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## Magnetic order and disorder environments in superantiferromagnetic NdCu<sub>2</sub> nanoparticles

E. M. Jefremovas<sup>1✉</sup>, P. Svedlindh<sup>2</sup>, F. Damay<sup>3</sup>, D. Alba Venero<sup>4</sup>, A. Michels<sup>5</sup>, J. A. Blanco<sup>6</sup> & L. Fernández Barquín<sup>1</sup>

Magnetic nanoparticles exhibit two different local symmetry environments, one ascribed to the core and one corresponding to the nanoparticle surface. This implies the existence of a dual spin dynamics, leading to the presence of two different magnetic arrangements governed by different correlation lengths. In this work, two ensembles of NdCu<sub>2</sub> nanoparticles with mean sizes of 18 nm and 13 nm have been produced to unravel the magnetic couplings established among the magnetic moments located within the core and at the nanoparticle surface. To this end, we have combined neutron diffraction measurements, appropriate to investigate magnetically-ordered spin arrangements, with time-dependent macroscopic AC susceptibility measurements to reveal memory and aging effects. The observation of the latter phenomena are indicative of magnetically-frustrated states. The obtained results indicate that, while the Nd<sup>3+</sup> magnetic moments located within the nanoparticle core keep the bulk antiferromagnetic commensurate structure in the whole magnetic state, the correlations among the surface spins give rise to a collective frustrated spin-glass phase. The interpretation of the magnetic structure of the nanoparticles is complemented by specific-heat measurements, which further support the lack of incommensurability in the nanoparticle state.

Magnetically-frustrated systems constitute a vast and fascinating research topic in condensed-matter physics. Terms such as disorder, competing interactions, randomness, or broken inversion symmetry are at the heart of many complex magnetic phenomena and spin textures, as they are encountered e.g., in spin glasses (SG), spin ices, spin liquids, pyrochlore oxides, multiferroics, or skyrmion crystals<sup>1–17</sup>. In recent years, ensembles of magnetic nanoparticles (MNPs), where structural and ensuing magnetic disorder is inherently present due to the finite particle size, are attracting growing attention owing to their enormous potential for technological applications (see, e.g., Refs.<sup>18–22</sup> and references therein). In particular, the spin dynamics and collective excitations of MNPs are the subject of intensive studies, where the antiferromagnetic (AF) systems stand out due to their relevance for data-storage applications and for the emerging fields of skyrmionics and spintronics<sup>23–35</sup>.

MNPs combine, in one single system, two different spin dynamics ascribed to two different symmetry environments—the particle core and the surface. Generally, it is found that the symmetry environment and the coordination number of the magnetic moments located within the nanoparticle core remain essentially the same as the ones found in the bulk counterpart<sup>36</sup>. For the surface spins, however, the situation is significantly different due to the existence of a non-negligible lattice distortion (strain) and reduced coordination numbers<sup>37–39</sup>. As a result, the magnetic interactions among surface spins will be changed and even frustrated, yielding disordered spin arrangements in the vicinity of the surface. By this token, minimal unit cell distortions might account for the switching between different types of magnetic orderings, such as, ferromagnetic (FM) and AF long-range orders akin to the achievement of an uncompensated magnetic moment or net magnetic signal found in Cr<sub>2</sub>O<sub>3</sub><sup>40</sup>, NiO<sup>41</sup>, and CoO–Pt<sup>42</sup>. However, much less attention has been paid to the case of nanoparticles based on rare-earth elements.

<sup>1</sup>Department CITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain. <sup>2</sup>Department of Materials Science and Engineering, Uppsala University, Box 35, 751 03 Uppsala, Sweden. <sup>3</sup>Laboratoire Léon Brillouin, Université Paris–Saclay, CEA–CNRS, 91191 Gif–sur–Yvette Cedex, France. <sup>4</sup>ISIS Neutron and Muon Facility, Rutherford Appleton Laboratory, Didcot OX11 0QX, UK. <sup>5</sup>Department of Physics and Materials Science, University of Luxembourg, 1511 Luxembourg, Luxembourg. <sup>6</sup>Department of Physics, University of Oviedo, 33007 Oviedo, Spain. ✉email: martinjel@uican.es

In this work, we use neutron diffraction, AC susceptibility, and specific-heat measurements to investigate the structure and spin dynamics of two ensembles of NdCu<sub>2</sub> MNPs with average particle sizes of 18 nm and 13 nm. Previous investigations have showed that NdCu<sub>2</sub> hosts a complex magnetic phase diagram in the bulk state, with AF-coupled magnetic moments along the *a*-direction and FM-coupled *b*-*c* planes (with a Néel temperature of  $T_N = 6.5$  K)<sup>43</sup>. In the low-temperature AF phase, a commensurate square-up modulation is established, whereas the rise in temperature provokes slight deviations from the equilibrium positions of the FM-coupled magnetic moments. At  $T_R = 4.5$  K a reorientation of the magnetic moments takes place, and an incommensurate structure is present up to  $T_N$ . Concerning NdCu<sub>2</sub> MNPs, these have evidenced a superantiferromagnetic (SAF) structure, where (at  $T = 1.5$  K) the *core* magnetic moments exhibit the commensurate square-up modulation of bulk NdCu<sub>2</sub><sup>22,39,44</sup>. By contrast, the magnetic moments located at the *surface* feature a collective freezing mechanism, following a SG dynamics. This AF-core/SG-surface arrangement is similar to the one reported for TbCu<sub>2</sub><sup>22,44</sup>, GdCu<sub>2</sub><sup>38</sup>, Cr<sub>2</sub>O<sub>3</sub>, NiO or CoO–Pt MNPs<sup>40–42</sup>. However, it is important to point out that, while for the case of the 3*d*-based MNPs, large exchange bias effect has been reported (up to several hundred mT<sup>40–42,45,46</sup>), the magnitude of the exchange bias in the 4*f*-based is remarkably reduced by two orders of magnitude (see Fig. S5 included in Supplementary Section “Exchange bias effect” in Ref.<sup>47</sup>). This evidences the enhanced role that the magnetically-disordered surface moments play into the magnetic dynamics of the system. These magnetically-disordered moments could lead to a modification of the complex AF structure that takes place within the nanoparticle core. Therefore, the microscopic analyses presented here will be focused on addressing the question whether the aforementioned commensurate-incommensurate transition also takes place in the MNP regime. Besides, we will evaluate quantitatively the surface disorder by evaluating the robustness of the collective SG state. For this purpose, the time-dependent magnetic susceptibility response will be analyzed. This approach, which has been employed previously to study the well-known power-law scaling of the critical behavior close to an anticipated SG temperature<sup>48–55</sup>, allows for the interpretation of subtle (very low magnetic signal) dynamic responses depending on the magnetic history (memory effects) and the time-dependent susceptibility (aging).

