## Relationship between weak ferromagnetism and magnetic irreversibilities in $Gd_2CuO_4$

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Detailed dc and ac magnetic susceptibility measurements have been made on a series of polycrystalline  $Gd_2CuO_4$ . This system crystallizes in a distorted T' phase with a reduced orthorhombic symmetry and exhibits a weak ferromagnetic (WF) behavior. The samples were synthesized at different temperatures both by solidstate reaction and by a sol-gel technique allowing control of the final size of the sample particles. Changes in the magnetothermal dependence of dc magnetization and in the frequency dependence of the ac susceptibility, are observed for the ceramic samples. We regard the starting temperature of irreversibilities in dc magnetization as a blocking temperature for a system of WF domains or clusters. In the sol-gel particles a size reduction depresses the blocking temperature, which is interpreted as the limitation of the WF domains extension by the particle size. The results are discussed in a framework that accounts for coherent displacements of the oxygen in the  $CuO_2$  planes as the origin of the WF domains.

## I. INTRODUCTION

In recent years the study of the magnetic properties of the rare-earth cuprates  $R_2$ CuO<sub>4</sub> (R=rare earth) has attracted considerable interest because of their relationship with the electron-doped superconductors  $R_{2-x}A_x$ CuO<sub>4</sub>, R = Pr, Nd, Sm, Eu; A =Th, Ce,<sup>1</sup> in the search for connections between the superconducting phenomena and the magnetism of the undoped material. These cuprates form in the tetragonal (T') crystal structure<sup>2</sup> and can be prepared in air at atmospheric pressure for the light rare earths R = Pr, Nd, Sm, Eu, and Gd. For R = Tb and heavier ones the T' phase can only be achieved under high pressure.<sup>3</sup> Neutron diffraction studies for R = Pr, Nd, Sm (Ref. 4) have indicated that the Cu moments order in them in a three-dimensional (3D) antiferromagnetic (AF) phase at a Néel temperature  $T_N \sim 260-290$  K. Other members of the series, with R = Gd, Tb, and heavier rare earths, also present a weak ferromagnetic component<sup>5,6</sup> and do not show superconductivity (SC) when doped with Th or Ce.<sup>7</sup> This fact suggests that superconductivity and weak ferromagnetism (WF) are mutually exclusive in these systems. An extensive investigation of several  $(R, R')_2$ CuO<sub>4</sub> solid solutions<sup>8</sup> supports a boundary for WF in the cuprates associated with the size of the planar CuO<sub>2</sub> lattice at a value of a = 3.910(1) Å. The boundary for WF is associated with a displacement of the oxygen atoms within the  $CuO_2$  planes, O(1), from their symmetric position. Electron paramagnetic resonance, x-ray, Mössbauer, and Raman techniques have confirmed this picture.<sup>9-11</sup> From those results it was concluded that the local symmetry at the R site is orthorhombic for the WF compounds.<sup>9</sup> The O(1) distortion is intraplanar and perpendicular to the Cu-O(1)-Cu bond.<sup>12</sup> The lower symmetry associated with displacements of O(1) allows a Dzyaloshinskii-Moriya<sup>13</sup> (DM) exchange term between adjacent copper moments,

$$H_{ii}^{\rm DM} = \mathbf{D}[\mathbf{S}_{\mathbf{i}} \times \mathbf{S}_{\mathbf{i}}],\tag{1}$$

