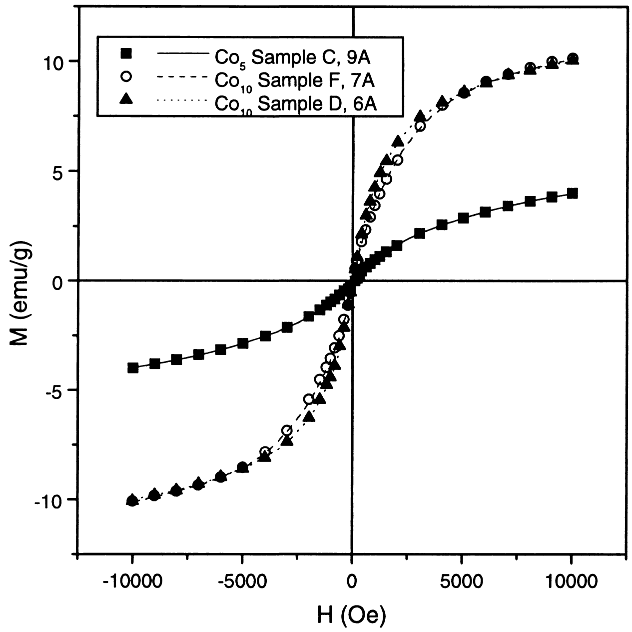

Figure 7. Behaviour of the experimental Σ (H) functions (lines) and experimental anhysteretic curves (symbols) for selected $Cu_{95}Co_5$ and $Cu_{90}Co_{10}$ samples.

performed on all samples reported in Figs. 4 and 5. The M_R/M_S vs H_c data for two selected Joule-heated samples are reported in Fig. 6(a). A linear behaviour is observed in both cases. In all examined systems, the dependence of reduced remanence on coercivity is always described by a linear law; all measured straight lines lie between the reported ones. However, a well-defined universal curve emerges by plotting M_R/M_S as a function of the ratio $\mu_o H_c/kT$, k being the Boltzmann constant and T the absolute temperature (see Fig 6(b), where all data are plotted), in perfect agreement with the prediction of the interaction model [12].

A Novel Representation of Hysteresis Loops

A novel graphical representation method can be introduced to make more apparent the features of narrow and slender hysteresis loops, like the ones observed in the $Cu_{100-x}Co_x$ system. First, the two branches of a symmetric hysteresis loop (both major or minor) are linearly combined to get the half-sum Σ:

$$\sum = \frac{1}{2}\left[M_+(H) + M_-(H)\right] \tag{1}$$

where $M_\pm$ refers to the upper (lower) loop branch, respectively. The function Σ(H) is an odd function of H, taking the value $\Sigma = 0$ for H = 0; therefore, it is closely similar to an experimental anhysteretic curve, i.e., to the magnetisation curve obtained as the locus of the vertices of minor loops measured in sequence. As a matter of fact, the curve Σ(H) turns out to be perfectly coincident (within the experimental errors, which are however very small in this case) with an anhysteretic curve obtained according to the above-mentioned experimental procedure. This result is reported in Figs. 7 and 8,

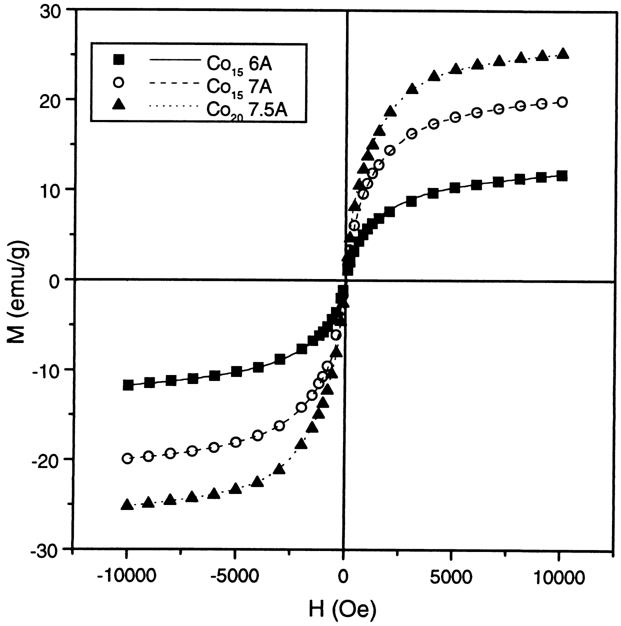

Figure 8. Same as in Fig. 7 for selected $Cu_{85}Co_{15}$ and $Cu_{80}Co_{20}$ samples.

where the Σ(H) curves obtained from Eq. (1) (lines) are reported together with directly measured anhysteretic curves (symbols) for selected samples of all considered systems. As a consequence, the function Σ(H) will be referred to in the following as the anhysteretic magnetisation. Such a curve may be fitted by a superposition of Langevin functions, representing the weighted contributions from particles having different size [4]. Such a fitting procedure allows one to derive an accurate value of the average magnetic moment μ_o, also providing an estimate of the saturation magnetisation of these samples, which is experimentally not attained unless very high field values ($H > 3 \times 10^4$ Oe) are available. The advantages and limits of such a procedure were discussed elsewhere [4].