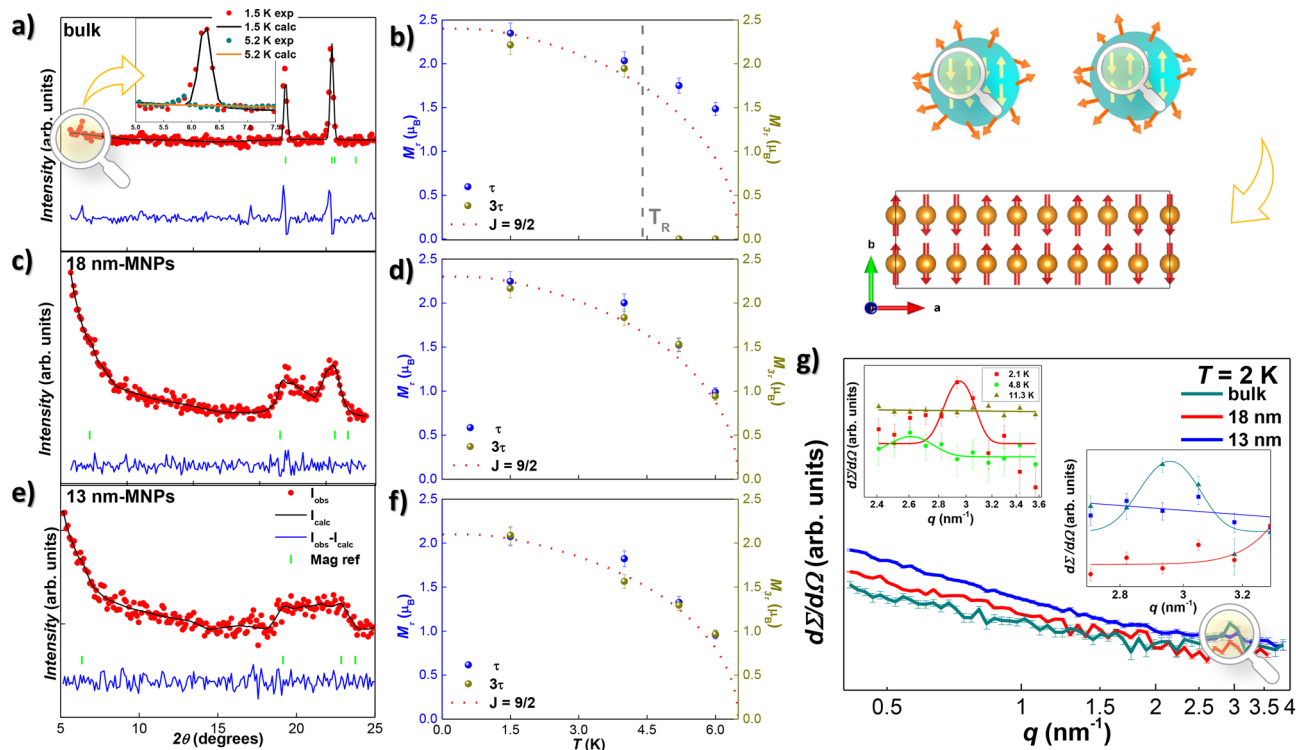
## Results and discussion

### Microscopic structural characterization: neutron diffraction and small-angle neutron scattering.

The nonmagnetic neutron diffraction (ND) (above  $T_N$ ) and the X-ray diffraction patterns have been discussed previously (Ref.<sup>39</sup>). This study showed that the bulk orthorhombic *Imma* structure is maintained also at the MNPs, with lattice parameters close to those of the bulk alloy reported in Ref.<sup>56</sup>. For the MNPs, Rietveld refinements indicated a mean nanoparticle size of  $\langle D \rangle = 18.3(1.0)$  and  $13.0(5)$  nm for 2h and 5h-milled MNPs; together with microstrain  $\eta$  values of  $\eta = 0.62(7)\%$  and  $\eta = 0.59(1)\%$ , respectively<sup>39</sup>. These values agree with the ones obtained from the nuclear magnetic structure, where  $\langle D \rangle = 16.5(4)$  nm and  $12.6(6)$  nm, respectively, as with the ones pointed from TEM characterization (see Supplementary Fig. S1 in Ref.<sup>57</sup>). Given the existence of this previous study, in this paper we will focus on the variation of the magnetic moment on the Nd<sup>3+</sup> sites. Figure 1a, c, and e include the ND patterns together with the Rietveld refinements (Bragg factor  $R_B < 10\%$  in all of the cases) for the three NdCu<sub>2</sub> alloys (bulk, 18 nm, and 13 nm) measured at  $T = 5.2$  K (i.e., in the region between  $T_R$  and  $T_N$ ). Particularly, we want to focus on the region between  $5^\circ < 2\theta < 25^\circ$ , as this angular range encompasses only magnetic reflections. The complete diffractograms can be inspected in Supplementary Fig. S2 in Ref.<sup>57</sup>. The indicated values of the MNP sizes inserted in Fig. 1c and e, 18 nm and 13 nm, respectively, have been obtained by means of Rietveld refinements of the pattern in the paramagnetic region at  $T = 10$  K<sup>39</sup>.

The magnetic unit cell of the bulk alloy included in Fig. 1a is well described using the propagation vector  $\tau = (0.612, 0.042, 0)$  (i.e., an incommensurate description). No higher harmonics are detected within the experimental resolution. Although the Rietveld refinements indicate a description with a pure incommensurate phase to be the most suitable for the magnetic cell arrangement, a minor fraction of the magnetic moments (below 5%) still keeps the commensurate modulation, just in the same way as reported in Ref.<sup>43</sup>. The survival of the commensurate structure above  $T_R$  can be clearly detected thanks to the emergence of a peak located at  $2\theta \sim 6.3^\circ$  (blue-shadowed region), which corresponds to the (200) Bragg reflection of the commensurate arrangement. The huge reduction of the magnetic commensurate moments at  $T = 5.2$  K accounts for the drop in the peak intensity compared to the situation at  $T = 1.5$  K, as it can be observed in the inset. In the case of the MNPs, this reflection is masked, as there is an increasing scattering signal below  $2\theta \sim 7^\circ$  ( $q < 0.316 \text{ \AA}^{-1}$ ). The rise of the magnetic intensity in the MNPs comes as a consequence of the incipient interparticle correlations, which has also been found in other SAF RCu<sub>2</sub> MNPs<sup>22,39,44</sup>.

On the other hand, the description of the magnetic unit cell corresponding to the MNPs keeps the commensurate arrangement up to  $T_N$ , as it can be observed according to the Rietveld refinements included in Fig. 1c and e. This has been sketched at the right-hand side of Fig. 1. The absence for the commensurate-incommensurate transition at the MNP state will be further confirmed by our specific-heat analysis, as no trace for a transition at  $T_R$  was observed. The suppression of magnetic order transitions has already been argued as a consequence of finite size effects<sup>58–60</sup>. Although finite-size effects are indeed affecting the magnetic state of the alloys (note the broadening of the magnetic peaks located between  $18^\circ < 2\theta < 25^\circ$ , corresponding to the (000) and (110) reflections, as the MNP size reduces, revealing a progressive loss of the AF ordering), in this case, it is the increasing inhomogeneous microstrain which is playing a key role in the lack of reorientation transition. Incommensurate structures are very subtle, meaning that, although slight deviations from commensurate phases are very common, transitions to a global incommensurate magnetic structure are less favored<sup>61</sup>. Therefore, it should not be surprising that the existence of inhomogeneous microstrain within the nanoparticles, including the nanoparticle core, may provoke slight deviations from a pure incommensurate arrangement. What is more, these deviations from a pure incommensurate phase, even if minor, already exist at bulk state (5% kept the commensurate



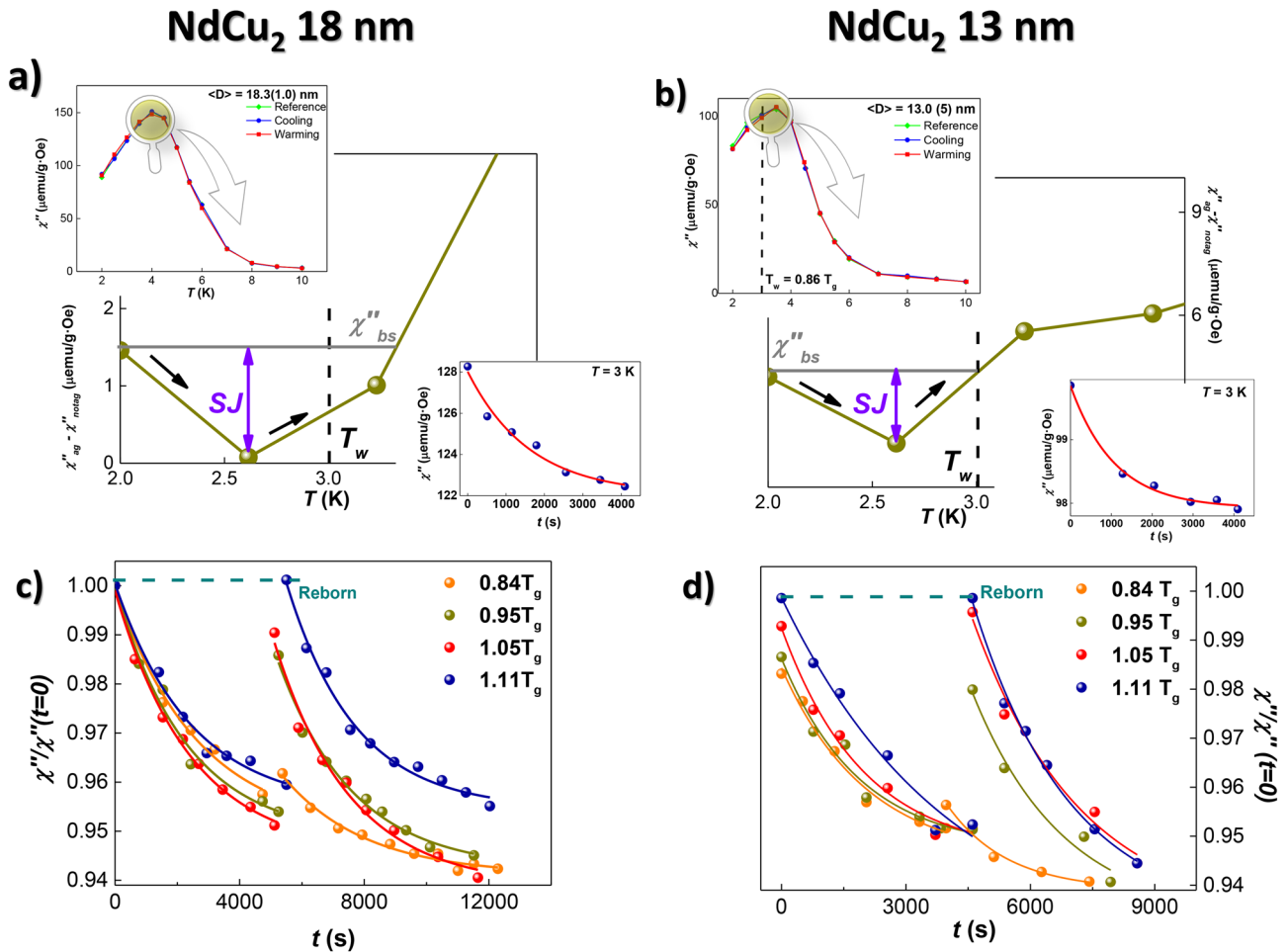
**Figure 1.** Neutron diffraction results. (a, c, e) Experimental neutron diffraction patterns at  $T = 5.2$  K (red dots), together with the Rietveld refinements (black lines) measured for bulk  $\text{NdCu}_2$ , 18 nm and 13 nm-sized MNPs, respectively. Inset in (a) zooms the commensurate (200) magnetic reflection, present at  $T = 1.5$  K, and absent at  $T = 5.2$  K. (b, d, f): Temperature dependence of the magnetic moment  $M$  per unit cell. The position of the commensurate-to-incommensurate transition temperature is only marked for the bulk alloy [vertical gray dashed line in (b)]. (g) Differential SANS cross section  $d\Sigma/d\Omega$  as a function of the momentum transfer  $q$  (log-log scale) measured for bulk (dark cyan), 18 nm (red), and 13 nm-sized (blue)  $\text{NdCu}_2$  MNPs at zero field and at  $T = 2$  K (commensurate AF phase). Right inset zooms into the region nearby  $2.6 \lesssim q \lesssim 3.3 \text{ nm}^{-1}$  at  $T = 2$  K. This region has been studied at  $T = 2.1$  K and 4.8 K (incommensurate AF phase) and at 11.3 K (paramagnetic phase) for the bulk alloy (top left inset). Sketches of the MNPs and of commensurate magnetic structure are showed on the top right.