to be effective. The direction of the Dzyaloshinskii vector **D** is determined by the point symmetry at the point bisecting the straight line between the Cu atoms coupled by the interaction. According to the criteria given by Moriya, for distorted Cu-O(1) planes the direction of  $\mathbf{D}$  is parallel to the crystallographic c axis. Thus, by Eq. (1), that antisymmetric exchange term involves only components of the Cu moments in the Cu-O(1) plane. This is in agreement with the conclusion that the WF moment, and thus the canting of Cu moments, is parallel to these planes, as derived from studies of  $Gd_2CuO_4$  single crystals.<sup>5,8</sup> The real part of the ac susceptibility  $\chi'$  as a function of temperature presents three main maxima, plus other anomalies at low temperatures.<sup>14</sup> One at 7 K, associated with the AF order of the rare-earth sublattice.<sup>15</sup> It has been suggested that this temperature is too high for AF ordering of the rare-earth and a pseudodipolar magnetic interaction has been proposed to explain the rareearth magnetic ordering.<sup>16</sup> Another, at about 20 K for small measuring fields, shifts to lower temperatures when the external field is increased. It is associated with a spin reorientation transition of the Cu moments due to a R-Cu

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interaction.<sup>5</sup> This peak does not appear for pressuresynthesized  $R_2$ CuO<sub>4</sub>, which may indicate a freezing of the copper WF components for the heavier R, <sup>16</sup> unlike in Gd<sub>2</sub>  $CuO_4$ . The third maximum, in the vicinity of 270 K, has been associated to the 3D AF Cu ordering at  $T_N$ , also detected by an abrupt change in dc magnetization in  $T_N$ .<sup>5</sup> Below it, a dependence of dc magnetization on the magnetothermal history has been reported,<sup>5</sup> however, no detailed study has been presented. In ceramic samples these irreversibilities are significantly enhanced, showing large differences between zero-field-cooled (ZFC) and field-cooled (FC) dc magnetizations, with the presence of slow relaxation processes.<sup>17</sup> Recently, we reported an ac study on ceramic samples annealed at two different temperatures that showed a high-temperature  $\chi'$  maximum whose position depends on the annealing temperature, with respect to the Cu AF ordering point.<sup>18</sup> We suggested an influence of the annealing conditions on the homogeneization of the O(1) distortions. This varies with the annealing and is associated with the coherence length of the O(1) distortion. The purpose of this work is to verify that hypothesis. For this reason we have prepared Gd<sub>2</sub>CuO<sub>4</sub> particles by sol-gel methods in order to control particle size and subsequently the hypothetic domain-cluster size. The data obtained by dc and ac magnetization in this work are compared with those of ceramic samples.

# II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

#### A. Sample preparation

In order to establish comparisons with the sol-gel technique we have synthesized Gd<sub>2</sub>CuO<sub>4</sub> samples by solid state reaction, using Gd<sub>2</sub>O<sub>3</sub> and CuO oxides as starting materials, at different temperatures. Stoichiometric amounts of the oxides were ground for several hours and, for the so-called sample C1, thermal treated at 850 °C with frequent intermediate grindings. Around 400 h were required to obtain the pure phase. Other ceramic samples, named C2, C3, C4, and C5, were prepared in several steps with intermediate grindings at different synthesis temperatures, 950, 1000, 1040 and 1080 °C, respectively. For the sol-gel technique, using urea as gelificant agent, nitrate salts were used as starting materials, due to their high solubility in water. The solvent was evaporated on a hot plate with continuous stirring. When cooling, a gel is formed which is decomposed in an oven at 250 °C, yielding the precursor of these samples. After grinding the precursor, it was submitted to several annealings at different temperatures, from 600 °C (sample S4) to 950 °C (sample S1), in order to obtain particles of different sizes. Details of this process have been previously reported.<sup>19</sup>

#### **B.** Experimental techniques

The polycrystalline powders were characterized analyticaly by inductive coupled plasma atomic emission spectroscopy (ICP-AES), using an ICP Perkin-Elmer 5000 with Ar plasma. The structural characterization was carried out by x-ray powder diffraction, using a diffractometer Philips PW-1710 with Cu anode (radiation Cu  $K\alpha l$  of  $\lambda = 1.540$  60 Å). The measurements were performed in air at room temperature. The lattice parameters were determined using a standard least-squares reduction method to fit the positions of the diffraction peaks. In order to determine the size distribution, measurements of photon correlation spectroscopy (PCS) and transmission electron microscopy (TEM) were carried out. The PCS measurements were performed with an Ar laser Liconix series 5000 of 5 W operating at  $\lambda = 488$  nm and a goniometer ALV-SP80 controlled automatically by means of an ALV-LSE unit. For those measurements, particles were dispersed in ethylene glycol using Triton X-100 as dispersing agent.

