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Study of magnetic interactions in a sample of Fe_3O_4 magnetic nanoparticles in DC and AC fields

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Summary. — The study conducted on a sample of Fe_3O_4 nanoparticles coated with oleic acid has been performed by using DC and AC field techniques useful to determine the presence of a mixed state of interactions within the same sample, confirmed by the qualitative comparison between the results of the two techniques. In particular, a thorough study of the AC response of the sample, in presence of an overlapping DC field, allowed to determine the types of interactions observed by the DC analysis.

1. – Introduction

In the last few years, interest in magnetic nanoparticles (MNPs) has increased due to the large possibility of applications for these materials, showing their versatility from biomedical aspects to applications connected to sustainability, energy storage, and data storage [1, 2]. The large number of possible applications has also increased interest in understanding their properties, in particular the magnetic ones, and their connection to different aspects such as the synthesis process, shapes of MNPs, dimensions, coating, and interactions between them. The interest in all of these is connected to the possibility of finding features that can improve the applications and tuning the synthesis and coating processes to the specific application. In this framework, the study presented in this paper has the aim of showing the characterization performed on a sample of iron oxide MNPs coated with oleic acid Fe_3O_4-OA both in the DC and AC fields. The combination of these techniques gives the possibility to study the presence of a double peak in the distribution of blocking temperature (T_B) and represents a possible approach to distinguish between different states of the aggregation of MNPs in the same sample. These results can be useful to select the desired samples of MNPs for the proper application.

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2. – Experimental details

The sample analysed in this work was synthesised by the thermal decomposition of organic precursors as described in ref. [3]. The obtained sample of MNPs has been characterised by TEM, from which a monomodal distribution of MNPs diameter has been observed [3]. The magnetic characterization of the sample has been performed by a Physical Property Measurement System (PPMS) from Quantum Design. The characterization in the DC field has been performed by using the Vibrating Sample Magnetometer (VSM) insert. The magnetization has been measured at different temperatures, $M(T)$, from 5 K to 300 K with a sweep rate of 0.5 K/min, both in the Zero Field Cooling (ZFC) and Field Cooling (FC) protocols with an applied DC field of 100 Oe, as described in ref. [4]. The magnetization *versus* magnetic field, $M(H)$, has been performed as described in ref. [4] at 5 K and at 300 K. The AC characterization has been performed by using the AC Measurement System (ACMS) insert of PPMS. The AC susceptibility of the sample has been measured by applying an AC field of 12 Oe of amplitude at a frequency of 107 Hz and 1077 Hz by varying temperature from 10 K to 300 K, $\chi(T)$, only in the ZFC protocol [5], and at 100 Oe of superimposed DC field. The $\chi(T)$ at 107 Hz has been performed at different superimposed DC fields (100 Oe, 400 Oe, 700 Oe, and 1000 Oe).

3. – Results and discussion

3·1. *DC characterization.* – The DC characterization of MNPs allows to estimate the T_B of the sample, above which it shows a superparamagnetic state. Different approaches can be used for the estimation of T_B [4, 6]. For non-interacting MNPs, the first one is to consider the temperature associated with the maximum of the ZFC curve as the T_B. In general cases, this method gives a rough estimation of T_B because it does not take into account effects connected to size and anisotropy ditribution [7]. In the case of the sample of Fe_3O_4-OA studied in this work, the maximum of the ZFC curve is associated with a temperature (T_{Max}) of (210 ± 2) K as can be seen in fig. 1(a). Another clear evidence of the superparamagnetic behaviour is provided by the comparison of the two $M(H)$ at 5 K and at 300 K in the region of zero field, reported in fig. 1(b). From this, it is possible to see that the sample has an hysteretic behaviour at low temperatures, with a coercive field (H_C) of (347 ± 1) Oe, and a paramagnetic-like behaviour at room temperature, with a H_C close to zero (around 2 Oe). These considerations confirm the presence of a superparamagnetic behaviour for the studied sample, but more information can be obtained from the derivative of the difference between the ZFC and FC curves. The obtained curve is associated with the distribution of T_B, which gives an estimate of the anisotropy energy barrier distribution for non-interacting MNPs [8, 9]. The T_B distribution obtained for the studied sample is reported in the inset in fig. 1(c) and shows two peaks. The presence of this double peak has to be interpreted as an effect of the magnetic properties of the sample and not connected to the presence of a double distribution of MNPs since the dimension distribution obtained with TEM is monomodal [3]. In order to shed light on the origin of the double peak, the AC susceptibility of the sample has been studied.

3·2. *AC characterization.* – The imaginary (χ'') component of the first harmonic of AC susceptibility as a function of temperature and at different frequencies and superimposed DC fields is reported in fig. 2(a) and (b).