On the other hand, the hysteretic character of these magnetisation curves is best evidenced by introducing another linear combination of the loops branches, i.e., the half-difference Δ:

$$\Delta = \frac{1}{2}\left[M_+(H) - M_-(H)\right] \tag{2}$$

Using the value of M_s obtained from anhysteretic curve analysis, the reduced half-sum Δ_R and reduced anhysteretic $\Sigma_R \equiv m$ are easily derived:

$$m = \frac{1}{2}\left[m_+(H) + m_-(H)\right] \tag{3}$$

$$\Delta_R = \frac{1}{2}\left[m_+(H) - m_-(H)\right]$$

where $m_\pm = M_\pm/M_s$. The reduced half-~~sum~~ difference is an even function of H, attaining its maximum value at H = 0, and monotonically decreasing to zero for $H \to \pm\infty$. The maximum value of Δ_R is coincident with the reduced remanence of the sample. The quantity Δ_R may be plotted either as a function of H (as shown in Fig. 9(a) for two selected samples) or as a function of the reduced

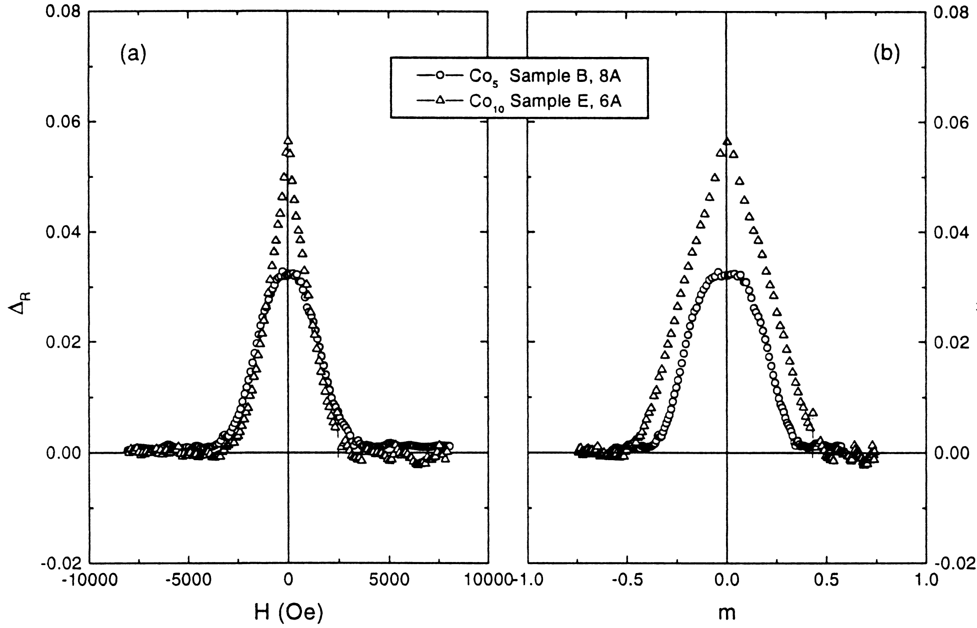

Figure 9. Reduced half-difference Δ_R as a function of H (a) and of m (b) for Joule heated $Cu_{95}Co_{05}$ (open circles; I = 8A) and $Cu_{90}Co_{10}$ (open triangle; I = 6A).

anhysteretic m, as shown in Fig. 9(b), which refers to the same samples of Fig. 9(a). It may be concluded that the latter form of representation provides the best way of evidencing the hysteretic characters of magnetisation in granular systems. It will be referred to as the "m, Δ_R(m) representation." Such a method is particularly effective in highlighting peculiar features of hysteresis loops in these systems: as an example, two main classes of loop shapes have been evidenced, i.e., loops characterised by a particularly flat behaviour of Δ_R around m = 0 (see, e.g., the $Cu_{95}Co_5$ sample in Fig. 9(b)), and loops displaying a steeper descent of Δ_R for small m values (see, e.g., the $Cu_{90}Co_{10}$ sample in the same Figure). These features correspond to loop branches staying parallel over an extended region of H values (first case), or immediately converging (second case). Note that relevant details of the measured loops may be particularly evidenced by using the m, Δ_R(m) representation; in particular, the possible asymmetries of the measured loops are naturally magnified by such a representation, which is therefore useful for a first check of the validity of a measurement. In addition, it is possible to infer that the loop branches in different systems merge at closely similar, although not exactly the same, values of the external field H, but they are definitely not merging at the same value of anhysteretic magnetisation.