The dc magnetization data were obtained using a Quantum Design superconducting quantum interference device (SQUID) and a DMS-1660 vibrating sample magnetometer (VSM) in the temperature range  $4 \le T(K) \le 300$ . The real and imaginary part components  $\chi'$  and  $\chi''$  of the external complex ac susceptibility were measured as a function of temperature using the mutual inductance technique, with a coaxial assembly consisting of a primary solenoid and two identical, oppositely wound, sensing coils connected in series and separated approximately 3.8 cm center to center. The sample is positioned within one of the secondary coils and driven with an applied ac magnetic field. The resultant variation in flux produces an output voltage, proportional to the sample susceptibility, which is measured by a phase-sensitive lock-in detector down to approximately 0.01  $\mu$ V, corresponding to a sensitivity for the variation of the magnetic moment of  $10^{-7}$  emu. Measurement accuracy and resolution are increased by moving the sample between the two sensing solenoids, in order to eliminate the offset voltages due to imperfect compensation of the secondary circuit. The calibration was performed using a Gd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O paramagnetic standard with the same shape and size as the investigated samples. Demagnetizing effects have been taken into account in the calculation of the internal susceptibility. Data were collected on warming from 13 K to 300 K, after zerofield cooling the sample. For each run of measurements, the ac field was applied with a fixed amplitude of  $H_{\rm ac}$  = 300 A/m (3.75 Oe) at fixed frequencies f, ranging from 5 Hz to 1000 Hz. A dc field,  $H_{dc}$  from 0 to 800 A/m (10 Oe), was generated by applying a dc current to the primary coil. The temperature of the samples was controlled with an accuracy of about 0.1 K.

## C. Size and structural characterization

For samples obtained by solid state reaction x-ray diffraction indicates a pure  $Gd_2CuO_4$  phase. By means of gravimetric pyrolisis it was determined that the proportion of C, H, and N in the final sol-gel samples is lower than the inferior detection limit of this technique. This indicates that the urea decomposes almost completely and does not contaminate the final samples. The results from inductively coupled plasma (ICP) measurements show that the molar ratio Gd/Cu is  $2.1\pm0.1$ ; i.e., the stoichiometry of the starting solutions is kept in the final samples. X-ray-diffraction data for the solgel samples show that the time necessary to obtain the right phase decreases considerably as the calcination temperature increases. We used 50 h for 600 and 650°C, 24 h for

Sol-gel samples	Calcination temperature	a (Å)	Size (nm)
S1	950 °C	3.894(1)	$350 \pm 60$
S2	900 °C	3.894(1)	$280~\pm~50$
S3	850 °C	3.894(1)	$270~\pm~40$
S4	800 °C	3.895(1)	$200 \pm 30$
S5	750 °C	3.895(1)	$160 \pm 30$
S6	700 °C	3.896(1)	$130 \pm 20$
S7	650 °C	3.896(1)	$110 \pm 20$
S8	600 °C	3.896(1)	$85 \pm 20$
Ceramic C5	1080 °C	3.894(1)	500-1000