It is possible to observe that at every frequency and field there is the presence of a

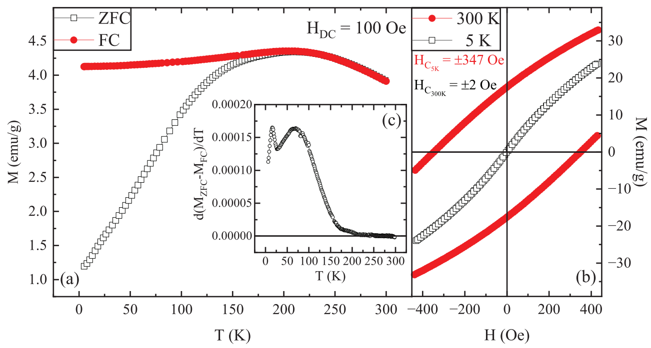

Fig. 1. – In panel (a) the magnetization as function of temperature under an applied DC field of 100 Oe is reported. In panel (b) the detail of the $M(H)$ around the origin of the axis is showed. The difference of H_{C} at 5 K and 300 K can be observed. In panel (c) the T_{B} distribution extracted by the derivative of the difference between the ZFC and FC curves reported in panel (a) is showed.

double peak, in agreement with what was observed in fig. 1(c) since the peak of the $\chi''(\mathrm{T})$ is generally used as an estimation of the mean T_{B} of the sample [5]. In particular, both the temperature associated with the peak at the lower temperature ($T_{\mathrm{Peak}\ 1}$) and the peak at the higher temperature ($T_{\mathrm{Peak}\ 2}$) decreased with the increase in the applied DC magnetic field. This can be more clearly observed in fig. 2(c) and (d), in which $T_{\mathrm{Peak}\ 1}$ (c) and $T_{\mathrm{Peak}\ 2}$ (d) are plotted as functions of the applied DC field (H_{DC}). The application of an external magnetic field has the effect of lowering the T_{B} [10]. The equation [10, 11]

$$(1) \qquad T_{\mathrm{P}}(H_{\mathrm{DC}}) = T_0(1 - (H_{\mathrm{DC}}/H_{\mathrm{k}})^d) \begin{cases} d = 2, & \text{for non-interacting nanoparticles,} \\ d = 2/3, & \text{for spinglass-like interaction} \end{cases}$$

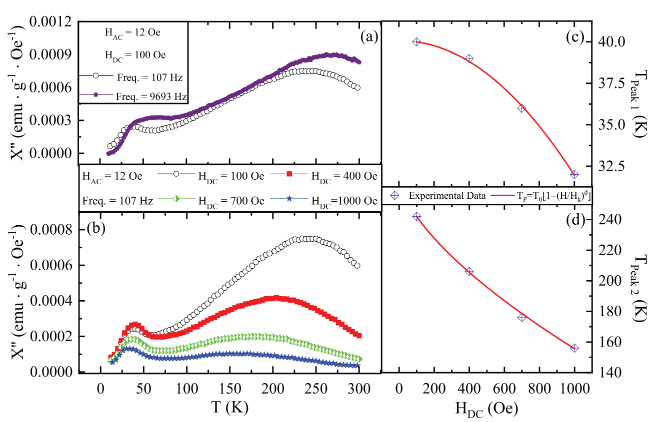

Fig. 2. – In panel (a) and (b) χ'' is reported as a function of temperature at different frequency (107 Hz and 1077 Hz) (a) and different H_{DC} (100 Oe, 400 Oe, 700 Oe and 1000 Oe) (b). In panels (c) and (d), respectively, the $T_{\mathrm{Peak}\ 1}(H_{\mathrm{DC}})$ and $T_{\mathrm{Peak}\ 2}(H_{\mathrm{DC}})$ are plotted. The red lines in panel (c) and (d) represent the fit performed with eq. (1).

describes how the temperature associated with the peak in $\chi''(\mathrm{T})$ is affected by the presence of an external magnetic field. In eq. 1, T_{P} is the temperature associated to the peak of $\chi''(\mathrm{T})$, T_0 is the T_{B} in the absence of an external magnetic field and H_{k} is the anisotropic field, in the case of non-interacting MNPs [10], while T_0 is the extrapolated temperature associated with the peak at zero field and H_{k} is the theoretical transition field at zero temperature, in the case of spin-glass like behavior [11]. The data reported in fig. 2(c) and (d) have been fitted with eq. (1). The behaviour of $T_{\mathrm{Peak\ 1}}(H_{\mathrm{DC}})$ follows eq. (1) with an exponent $d = 2.03$, near to the expected 2, so indicating non-interacting MNPs behavior. On the other side, $T_{\mathrm{Peak\ 2}}(H_{\mathrm{DC}})$ follows eq. (1), but with a $d = 0.65$, near to the expect 2/3 for a system of spinglass-like interaction. The analysis of the double peak at different applied fields shows that the sample is characterised by different states of aggregation of MNPs, the first peak is due to a low or absent interaction at low temperatures while the second one is due to a strong and spinglass-like interaction at higher temperatures. This result can be enforced by calculating the Mydosh's parameter ϕ starting from the curves in fig. 2(a) [12]. For $T_{\mathrm{Peak\ 1}}$ (Freq.), $\phi = 0.393$, as expected for non-interacting MNPs, then for $T_{\mathrm{Peak\ 2}}$, $\phi = 0.059$, as expected for a system of spinglass-like interaction.

4. – Conclusion

A sample of Fe_3O_4 MNPs has been characterised both in DC and AC fields. A bimodal T_{B} distribution associated with the sample has been obtained by the DC measurements. The presence of a double peak has also been observed directly by the measurement of the imaginary part of the AC susceptibility. From the effect of different superimposed fields, the temperature associated with the peak at lower temperatures has been observed to follow a behaviour typically associated to a system of non-interacting MNPs, while the temperature associated with the peak at higher temperature follows a behaviour typical of a system of MNPs with spinglass-like interaction.

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