structure), and are enhanced in the nanoparticle state, preventing the magnetic moments to transition from a pure commensurate to an incommensurate magnetic arrangement.

The middle panels (Fig. 1b,d,f) depict the evolution of the magnetic moment  $M$  with temperature. These data were obtained as  $M = \frac{\pi}{4}\mu_{\tau}$  and  $M = \frac{3\pi}{4}\mu_{3\tau}$  for the fundamental (left axis) and third-harmonic contribution (right axis), respectively. It should be noted that, when the magnetic structure changes from the commensurate to the incommensurate arrangement at  $T_R = 4.5$  K (and only for the bulk alloy), the  $3\tau$  contribution vanishes. Following the loss of AF order revealed by the broadened magnetic peaks (see Fig. 1c,e), a drop in the value of the magnetic moment with decreasing MNP size can be detected. This is well-understood as the amount of AF-coupled entities decreases progressively along with the size reduction. The comparison with the Brillouin function calculated with a total angular momentum of  $J = 9/2$  (red dotted line) shows a reasonable agreement, as it has been already reported in other  $\text{RCu}_2$  MNP systems<sup>22,47</sup>.

In order to access the low- $q$  region (to better define the magnetic structure of  $\text{NdCu}_2$  bulk and MNPs), we have performed small-angle neutron scattering (SANS) measurements. Figure 1g displays the experimental total (nuclear and magnetic) differential SANS cross section  $d\Sigma/d\Omega$  as a function of the momentum transfer  $q$ . There, it can be observed the onset of a structure, which diffracts as a peak, at  $T = 2$  K and  $q \cong 2.93 \text{ nm}^{-1}$ , only for the bulk alloy. This  $q$ -value corresponds to a real-space distance of about 2.14 nm, which is nearly 5 times the  $a$  parameter of the crystallographic unit cell<sup>39,43</sup>. This finding reveals that the RKKY-interaction-mediated spin structures are correlated up to a length scale corresponding to 5 nuclear cells. Complementary  $\chi_{AC}(T)$  measurements on the bulk alloy (see Supplementary Fig. S6 in Ref.<sup>57</sup>) further support the existence of such a correlation, as the presence of a cusp in the  $\chi''(T, f)$  component at  $T \lesssim T_N$  reveals that a large number of individual magnetic moments exhibit a different spin-spin correlation than that of the long-range AF-ordered spin. These short-range AF interactions are robust, since this peak remains almost unaffected even when a field of 3 T is applied (see supplementary figure Fig. S3 in Ref.<sup>57</sup>). The fact that this contribution is wiped out for the MNPs indicates that the size reduction towards the nanoscale destroys this additional correlation.

Unfortunately, in the present SANS experiments, we could only access large momentum-transfer values  $q$ , meaning that we could not measure the structure factor over the whole range of scattering vectors, necessary



**Figure 2.** AC susceptibility results. Memory effects and aging phenomena measured at  $f = 0.2$  Hz and  $\mu_0 h_{ac} = 0.313$  mT for 18 nm-sized (a, c) and 13 nm-sized (b, d) NdCu<sub>2</sub> MNPs. In (a, b), the drop in  $\chi''_{ag} - \chi''_{notag}$  at  $T \lesssim T_w$  (marked SJ in purple) evidences memory effects. Bottom insets in both figures depict the relaxation behavior of  $\chi''(t)$  at  $T_w$ . Note that the Y-axis are expressed in  $\mu\text{emu/gOe}$ . (c, d) depict  $\chi''(t)$  measured at  $T_w$  before and after applying  $4\Delta T$  (cycles). Note that the SG state is completely reborn for  $\Delta T = 1.11 T_g$ .

to also establish the AFM/SG structure via SANS, similar to what has been done on iron oxide, cobalt ferrite, and manganese–zinc–ferrite nanoparticles in Refs.<sup>18,21,62</sup>. Therefore, the present analyses will be constrained to the high- $q$  peak, that was only present for the bulk alloy. The magnetic nature beneath the SANS peak observed for the bulk alloy is further confirmed by monitoring the change in  $d\Sigma/d\Omega$  as the different magnetic states are traversed. This way, by changing the temperature from the commensurate structure ( $T = 2.1$  K) to the incommensurate phase ( $T = 4.8$  K), and then, to the paramagnetic state ( $T > 6.5$  K), it can be observed how the peak found at  $q \cong 2.93 \text{ nm}^{-1}$  moves towards lower momentum transfers ( $q \cong 2.61 \text{ nm}^{-1}$ ) and softens (see left inset in Fig. 1g). This indicates that the transformation from a commensurate to an incommensurate phase also implies a change of the short (additional) correlation length, which now correlates spin structures up to a length scale corresponding to 6 nuclear cells. This is in good agreement with the enlarged magnetic cell of the incommensurate phase, which grows from 10 to 23 crystallographic unit cells, driven by the change of the propagation vector from  $\tau = (0.6, 0, 0)$  to  $\tau = (0.612, 0.042, 0)$ <sup>43</sup>. Both SANS contributions corresponding to the magnetic state ( $T = 2.1$  K and  $T = 4.8$  K) are well below the one corresponding to the paramagnetic phase ( $T = 11.3$  K). This is expected, since a rise in the scattering signal due to the increasing disorder should be recovered in the nonmagnetic state<sup>63</sup>.

Summarizing this section, the diffraction results unambiguously reveal that the core of the nanoparticle arranges following a commensurate structure, with no reorientation. In which concerns the surface ones, a magnetically disordered phase is taking place. The existence of interparticle correlations observed in the neutron diffraction patterns, together with the evidenced SG state in NdCu<sub>2</sub> MNPs<sup>39</sup> allow us to state such a magnetically-disordered SG-like phase for these outer magnetic moments.

**Rejuvenation and memory effect measurements.** In order to quantify the robustness of the SG phase settled for the magnetic moments located at the surface, we have analyzed the time-dependent  $\chi_{AC}(t)$  response. Given that these phenomena are better determined on the out-of-phase component, we will restrict our analyses to the  $\chi''(T, t)$ . We refer the reader to supplementary Fig. S7 for a brief comment on the in-phase component of the MNPs. Figure 2 includes the memory effect (Fig. 2a,b) and temperature-cycling protocols (Fig. 2c,d)

corresponding to the 18 nm [(a) and (c)] and the 13 nm-sized [(b) and (d)] MNPs, respectively. The measurements are focused on the temperature region  $T < 10$  K, given that both MNP ensembles enter the paramagnetic region already at  $T = 7$  K<sup>39,64</sup>. The glass temperature  $T_g$  of these MNPs, determined according to the emergence of a peak in the out-of-phase  $\chi''(T, f)$  component [see top insets in (a) and (b)], was located at  $T_g = 3.8(1)$  K for both particle sizes. Therefore, the waiting temperature  $T_w$  was fixed at  $T_w = 3$  K, which corresponds to  $T_w = 0.796 \approx 0.8 T_g$ . As can be deduced from Fig. 2a and b, memory effects appear when a stop is made at  $T_w = 0.8 T_g$ , as a drop is measured for the difference between the out-of-phase  $\chi_{AC}$  component measured on cooling for the following two scenarios: (i) waiting at  $T_w$  for about  $10^4$  s and then resuming the cooling down to  $T = 2$  K (denoted as  $\chi''_{ag}$ ), and (ii) cooling without waiting at  $T_w$  (denoted as  $\chi''_{notag}$ ). The drop in the  $\chi''_{ag} - \chi''_{notag}$  difference data is revealed for  $T \lesssim T_g$  in both MNP sizes. The relaxation of  $\chi''(t)$  (bottom insets) follows the same trend as the one found in SGs<sup>65–67</sup>. There, a faster decay can be observed for the smallest MNPs (13 nm).