700 °C, 12 h for 750 °C, 6 h for 800 °C, and 3 h or less time for the higher temperatures (850, 900, and 950 °C). Above 950 °C the samples decompose. The  $Gd_2CuO_4$  phase is not unique at low temperatures, remaining rests of Gd<sub>2</sub>O<sub>3</sub> and CuO. The percentage of the correct phase is improved with higher calcination temperature, being 85%, 90%, and 92% for 600, 650, and 700 °C respectively. For calcination temperatures above 700 °C more than 95% is achieved. The presence of such oxides has been proved to have nonimportant effects on the measured properties. The Rietveld refinement of the spectra shows a slight increase of the lattice parameters (see Table I). A detailed description has been recently reported.<sup>20</sup> This fact must be specially stressed because of the influence of the a parameter on the magnetic properties of the  $R_2$ CuO<sub>4</sub> family. In our case the maximum a parameter observed, 3.896(1) Å, is relatively far from the value 3.910 Å quoted as the boundary for WF.8 In Table I it is shown the evolution of the average size for samples prepared via sol-gel techniques versus final calcination temperature, obtained by TEM. As can be seen the particle size increases with the annealing temperature. The data are in agreement with those obtained by PCS, which also shows that the size distribution is reasonably monodisperse. The polydispersity goes from  $85\pm20$  nm for 600 °C to  $350\pm40$ nm for 950 °C.

#### **III. RESULTS**

The ZFC and FC dc magnetization  $M_{dc}$  of the ceramic samples obtained at the two extreme temperatures 850 °C (C1) and 1080 °C (C5) is shown in Figs. 1(a) and 1(b) respectively. The FC data have been obtained while cooling down from 300 K to 4 K under an applied field  $H_a \approx 5$  Oe. The ZFC data were measured during heating with an applied field  $H_a \approx 5$  Oe, on samples cooled under a magnetic field smaller than 1 Oe. In these figures, two differences are seen:  $M_{dc}$  for C1 is smaller than that of C5 in an interval of ~70 K under  $T_N$ , although the points where a rapid increase of signal occurs remain the same, supporting a similar  $T_N$  for the Cu sublattice. The reversible character of  $M_{dc}$  for C1 extends over a large region of T below  $T_N$ . Instead, for C5, a strong dependence on the magnetothermal history is seen for almost all  $T < T_N$ .

The magnetization parallel to the CuO<sub>2</sub> planes at high



FIG. 1. dc magnetization versus temperature curves (FC and ZFC) for samples (a) C1 and (b) C5, under an applied field  $H_a \approx 5$  Oe.

fields in the case of single crystals of these weak ferromagnets can be reasonably well described by the expression<sup>5</sup>

$$M_{\rm dc}(T) = M_{\rm Cu}(T) + \frac{C_R}{T+\theta} [H_a + H_i^R(T)],$$
 (2)

with  $M_{Cu}$  being the net magnetization of the CuO<sub>2</sub> planes due to the canting of the Cu moments,  $C_R$  the Curie constant for the paramagnetic  $R^{3+}$  ion,  $\theta$  the Curie-Weiss temperature, and  $H_i$  an "internal field" that polarizes the rare-earth site, which results from the magnetic coupling to the ordered Cu lattice.<sup>21</sup> In the perpendicular direction, c axis, the only contribution to  $M_{dc}$  is due to the rare-earth ion paramagnetism. For a powder these effects are averaged, yielding an expression similar to (2). A departure from (2) is found at low field because of the magnetothermal dependence of the term

$$M_0(T) = M_{\rm Cu} + \frac{C_R}{T+\theta} H_i(T).$$
(3)

Due to the large effective moment of  $\text{Gd}^{3+}$  (7.94 $\mu_B$  for  $\text{Gd}^{3+}$ , in the absence of interactions, close to the measured at high fields in this material) and the small value of  $M_{\text{Cu}} \approx 3.5 \times 10^{-3} \mu_B/\text{mol}$ ,<sup>22</sup> this term can be neglected to obtain an estimate value of  $H_i$  from the high field linear part of M vs H curves, extrapolating to zero magnetization. That is shown in Fig. 2, where it is observed that the internal field is lower, in the vicinity of  $T_N$ , for C1. Its  $H_i$  value tends to reach that of C5 at low temperatures. Below the T at which FC and ZFC split,  $T_{\text{on}}$ , we observed hysteresis loops with coercive fields up to 15 Oe at 77 K. Besides,  $T_{\text{on}}$  decreases from 290 K for C5 and ~200 K for C1.