Another interesting example of the m, Δ_R(m) representation is illustrated on Fig. 10, where selected minor loops measured on the alloy $Cu_{85}Co_{15}$ are compared with the corresponding major loop. It is apparent that the minor loop with $H_V = 4 \times 10^3$ Oe ($>H_V^* \approx 3 \times 10^3$ Oe) is identical in shape to the major loop (small differences in proximity of m = 0 give a measure of the experimental uncertainties), indicating that when H_V overcomes H_V^* all loop features remain essentially the same, while minor loops performed using $H_V < H_V^*$ are clearly different in amplitude and (to a lesser extent) in shape. These properties are observed with much more difficulty using the conventional H, $M_\pm$(H) representation.

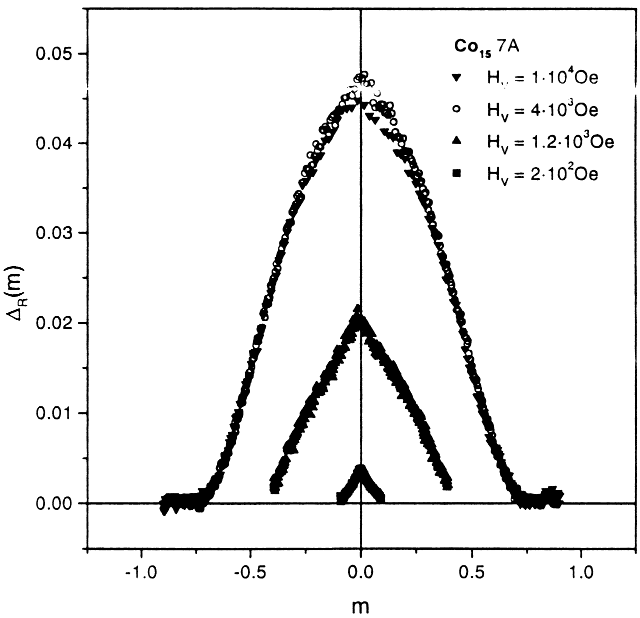

Figure 10. $\Delta_R(m)$ vs m representation for major loop and selected minor loops of Joule-heated $Cu_{85}Co_{15}$.

Conclusions

It may be concluded that the hysteretic features in the magnetisation behaviour of the granular system $Cu_{100-x}Co_x$ may vary depending on the actual structure of the system (mean particle diameter, extension of particle distribution, mean interparticle distance) which can be in turn modified, with relative ease, by changing the process parameters and/or by thermal treatment. From this viewpoint, the $Cu_{100-x}Co_x$ system is particularly apt to be used in tests of conflicting theories of magnetic hysteresis in granular materials.

The problems posed by the peculiar shape and small separation of measured hysteresis loops, constituting so far a serious obstacle to their accurate analysis, have been circumvented by introducing an alternative method of representation of the loop. The procedure leading to the novel representation does not imply any alteration of real experimental data. The validity of the m, $\Delta_R(m)$ representation has been put into evidence by proper examples.

Finally, let us explicitly state that in all examined cases (concerning more than 40 different samples of all compositions, i.e., a much larger number than referred to in this paper), the shape of room-temperature hysteresis loops emerging from both the H, $M_\pm(H)$ and the m, $\Delta_R(m)$ representation seems to be very different from the one predicted by a conventional Stoner-Wohlfarth theory [14], which should be applicable when magnetic hysteresis arises from non-interacting, blocked spherical particles. Of course, this indication cannot completely rule out such a hypothesis, because the fraction of blocked particles invoked to explain these hysteretic properties is really low, so that superparamagnetic features may dominate over the Stoner-Wohlfarth contribution, therefore modifying its peculiar shape.

On the other hand, the same circumstance may also indicate that the magnetic hysteresis has an entirely different origin. The theory of interacting superparamagnetic particles, successfully predicting a universal relation between reduced remanence and coercivity, is being further developed and appears to be particularly promising even from this viewpoint. The results will be the subject of future work.

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