With the aim of accessing more information about the robustness of the magnetically frustrated and disordered SG surface moments, temperature cycles have been performed, following the protocol described in the “Magnetic characterization” subsection of the “Methods” section. Figure 2c and d include such measurements, performed at  $T = 3$  K with cycles of  $\Delta T = 0.84, 0.94, 1.05,$  and  $1.11 T_g$ . As it can be seen, the smaller the  $\Delta T$ , the slower the relaxation (decay). An interpretation of this effect is based on the results of the droplet model for SGs<sup>68</sup>. Within this framework, the correlated spins are assumed to form a *droplet* (or, equivalently, a *domain*) of a certain length, which behaves independently from the rest of the spins<sup>69</sup>. In our case, the slower relaxation implies that the *domains* (droplets) of correlated spins are larger<sup>66</sup>. Paying attention to the rise in the  $\chi''(t)$  value after having resumed the temperature rise (i.e.,  $t > t_{\Delta T}$ ), the effect of a finite domain length scale  $\ell_{\Delta T}$  can already be seen at  $\Delta T = 0.84 T_g$ , as the  $\chi''(t = t_{\Delta T})$  increases with respect to  $\chi''(t \lesssim t_{\Delta T})$ . This rise is enhanced as the step  $\Delta T$ , until the initial value is met, i.e.,  $\chi''(t = t_{\Delta T}) = \chi''(t = 0)$ . The situation can be explained taking into account that the magnetic moments freeze at  $t = 0$  in some particular disordered configuration (domain). Such a configuration is imposed by the frustration of the oscillatory RKKY interactions. Thus, a particular *metastable* initial spin configuration of the droplet is established. When  $\Delta T$  is increased, the larger droplets will start to break down, while a new overall droplet configuration appears. In this way, at least two SG domain configurations coexist, implying the existence of different length scales (conversely, time scales). It is noticeable that in our case, the spin domains are located at the nanoparticle surface, arranged quasi-spherically as a whole, while previous evidence have been reported in well-defined SGs (e.g., the Ising system  $\text{Fe}_{0.5}\text{Mn}_{0.5}\text{TiO}_3$ <sup>70</sup> or the Heisenberg-like material  $\text{CdCr}_{1.7}\text{In}_{0.3}\text{S}_4$ <sup>66</sup>). Spin-glass correlations in the  $\text{NdCu}_2$  MNPs exist even at temperatures above  $T_g$ , as  $\chi''(t = t_{\Delta T})$  is still below  $\chi''(t = 0)$  for  $\Delta T = 1.05 T_g$ . This underlines the robustness of the SG interactions. Then, when  $\Delta T = 1.11 T_g$ , the energy barriers of the larger initial clusters become smaller compared to the thermal energy, meaning that the domain landscape established at  $T = 3$  K prior to the temperature cycling is completely destroyed, and thus, the SG state is said to be completely reborn (*rejuvenation*), as it has already been showed in other ensembles of MNPs evidencing complex magnetic structures (e.g.,  $\text{SrFe}_{12}\text{O}_{15}$ <sup>54</sup>). This rejuvenation of the moments sitting at the surface of the MNPs is somehow surprising, considering that the coupling between neighboring moments is not so well defined, compared to the archetypal Ising or Heisenberg systems mentioned above, where the aging and rejuvenation analyses have been carried out in great detail<sup>71–73</sup>.

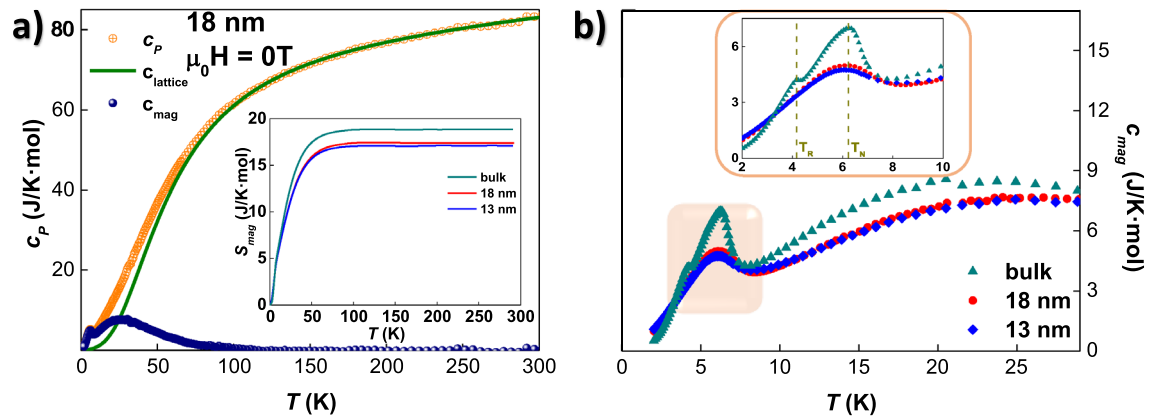
It is worth mentioning that both memory and temperature cycling measurements have been performed for the bulk alloy as well in order to check whether the incommensurate-to-commensurate transition of the magnetic structure could imply frustration that might give rise to a SG state. Not surprisingly, neither traces of memory effects nor relaxation effects are evidenced in the bulk alloy at any temperature surrounding  $T_R = 4.5$  K. This ensures that the transition from the commensurate phase to the incommensurate one is accomplished without the weakening of any magnetic AF order, as the magnetic moments keep well-aligned in the square-up structure.

In order to put into context the onset of memory effects connected to SAF MNPs, we have worked out a simple procedure to compare the robustness of such effects among different SG systems. For this purpose, we define the SG rejuvenation jump ( $SJ$ ) parameter as follows:

$$SJ = \left| \frac{\chi''_{memory} - \chi''_{bs}}{\chi''_{bs}} \right|, \quad (1)$$

where  $\chi''_{memory} = \chi''_{ag} - \chi''_{notag}$ , and  $\chi''_{bs}$  is defined as the  $\chi''_{memory}$  value corresponding to the temperature at which memory effects emerge (see gray line in Fig. 2a,b). We have estimated also the  $SJ$  values corresponding to the canonical SGs CuMn ( $SJ = 7.5$ ) and  $\text{CdCr}_{1.7}\text{In}_{0.3}\text{S}_4$  ( $SJ = 12$ )<sup>66,74</sup>, and also for SG NiFe nanoparticles of 12 nm size embedded in a  $\text{SiO}_2$  matrix ( $SJ = 0.8$ )<sup>52</sup>. Our  $\text{NdCu}_2$  ensembles showcase  $SJ = 0.5$  and  $SJ = 0.6$  for 18 nm and 13 nm-sized MNPs, respectively. As it can be seen, these values are smaller than those of the canonical bulk SGs. This can be readily understood as the magnetically-frustrated RKKY interactions are better accomplished in the bulk systems, where the unit cell distortion and microstrain are minim. But compared to other nanoparticle ensembles, the values obtained for our  $\text{NdCu}_2$  MNPs are in good agreement with this of NiFe nanoparticles of a similar size. Here, we can comment on the positive tendency for the  $SJ$  values as the nanoparticle size decreases. This effect can be understood in terms of an increasing surface-to-core ratio, i.e., the amount of magnetically-frustrated moments increases when reducing the nanoparticle size, which easily translates into the enhancement of memory effects.

**Specific heat measurements.** Specific heat measurements have been performed in order to complete the information about the magnetic transitions undergone by the  $\text{NdCu}_2$  ensembles. Following common practice (e.g., Refs.<sup>56,75,76</sup>),  $c_p$  is assumed to consist of three additive contributions:



**Figure 3.** Zero-field specific-heat results. **(a)** Experimental  $c_p$  (orange), calculated  $c_{lattice}$  (green) and  $c_{mag}$  (blue) contributions corresponding to 18 nm-sized NdCu<sub>2</sub> MNPs. Inset compares  $S_{mag}$  calculated for bulk (dark cyan), 18 nm (red), and 13 nm-sized (blue) MNPs. **(b)**  $c_{mag}$  contribution of bulk, 18 nm, and 13 nm-sized MNP alloys. The inset provides a closer view on the magnetic transition region, where the positions of the Néel ( $T_N$ ) and reorientation ( $T_R$ ) temperatures have been marked by dashed vertical lines.

$$c_p = c_{ph} + c_{el} + c_{mag}, \quad (2)$$

where  $c_{ph}$  is the phonon contribution, which is assumed to obey a Debye model,  $c_{el}$  is the electronic term (depending linearly on  $T$ ), and  $c_{mag}$  represents the magnetic contribution, including the effect of the crystalline electric field (CEF). To extract the  $c_{mag}$  term, we have combined both  $c_{el}$  and  $c_{ph}$  contributions into a single term, labeled as  $c_{lattice}$ , which has been estimated taking into account the existence of two different symmetry environments: one for the magnetic moments located within the core, and one for those located at the nanoparticle surface. To separate both contributions, we have employed the procedure explained in Ref.<sup>39</sup>, where  $c_{lattice}$  is taken from the nonmagnetic isostructural YCu<sub>2</sub> compound<sup>77,78</sup>, including a renormalization factor to account for the different molar masses between the magnetic (Nd<sup>3+</sup>) and nonmagnetic (Y<sup>3+</sup>) ions<sup>75</sup>. The surface contribution to  $c_{lattice}$  is fitted according to the phonon and electronic contributions. Indeed, the latter ones are weighted by a factor  $N_c$  that accounts for the core-to-volume ratio<sup>39</sup>. In this way, the  $c_{lattice}$  contribution is calculated as

$$c_{lattice} = N_c \left[ \gamma_c T + 9R \left( \frac{T}{\theta_D^c} \right) \int_0^{\theta_D^c/T} dx \frac{x^4 e^x}{(e^x - 1)^2} \right] + N_s \left[ \gamma_s T + 9R \left( \frac{T}{\theta_D^s} \right) \int_0^{\theta_D^s/T} dx \frac{x^4 e^x}{(e^x - 1)^2} \right], \quad (3)$$

where  $R = 8.314 \text{ J}/(\text{K mol})$ , and  $\theta_D^c$  and  $\theta_D^s$  denote the Debye temperatures corresponding, respectively, to the core and surface contributions. The fraction of magnetic moments located within the core,  $N_c$ , is 0.47 and 0.34 for the 18 nm and 13 nm-sized MNPs, respectively (indeed, the surface moments,  $N_s = 1 - N_c$ ). We refer the reader to Supplementary Section “Estimating the core-to-volume ratio” for a brief comment on the estimation of the  $N_c$  values.