FIG. 2. Internal fields, obtained as described in the text, versus temperature for samples C1 and C5. The lines are guides for the eye.

In Fig. 3 hysteresis loops measured at 77 K for sample C1 after a ZFC and a FC under an applied field of 13 kOe are shown, the former beign displaced with respect to the latter by  $\approx 5$  Oe. The FC loop does not close for this T and field. As expected, the irreversibilities of  $M_{\rm dc}$  depend strongly on the magnitude of  $H_a$ .<sup>23</sup> In Fig. 4 we observe from VSM measurements that  $M_{\rm FC}$  and  $M_{\rm ZFC}$  separate at a  $T_{\rm on}$  near  $T_N$  for  $H_a \approx 0.5$  Oe for sample C5. Instead, for a field as low as 5 Oe the splitting occurs at a  $T_{\rm on}$  about 20 K lower than  $T_N$ .  $T_{\rm on}$  decreases monotonically with the calcination temperature of the sample. However,  $T_N$  remains the same within experimental error.

In Fig. 5 we show the real  $(\chi')$  and imaginary  $(\chi'')$  parts of the ac magnetic susceptibility for samples C1 and C5 with an ac field of amplitude  $(H_{ac})$  of 300 A/m and frequencies of 10 Hz and 1000 Hz.  $\chi'$  is the dispersive response of the system and may be associated with the ZFC susceptibility obtained via dc measurements. Two maxima in  $\chi'$  are observed. The first is at ~20 K for both samples. The second



FIG. 3. Hysteresis loops measured at 77 K for sample C1 under FC and ZFC conditions.



FIG. 4. dc magnetization versus temperature curve (FC and ZFC) for sample C5 at fields of 0.5 and 5 Oe.

maximum  $T_M$  is at 290 K and 210 K for samples C5 and C1, respectively. The maximum for sample C5 is frequency independent and is close to the Néel temperature of the Cu sublattice. Instead, the maximum of sample C1 is much broader, larger, and it is frequency dependent, as previously reported by us.<sup>18</sup>

The ac susceptibility for the larger particle size sol-gel sample, S1, is presented in Fig. 6. It resembles the  $\chi_{ac}$  of sample C1. The maximum at 20 K is double-peak structured (see inset), which is also observed in ceramic samples. It is



FIG. 5. ac magnetic susceptibility versus temperature for (a) the ceramic sample calcinated at the lowest temperature, sample C1, (b) the ceramic sample calcinated at the highest temperature, sample C5.



FIG. 6. ac magnetic susceptibility versus temperature for sample S1 (350 nm).

slightly frequency dependent when a dc field  $H_{dc}$  is superimposed. The second maximum  $T_M$  (also present in  $\chi''$ ), at temperatures between 200 and 210 K, is similar to those of sample C1. The superposition of  $H_{dc}$  results in a change in shape of both maxima, until they vanish for a value  $H_{dc} \approx 10$  Oe, as shown in Fig. 7, similar to what is also observed for sample C1. A field of the same order cancels FC and ZFC differences about 30 K below  $T_{on}$ .

For samples synthesized at lower temperatures, i.e., smaller particle size, significative changes in  $\chi_{ac}$  are observed. In Fig. 8(a) we present  $\chi'$  vs T for a sample synthesized at 800 °C (S4). In this case,  $T_M$  is less pronounced and it is displaced to lower T. It is quite frequency independent, as shown in Fig. 8(a). The addition of a dc field of 10 Oe depresses but does not eliminate the peak as shown in Fig. 8(b) and shifts it to lower T [Fig. 8(c)]. The onset for the FC and ZFC  $M_{dc}$  differences in this sample appears at  $\approx$  140 K for 5 Oe [Fig. 8(d)], very close to  $T_M$ . For smaller particles (sol-gel at 650 °C, S7),  $T_M$ , shifts to lower T and it is pos-



FIG. 7. Dependence of ac susceptibility under a superposed dc field  $H_{dc}$  for sample S1.

sibly hidden by the 20 K peak, which now is more field dependent (Fig. 9) than in the previous cases.

For the smaller particle size sample (S8), no presence of any peak, in both  $\chi'$  and  $\chi''$ , has been observed (Fig. 10). The data for this case can be fitted to a simple Curie-Weiss law with an effective moment of 7.6(4) $\mu_B$  and a Curie-Weiss temperature  $\theta_{Gd} = 17$  K. For this sample  $\chi'$  and  $\chi''$  are independent of frecuency, dc field, and no dependence on the magnetothermal history in  $M_{dc}$  has been observed.

## **IV. DISCUSSION**

The main goal of this work is to find the nature of the correlation between WF and the dynamic magnetic effects reported here. The features found here are not present for the  $R_2$ CuO<sub>4</sub> compounds where the Cu sublattice is perfectly AF arranged.<sup>8</sup> The origin of the irreversible behavior observed in the dc magnetization and ac susceptibility in some of the  $R_2$ CuO<sub>4</sub> is associated with the WF component.<sup>6,17</sup> That behavior has its origin in the O(1) distortion, resulting in the reduction of the tetragonal symmetry. Braden et al.24 reported recently a neutron-diffraction study on Gd<sub>2</sub>CuO<sub>4</sub> single crystals where it was claimed that the oxygen distortion forms a superstructure, which can be described by the Acam space group. In that case, the point bisecting the straight line between the interacting Cu ions is no longer an inversion center and a DM interaction is possible. The stabilization of such a superstructure is essential for the existence of a macroscopic WF.<sup>25</sup>

It is interesting to notice the differences found in the properties of Gd<sub>2</sub>CuO<sub>4</sub> when it is synthesized as a crystal or as a powder. In the first case the magnetothermal history is barely noticeable in the  $M_{dc}$  (Ref. 5) (for example, small differences between FC and ZFC loops), whereas in the ceramics it is easily observed as seen in Sec. III. Even more, the final annealing temperature affects the magnetic properties of the system. Sample C1 presents a characteristic that in principle could be thought to be in contradiction with the picture that states WF as the origin of irreversibilities in ac magnetization. Both the onset of the ZFC and FC,  $T_{on}$ , and  $T_M$  are at temperatures below  $T_N$ , unlike sample C5, which defines a certain independence of both onsets (as, in the reference sample C5,  $T_M$  is very close to  $T_N$ , it would have been the expected result). The precedent line does not mean the disconnection of magnetic irreversibilities and WF, as the former cannot exist unless the latter is present.

The analysis must be centered in the magnetism of the  $CuO_2$  planes. The WF moment in them, with  $M=S_1+S_2$  the ferromagnetic contribution of the copper lattice, represented by  $S_1$  and  $S_2$ , and  $L=S_1-S_2$  the AF vector, and provided that M, L, and D are mutually orthogonal, can be written as

$$\mathbf{M} \propto \frac{\mathbf{D} \times \mathbf{L}}{J}.$$
 (4)

The sign of  $\mathbf{M}$  is determined by the direction of the oxygen displacements through the sign of  $\mathbf{D}$ . The occurrence of macroscopic WF suggests a correlation of the oxygen distortions allowing a same  $\mathbf{D}$  vector. The annealing temperature varies the distances over which the oxygen distortion is coherent. We define coherence as the property that allows a distorted



FIG. 8.  $\chi'$  versus temperature for sample S4 (200 nm) (a) at frequencies of 33.3 and 1000 Hz with  $H_{dc}=0$ , (b) at 33.3 Hz and 1000 Hz under  $H_{dc}=800$  A/m, (c) at a frequency of 33.3 Hz and  $H_{dc}$  of 0 and 800 A/m, (d) dc magnetization under an applied field of 5 Oe.



FIG. 9.  $\chi'$  versus temperature for sample S7 (110 nm).