Following the above-mentioned fitting procedure, Fig. 3a showcases the measured  $c_p$  and the calculated  $c_{lattice}$  and  $c_{mag}$  contributions for the 18 nm-sized MNP ensemble. There, it can be seen how the calculated  $c_{lattice}(T = 300 \text{ K}) = 83.01 \text{ J}/(\text{K mol})$  matches well the expected value according to the Dulong–Petit law<sup>79</sup>. Values for  $\gamma^{bulk} = 12.14(13) \text{ mJ}/(\text{mol K}^2)$  and  $\theta_D^{bulk} = 224.7(6) \text{ K}$  have been obtained, in good agreement with the ones reported for polycrystalline bulk NdCu<sub>2</sub><sup>56</sup>. In the case of the MNP surface,  $\gamma^s = 22.82(2) \text{ mJ}/(\text{mol K}^2)$  and  $\theta_D^s = 281(4) \text{ K}$  for 18 nm, and  $\gamma^s = 21.5(5) \text{ mJ}/(\text{mol K}^2)$  and  $\theta_D^s = 240(6) \text{ K}$  for 13 nm MNPs, values that are greater compared to the bulk ones, as expected<sup>22,37,39</sup>. The inset in Fig. 3a includes the magnetic entropy  $S_{mag}$ , which has been calculated as follows:

$$S_{mag}^{exp} = \int_0^{300} \frac{c_{mag}}{T} dT \quad (4)$$

It can be seen, on the one hand, that the magnetic entropy of the bulk alloy,  $S_{mag}^{exp} = 18.8(1) \text{ J}/(\text{K mol})$ , lies slightly below the theoretical  $S_{mag}^{theo}(300 \text{ K}) = R[\log(2J + 1)] = 19.14 \text{ J}/\text{Kmol}$ <sup>79</sup>, so does compared to the MNPs, where  $S_{mag}^{exp} \approx 17 \text{ J}/\text{Kmol}$ . This reduction might be caused by the existence of short-range correlations and of a distorted surface, which both have been claimed to keep the  $S_{mag}^{exp} < S_{mag}^{theo}$ <sup>22,39,56,64</sup>. Additionally, the value of  $S_{mag}^{exp}$  around  $T_N$  for the MNPs is about  $3.6 \text{ J}/\text{Kmol}$ , which is also below the expected value  $S_{mag}^{theo}(T_N) = R[\log(2)] = 5.76 \text{ J}/(\text{Kmol})$  for a complete removal of the two-fold spin degeneracy of the CEF ground-state doublet<sup>80</sup>. The same picture holds for the bulk alloy, where  $S_{mag}^{exp} \approx 4.39 \text{ J}/(\text{K mol})$ . These facts (reduced  $S_{mag}^{exp}$  at 300 K and  $T_N$ ) were also found in polycrystalline bulk NdCu<sub>2</sub> and CeCu<sub>2</sub> alloys<sup>56,64</sup>.

Figure 3b shows the  $c_{mag}$  contribution corresponding to the three alloys at zero external field, while the  $c_{mag}$  obtained upon applying different magnetic fields can be inspected in Supplementary Fig. S8. The region nearby the low-temperature magnetic transitions has been enlarged in the inset to observe in closer detail the lack of a reorientation transition in the MNPs. Thereby, the  $c_{mag}$  reveals clearly how the bulk AF state survives in the

MNPs, according to the occurrence of an AF  $\lambda$ -anomaly in the MNPs. The  $T_N$  value is not affected by the nanoscaling, as it is kept constant at  $T_N = 6.2(1)$  K. This is in good agreement with what has already been reported in Ref.<sup>39</sup>. The most interesting change to be noticed with respect to the bulk alloy is the lack of a reorientation transition, which confirms the ND results, where the magnetic structure of the AF core moments follows a commensurate square-up antiferromagnetic structure in the whole magnetic region. The Schottky-like contribution found above  $T_N$  is not related to extra magnetic transitions, yet it arises from CEF effects. This reveals, in the same way as in Ref.<sup>39</sup>, that the energy level schemes are maintained in the nanoparticle regime in a way very similar to the bulk. A complete explanation for this finding can be found in Ref.<sup>39</sup>, where the joint analyses between specific heat and inelastic neutron scattering unveiled the prevalence of the CEF schemes despite the size reduction to the nanoscale.

## Conclusion

Two MNP ensembles of NdCu<sub>2</sub> with 18 nm and 13 nm particle size have been produced and characterized in order to scrutinize the dual spin dynamics driven by the core and surface environments. The core magnetic moments arrange into a commensurate square-up antiferromagnetic structure up to  $T_N$  without exhibiting any reorientation to an incommensurate phase, as it was the case for the bulk alloy. On the other hand, the magnetic moments located at the MNP surface give rise to a collective spin-glass phase, for which we have been able to determine quantitatively the time-dependent memory effects and aging phenomena. Such magnetically-frustrated correlations have been compared with those found in canonical and MNP spin glass phases by means of the  $SJ$  parameter. A strong reduction in the  $SJ$  value has been determined when passing from ideal Ising spin-glass systems to superantiferromagnetic MNPs. Finally, although NdCu<sub>2</sub> MNPs adopt an AF/SG core/surface arrangement very similar to the one reported in Cr<sub>2</sub>O<sub>3</sub>, NiO or CoO–Pt MNPs<sup>40–42</sup>, the magnetization dynamics of the presented 4f NdCu<sub>2</sub> MNPs is radically different from the one of transition metal-based MNPs, as the magnetically-frustrated moments play a key role in the global MNP magnetic dynamics response. Therefore, our work shows how the complex magnetic structure of bulk NdCu<sub>2</sub> evolves with decreasing particle size, as well as it provides a depiction on how the size-effects modify the magnetically-frustrated RKKY exchanged interactions taking place at the nanoparticle surface.

## Methods

**Sample production.** Polycrystalline NdCu<sub>2</sub> pellets have been obtained by melting the constituents in an arc furnace (MAM-1, Johanna Otto GmbH) under an Ar atmosphere (99.99%). The resulting alloy was sealed-off in a glove box under Ar pressure (99.99%) to avoid oxidation, and grinded for times of 2h and 5h in a Retsch PM 400/2 high-energy planetary ball mill (using WC containers). This technique allows to obtain easily a large amount (~ 5 g) of MNPs.

**Neutron diffraction and small-angle neutron scattering.** The microscopic structure of the NdCu<sub>2</sub> samples was studied using neutron diffraction (ND) and small-angle neutron scattering (SANS). ND measurements have been carried out at the G4.1 instrument (LLB, France) using a wavelength of  $\lambda = 2.426$  Å at temperatures between 1.5 K and 15 K. A measuring time of 8 h for each diffraction pattern has been chosen to assure a high signal-to-noise ratio. SANS measurements were performed at the ZOOM instrument (ISIS, UK). The following parameters were employed: sample-to-detector distance: 4 m, wavelength range:  $1.75$  Å  $< \lambda < 16.5$  Å, sample temperatures: 2–100 K, applied fields: 0–3 T.