CuO<sub>2</sub> plane to give a unique direction for the WF component; i.e., this local coherence defines a given WF domaincluster size. In this way,  $T_{on}$  and  $T_M$  (note that  $T_{on} \sim T_M$ ) are associated with a blocking temperature  $T_B$  for that WF domain size. The bigger the size, the higher the blocking temperature, limited by  $T_N$ , similar to that of ultrafine magnetic particles,<sup>26</sup> where magnetothermal dependences arise after size reductions which define a  $T_B$  for a given magnetized volume. We must note that in a perfect Acam-space-groupdescribed Gd<sub>2</sub>CuO<sub>4</sub> single crystal these dependences on the thermal history should not be present, as there is an unique WF component. The FC and ZFC differences reported in Gd<sub>2</sub>CuO<sub>4</sub> single crystals have their origin in small deviations from a perfect coherent oxygen distorted structure. A similar behavior is found in ferromagnetic materials, when their grain size is reduced.<sup>27</sup> We will use this idea to develop a simple model to interpret our data. A blocking temperature  $T_B$  can then be estimated as  $T_B = KV/25k_B$ , where V is the volume of the domain and K the anisotropy constant.<sup>27</sup> The effect of this constant can be represented by an anisotropy field  $H_a = 2K/M_0$  ( $M_0$  the sublattice magnetization). If we



FIG. 10.  $\chi'$  and  $\chi''$  versus temperature for sample S8 (85 nm).

neglect the paramagnetic contribution due to the rare-earth ion and consider only the effects of the copper sublattice, we can estimate  $H_a$  as the field at which the paramagnetic part begins to be the dominant one and  $M_0$  as the magnetization for that field. From initial magnetization measurements on single crystals we have estimated values of about 50 Oe and 100 emu/mol for  $H_a$  and  $M_0$ , respectively. A value of  $K \approx 45$  erg/cm<sup>3</sup> is obtained. We note that this calculation cannot be applied for C5, as, for it,  $T_{on}$  is limited by the disorder of the Cu AF arrangement. Substituting this value on the equality for  $T_B$ , with  $T_B = 210$  K [Fig. 5(a)], results in a value of  $V = 1.57 \times 10^{-14}$  cm<sup>3</sup>. As Gd<sub>2</sub>CuO<sub>4</sub> crystallizes in the T' phase, with a = 3.894 Å, c = 11.882 Å, we assume a tetragon with those proportions. Thus, the hypothetical tetragonal domain has a square basis with a side length of 170 nm. That length give us an estimate of the extension of the WF domain associated with the canted Cu ions. We note this because the reduction of this length would have effects on  $T_{\rm on}$ , as we will see later.

The coercive fields found in Gd<sub>2</sub>CuO<sub>4</sub> appear at about the T where ZFC and FC differences appear. They are dependent on the magnetothermal history of the sample, indicating a different nature from the coercive fields of an usual ferromagnet, where such character appears only in systems of fine particles.<sup>26</sup> The displacement of the hysteresis loop seen in Fig. 3 suggests the existence of an unidirectional anisotropy in the form  $E \propto K \cos \theta$  (where  $\theta$  is the deviation angle of the WF component with respect to the external field and K an anisotropy constant). In this case it would be superposed to a typical sinusoidal-quadratic one, which creates symmetric hysteresis loops with coercive fields related to the values of the anysotropy constants of the material. The effect of such unidirectional anisotropy is an M versus H loop displaced from the origin in a value related to the anisotropy constant and with no hysteresis.<sup>23</sup> The existence of such an anisotropy can be related to the pseudovectorial character of the Dzialoshinskii-Moriya vector. This pseudovector is defined by the cross product (1), which marks not only a preferred direction in space, but also an orientation. The anisotropy created by such a term, where there is not a fixed **D**, is in the aforementioned form.<sup>23</sup>