**Magnetic characterization.** The magnetic characterization was performed by means of dynamic  $\chi_{AC}(t, f, T)$  measurements in a QD-MPMS (SQUID) magnetometer located at the University of Cantabria, Spain. The ensembles of MNPs were measured between  $T = 2$ –300 K under an oscillating magnetic field amplitude of  $\mu_0 h_{AC} = 0.313$  mT and a frequency of  $f = 0.2$  Hz. To probe memory effects and aging phenomena, several protocols can be found in the literature, including both static  $M_{DC}$  and dynamic  $\chi_{AC}$  susceptibility measurements<sup>55,66,70,81,82</sup>. In this work, we have recorded the out-of-phase  $\chi''$  component of the dynamic  $\chi_{AC}$  susceptibility, as it allows to detect in more detail the subtleties concerning the spin dynamics<sup>55,70</sup>. Briefly, in order to trace the memory effects, we have compared the difference between the AC susceptibility measured upon warming (i) without making any stop (*reference*), and (ii) after having made a stop at the waiting temperature  $T_w$  (*warming*) for  $t > 10^3$  s. The occurrence of a drop in this difference at temperature values slightly below  $T_g$  will account for the memory effect. Concerning the aging phenomena, these are probed by inspecting the  $\chi''(t)$  data. Moreover, the *robustness* of the SG-like frustrated interactions has been further investigated by applying a *temperature cycling* protocol. This consists of measuring the  $\chi''$  versus  $t$  dependency at a certain  $T_w$  value within the SG phase (in our case,  $T_w \sim 0.8 T_g$ ) for a sufficiently long period of time ( $t \sim 10^3$  s). Once the waiting time is over, the temperature has been raised by a certain  $\Delta T$  up to temperature values close to that of  $T_g$  ( $\Delta T$  varies between  $0.85 T_g$  and  $1.1 T_g$ ). Immediately thereafter, the temperature is lowered down to  $T_w$ , and the  $\chi''(t)$  signal is measured again for  $t \sim 10^4$ – $10^5$  s. This cycling protocol mimics the one already reported in Ref.<sup>70</sup>, and allows to monitor adequately the robustness of the SG phase.

**Specific heat measurements.** The thermodynamic properties have been studied by means of heat capacity measurements. These were performed using a QD-PPMS instrument (University of Cantabria) in the temperature range between 2 and 300 K, under zero applied magnetic field, and at magnetic fields of 1 T and 8 T. Measurements were performed following the relaxation method<sup>83</sup>.

## Data availability

All data generated or analyzed during this study are included in this published article and its supplementary information files.

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## Author contributions

E.M.J., L.F.B., and P.S. conceived the experiments. E.M.J., P.S., L.F.B., F.D., and D.A.V. conducted the experiments. E.M.J., J.A.B., A.M., and P.S. analyzed the results. All authors reviewed the manuscript.

## Competing interests

The authors declare no competing interests.

## Additional information

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1038/s41598-022-13817-7>.

**Correspondence** and requests for materials should be addressed to E.M.J.

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# Supplementary Material to: Magnetic Order and Disorder Environments in Superantiferromagnetic NdCu<sub>2</sub> Nanoparticles

E. M. Jefremovas<sup>1,\*</sup>, P. Svedlindh<sup>2</sup>, F. Damay<sup>3</sup>, D. Alba Venero<sup>4</sup>, A. Michels<sup>5</sup>, J. A. Blanco<sup>6</sup>, and L. Fernández Barquín<sup>1</sup>

<sup>1</sup>Department CITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain

<sup>2</sup>Department of Materials Science and Engineering, Uppsala University, Box 35, SE-751 03 Uppsala, Sweden

<sup>3</sup>Laboratoire Léon Brillouin, Université Paris-Saclay, CEA-CNRS, 91191 Gif-sur-Yvette Cedex, France

<sup>4</sup>ISIS Neutron and Muon Facility, Rutherford Appleton Laboratory, Didcot, OX11 0QX, United Kingdom

<sup>5</sup>Department of Physics and Materials Science, University of Luxembourg, L-1511 Luxembourg

<sup>6</sup>Department of Physics, University of Oviedo, 33007 Oviedo, Spain

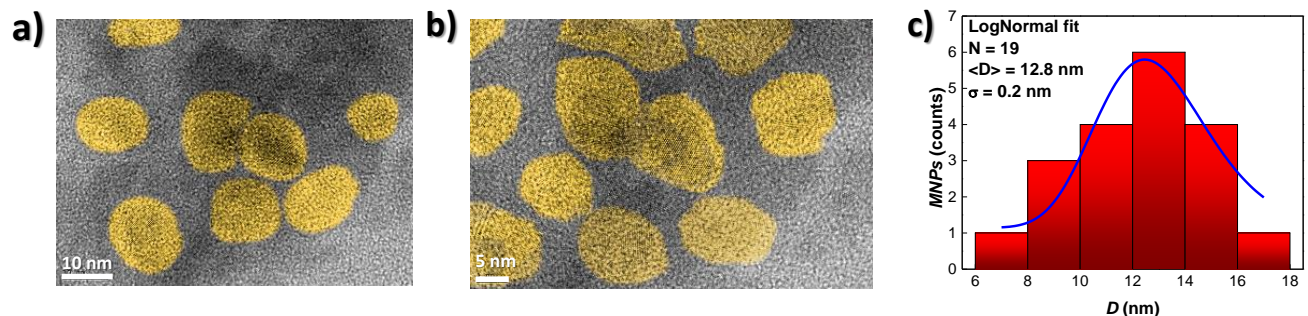
\*martinjel@unican.es

## ABSTRACT

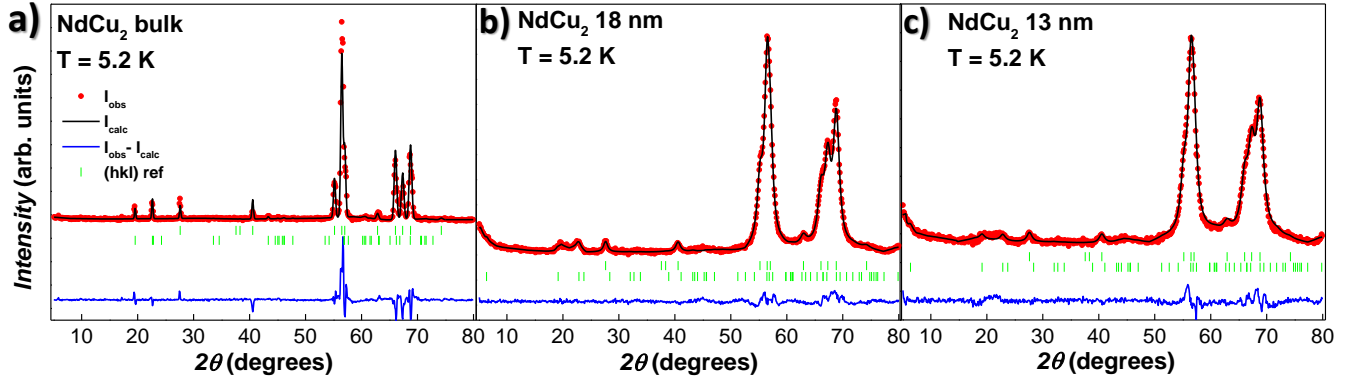
This Supplementary Material includes supporting information on the microscopic structure of the nanoparticles. In this way, two representative TEM images have been included to access more information on the MNP morphology, as well as supplementary neutron diffraction (ND) and small-angle neutron scattering (SANS) data. We are also including the estimation of the geometrical core-to-volume ratio for both MNP ensembles (18 and 13 nm-sized). Supplemental static and dynamic magnetization measurements are displayed, accounting for the exchange bias effect, the dynamic in-phase and out-of-phase susceptibility of bulk NdCu<sub>2</sub>, plus an overview of the in-phase  $\chi'(T)$  component for the 18 and 13 nm-sized MNPs. Finally, the field dependence of the  $c_{mag}$  contribution to the specific heat is displayed.

## Transmission Electron Microscopy analysis

Figs. S 1 (a) and (b) include two representative Transmission Electron Microscopy (TEM) images corresponding to NdCu<sub>2</sub> 5h-milled MNPs. The morphology of the MNPs can be considered as quasi-spherical, in good agreement with the previous morphology reported for TbCu<sub>2</sub> and Tb<sub>0.5</sub>Gd<sub>0.5</sub>Cu<sub>2</sub> MNPs produced by our group following the same route (ball milling)<sup>1,2</sup>. The statistical analyses of these images (19 nanoparticles counted) point to a mean nanoparticle size  $\langle D \rangle = 12.6$  nm with size dispersion  $\sigma = 2.6$  nm. This value is compatible with the ones obtained by means of both XRD [13.0(5)] and ND [12.7(1.0)] characterization, even if the number of MNPs counted is low.



**Fig. S 1.** (a) and (b) representative TEM images corresponding to NdCu<sub>2</sub> 5h-milled MNPs, and (c) their corresponding size distribution ( $N = 19$  MNPs). The fitting follows a LogNormal distribution, pointing to  $\langle D \rangle = 12.6(3)$  nm.



**Fig. S 2.** Neutron diffraction patterns for bulk  $\text{NdCu}_2$  (a), 18 nm (b), and 13 nm-sized (c) MNPs measured between  $5^\circ < 2\theta < 80^\circ$  at  $T = 5.2$  K, *i.e.*, above the bulk reorientation temperature of  $T_R = 4.5$  K. Red dots represent the experimental data, black lines are the calculated Rietveld refinements, and the blue lines at the bottom correspond to the difference between the calculated and experimental values. Green bars mark the position of the  $(hkl)$  positions of the nuclear (top) and magnetic (bottom) structures. The bulk magnetic structure is well-fitted according to an incommensurate description, while the MNPs (18 nm and 13 nm) maintain the commensurate square-up modulation at  $T = 5.2$  K.

## Neutron diffraction

Figure S2 represents the ND patterns corresponding to bulk (a), 18 nm (b), and 13 nm-sized (c) MNPs of  $\text{NdCu}_2$ . According to Ref. 3, the bulk magnetic structure at  $T = 5.2$  K has already undergone a phase transition from a commensurate to an incommensurate structure with a propagation vector of  $\tau = (0.612, 0.042, 0)$ . All the Bragg peaks are well-fitted according to this description. On the other hand, the ND data in Fig. S2(b) and (c) maintain the commensurate structure. The rise in intensity in the low-angle region ( $2\theta < 7^\circ$ ,  $q < 0.316 \text{ \AA}^{-1}$ ) indicates the occurrence of interparticle correlations which can be connected to a surface spin-glass phase.

## Small-angle neutron scattering

Figure S3 displays the field evolution of the total (nuclear and magnetic) SANS cross section  $d\Sigma/d\Omega$  of bulk  $\text{NdCu}_2$  in the neighborhood of the diffraction peak at  $q \cong 2.93 \text{ nm}^{-1}$  (with  $2\pi/2.93 \text{ nm}^{-1} \cong 2.14 \text{ nm}$ ). These short-range AF interactions are rather robust, since the peak remains almost unaffected even when a field of 3 T is applied (see inset in Fig. S3).

## Estimating the core-to-volume ratio

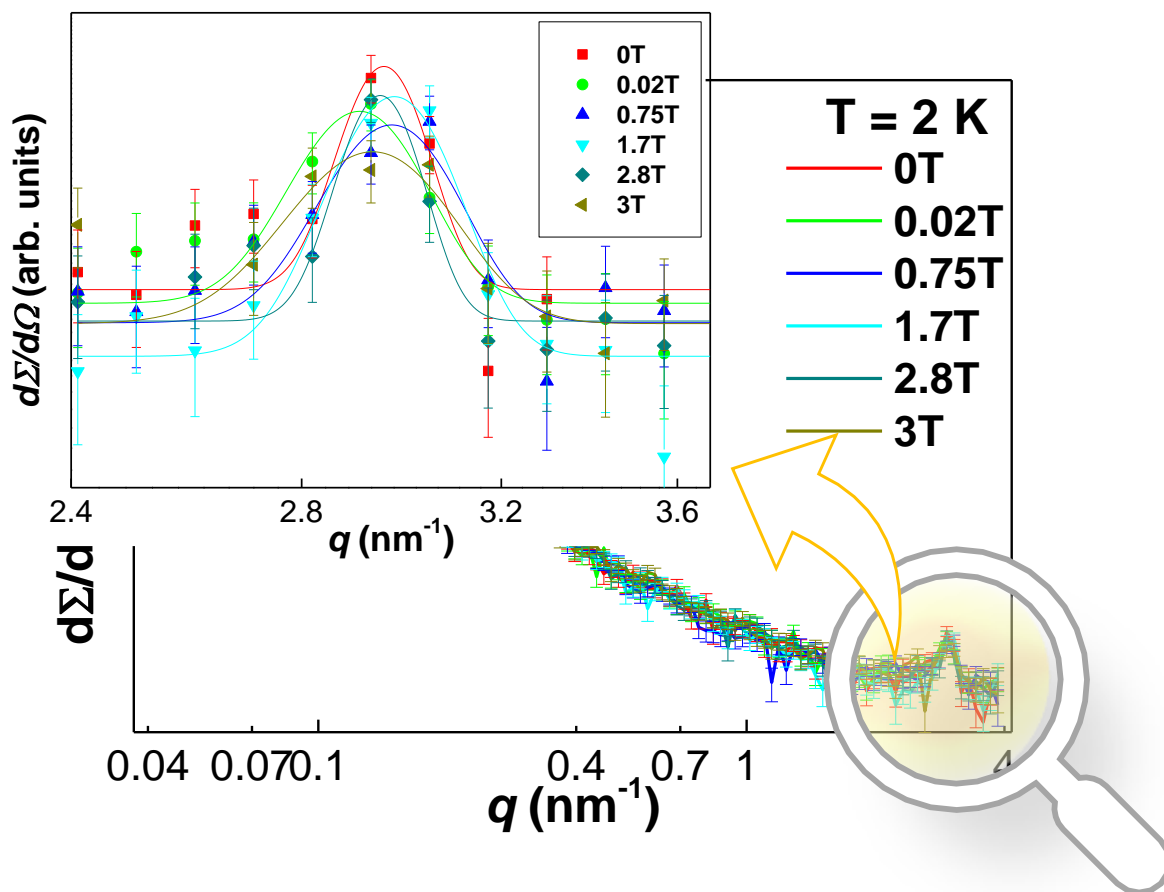
Following eq. S1 included in Ref.<sup>4</sup>, the geometrical core-to-volume ratio corresponding to a MNP size of  $\langle D \rangle = 18$  and 13 nm has been estimated as:

$$N_c = \frac{V_{core}}{V_{MNP}} = \left( \frac{D_{core}}{D_{MNP}} \right)^3 = \begin{cases} \left( \frac{14}{18} \right)^3 \approx 0.47 \\ \left( \frac{9}{13} \right)^3 \approx 0.33 \end{cases} \quad (1)$$

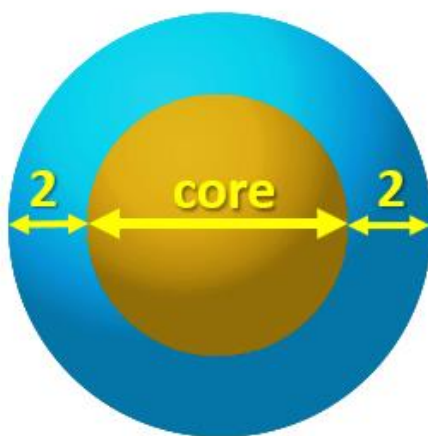
where the MNPs have been assumed to be spherical and a shell thickness of 2 nm is considered, as it is commonly found in MNPs<sup>1</sup> (see sketch in Fig. S4).

## Exchange Bias effect

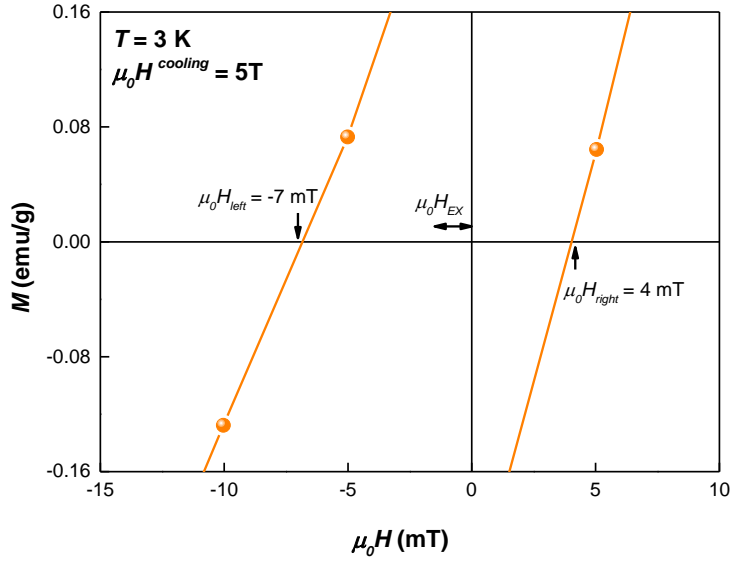
Fig. S 5 showcases the central region of the hysteresis loops performed on  $\text{NdCu}_2$  13 nm-sized MNPs. The sample has been cooled to  $T = 3$  K with applying an external field of 5T. A slight negative shift of cycles can be detected, accounting for an exchange bias field  $\mu_0 H_{EB} \sim 1.5$  mT. This value is two orders of magnitude below the one reported for transition metal-based MNPs, *e.g.*,  $\mu_0 H_{EB} \sim 120$  and 300 mT for  $\text{CoFe}_2\text{O}_4$  ( $T_f \sim 125$  K)<sup>5</sup> or  $\text{FeO/Fe}_3\text{O}_4$  ( $T_N \sim 200$  K) MNPs<sup>6</sup>; and even below that of 3 mT reported for 8 nm-sized  $\text{TbCu}_2$  MNPs<sup>7</sup>. The fact that  $\text{NdCu}_2$  displays extremely low values for its ordering ( $T_N \sim 6.5$  K) and freezing ( $T_f \sim 5.5$  K) transitions hampers the observation of large exchange bias field.