The study of sol-gel particles helps to understand this problem. For S1, the particle is larger than the domain size and the response is similar to sample C1 because of a lowtemperature annealing which does not allow a whole stabilization of the oxygen superstructure in the whole grain; so the onsets of WF and irreversibilities are different. A superposed dc field causes the dissapearance of local energy minima in the system, avoiding therefore metastable states, with the subsequent reduction of FC and ZFC onset points and supression of the  $\chi'$  maximum, regarded as a marker for the blocking temperature. We suggest that reducing the size in the sol-gel samples decreases  $T_B$  only when the particle is of the order of the WF domain. For the biggest size samples  $T_B$  remains approximately constant, but for S4 it begins to be affected. The average size of S4 is 200 nm, quite close to the value of 170 nm we had previously calculated. This indicates that for this sample the grain and domain sizes are coincident and further reductions in the particle size will depress  $T_B$ , as happens. But another factor enters into the scene. As mentioned,  $T_M$  for S1 is frequency dependent, whereas in S4 the dependence is quite smaller. The change of frequency dependence indicates that in S1 the maximum does not correspond to a phase transition, but in S4 it could be, like for sample C5, where  $T_M$  is close to  $T_N$  and is frequency independent. We have searched for the reason in the limitation of the 2D spin correlation length by particle size. In lamellar CuO<sub>2</sub> insulating antiferromagnets these correlations develop progressively with decreasing temperatures within the layers and there is then a crossover to 3D behavior when the interplanar coupling between correlated regions becomes of the order of thermal energy, at a temperature defining  $T_N$ .<sup>28</sup> Although the theory modeling the magnetism in these compounds is not still complete, it seems reasonable to think that eventual reductions of the 2D spin correlation length at  $T_N$ would reduce it. Such effect could be induced by direct restriction of the CuO<sub>2</sub> planar dimensions. So, in our case, once a certain point is reached, the particle size could be smaller than the required 2D spin correlation length to maintain the bulk  $T_N$ , causing its depression. This picture is being confirmed indirectly through measurements of the onset of WF.<sup>29</sup> Provided that WF appears once the 3D Cu order does, the dissappearance of the former would be telling the same for the latter. By microwave absorption experiments we have seen that the resonant mode associated with WF does reduce its onset point with decreasing sizes.<sup>29</sup> In the case of the 800 °C-annealed sol-gel sample the apparent frequency independence of the  $\chi'$  maximum could be indicating a depressed Néel temperature located at the maximum. This extreme must be confirmed by further experiments.

#### **V. CONCLUSIONS**

We have studied the relationship between WF and the irreversible magnetic properties in Gd<sub>2</sub>CuO<sub>4</sub> in ceramic samples prepared at different annealing temperatures and we have compared them with those of sol-gel particles of different sizes. A variation of a high-temperature maximum in the real part of ac magnetic susceptibility,  $T_M$ , related to the onset of irreversibilities on dc magnetization at a temperature  $T_{\rm on}$ , has been observed. Such irreversibilities consist of large differences between FC and ZFC dc magnetization curves as well as the presence of measurable coercive fields in M vs Hloops. These loops are not symmetric when measured under a FC starting above the 3D Néel temperature for the copper moments, which is interpreted as the presence of uniaxial anisotropies due to DM interactions with a nonunique D vector. Size reduction by sol-gel methods gives rise to a reduction of  $T_M$  as well as the elimination of it. In the case of ceramic samples annealed at low temperature, a noncoherent distortion of the O(1) oxygen in the grains but only in small parts of them is proposed. These local uniformly distorted parts of the CuO<sub>2</sub> planes are associated with the formation of WF domains or clusters. The sol-gel method does not affect the  $T_{\rm on}$  when the particle size is larger than the domain size. Instead, it does when the particle is smaller than the domain size. The depression of the Néel temperature of the Cu moments via reduction of 2D spin correlation lengths of the Cu sublattice order could be involved in the depression of  $T_{on}$ once reached a given size, smaller than the WF domain one.

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