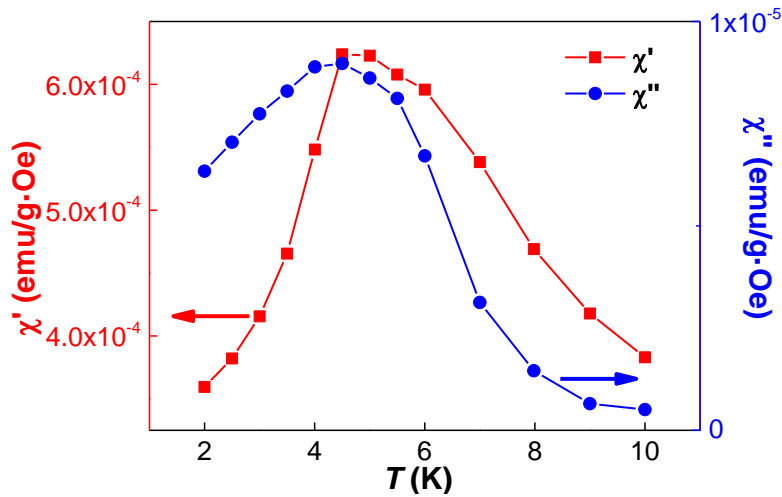
**Fig. S 3.** Field-dependence ( $\mu_0 H$  between 0 and 3 T) of  $d\Sigma/d\Omega$  of bulk  $\text{NdCu}_2$  at  $T = 2$  K (log-log scale). The inset enlarges the  $q$ -region in the vicinity of the magnetic diffraction peak at  $q \cong 2.93 \text{ nm}^{-1}$ .



**Fig. S 4.** Schematic representation of the nanoparticles, where the shell is considered to be of 2 nm thickness.



**Fig. S 5.** Central region of the hysteresis loops performed on 13 nm-sized NdCu<sub>2</sub> MNPs. An exchange bias field of  $\mu_0 H_{EB} \sim 1.5$  mT can be observed.



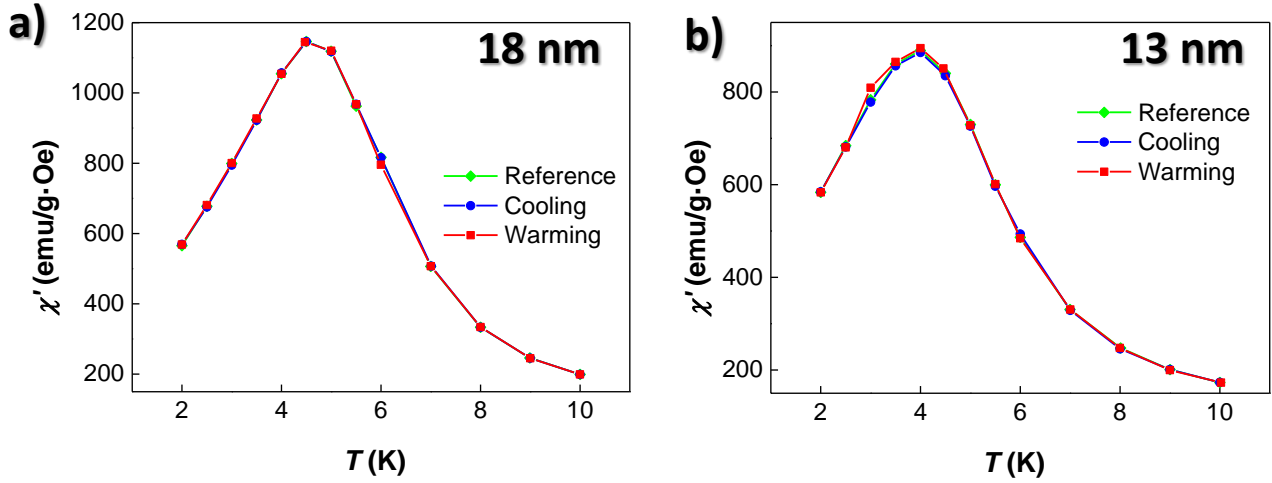
**Fig. S 6.** In-phase  $\chi'$  (red) and out-of-phase  $\chi''$  (blue) components of the dynamic susceptibility  $\chi_{AC}(T)$  measured at  $f = 0.2$  Hz and  $\mu_0 h = 0.313$  mT for NdCu<sub>2</sub> polycrystalline bulk alloy.

### Dynamic susceptibility of bulk NdCu<sub>2</sub>

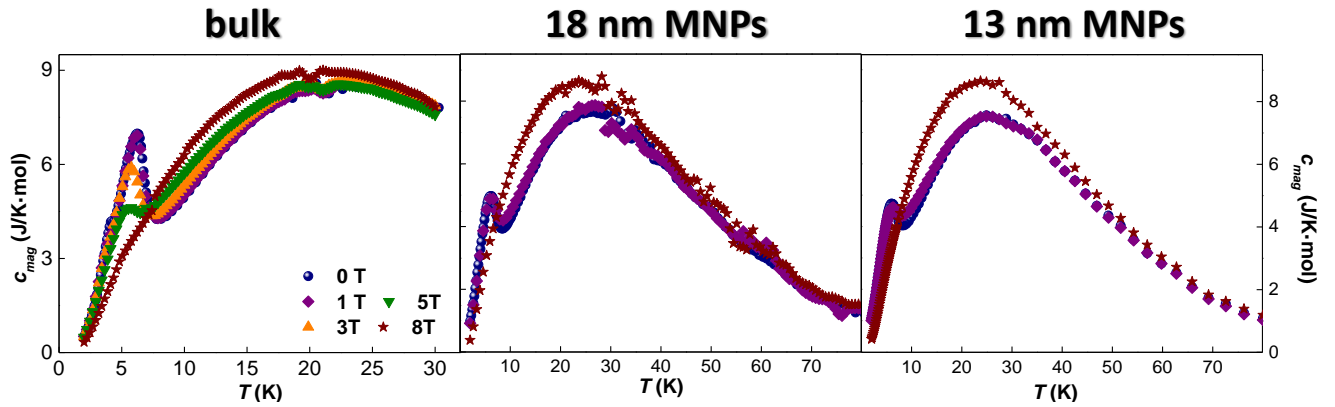
Fig. S 6 the in-phase and out-of-phase components for the bulk NdCu<sub>2</sub> alloy. The in-phase shows two peaks, at  $T \sim 4.5$  and  $T \sim 6.5$  K, which correspond to the  $T_R$  and  $T_N$  transitions. The out-of-phase displays a broad peak centered at  $T \sim 4$  K.

### In-phase $\chi'(T, f)$ component of NdCu<sub>2</sub> MNPs

Fig. S 7 includes the dynamic susceptibility in-phase  $\chi'(T, f)$  component corresponding to the 18 and 13 nm-sized MNPs, respectively. There, it can be seen the occurrence of a broad peak in the vicinity of  $T \approx 5$  K for both MNP ensembles. This maximum have evidenced a shift towards higher temperatures when increasing the frequency<sup>4</sup>, which is a characteristic behavior of freezing transitions<sup>8,9</sup>. Although additionally to this SG-cusp, a maximum in  $\chi'(T, f)$  corresponding to the AF Néel transition should be observed at  $T = T_N$ , only a single broad peak is detected, as a consequence of the proximity of both  $T_N$  and  $T_f$  transitions.



**Fig. S 7.** In-phase  $\chi'(T)$  component corresponding to (a) 18 and (b) 13 nm-sized NdCu<sub>2</sub> MNPs measured under  $f = 0.2$  Hz and  $h = 0.313$  mT.



**Fig. S 8.** Magnetic contribution to the specific heat,  $c_{mag}$ , as a function of temperature  $T$  for bulk (a), 18 nm (b), and 13 nm-sized (c) MNPs measured under external magnetic fields of 0, 1, and 8 T. Additionally, for the case of the NdCu<sub>2</sub> bulk alloy, data at 3 T and 5 T are shown.

### Magnetic contribution to the specific heat

Figure S8 shows the field dependence of the magnetic contribution to the specific heat,  $c_{mag}$ , corresponding to bulk (a), 18 nm-sized (b), and 13 nm-sized MNPs (c). First of all, it should be mentioned that, as for the case of the 13 nm-sized MNPs<sup>4</sup>, for which  $\gamma^s = 21.5(5)$  mJ/(mol K<sup>2</sup>) and  $\theta_D^s = 240(6)$  K were obtained<sup>4</sup>, the 18 nm-sized MNPs also do evidence alterations in the surface propagation, in the form of a softening of  $\gamma^s = 22.82(2)$  mJ/(mol K<sup>2</sup>) and  $\theta_D^s = 281(4)$  K. These values are, as expected, larger than the bulk ones, which have been obtained as  $\gamma^{bulk} = 12.14(13)$  mJ/(mol K<sup>2</sup>) and  $\theta_D^{bulk} = 224.7(6)$  K, in good agreement with the ones reported in Ref. 10.

The field dependence of the  $c_{mag}$  contribution allow to detect how the Néel transition is almost destroyed at an applied field of  $\mu_0 H = 3$  T for the bulk alloy [Fig. S8(a)], which is congruent with the existence of a metamagnetic transition found at  $2.7$  T<sup>11</sup>. According to both the modeling in Ref. 11 and the experimental magnetization study presented in Ref. 3, the magnetic moments are, above 2.7 T, ferrimagnetically-oriented. The fact that we could still recover a slight hump, even at 8 T, underlines the robustness of the AF-coupling, that still exists for some magnetic entities within the global F1 phase. In the case of the MNPs [Fig. S8(b) and (c)], the situation is very similar: the Néel transition is barely affected at 1 T, whereas it is completely wiped out at 8 T, in good agreement with  $M(H)$  results<sup>4</sup>.

## References

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