# Magnetic susceptibility studies in Gd<sub>2</sub>CuO<sub>4</sub> below 300 K

J. Mira, J. Castro, J. Rivas, D. Baldomir, C. Vázquez-Vázquez, J. Mahía, and A. López-Quintela Universidad de Santiago de Compostela, E-15706, Spain

D. Fiorani ICMAT-CNR, Roma, Italy

R. Caciuffo and D. Rinaldi Universita di Ancona, 60131 Ancona, Italy

T. Jones NR&D, San Diego, California

S. B. Oseroff San Diego State University, San Diego, California 92182

Measurements of the real  $(\chi')$  part of the ac magnetic susceptibility have been performed on two polycrystalline Gd<sub>2</sub>CuO<sub>4</sub> samples sintered at different temperatures, 850 °C and 1080 °C in the temperature range 10 < T(K) < 300. Two well-defined maxima have been observed in the temperature dependence of  $\chi'$ . One, located at about 20 K, that is frequency independent. The second is at about 280 K for the sample annealed at 1080 °C, and it is frequency independent. Instead, for the sample annealed at 850 °C the maximum appears at about 210 K, and it is frequency dependent. These results suggest the existence of magnetic domains, with their coherence lengths being a function of the thermal treatment.

## I. INTRODUCTION

Rare earth cuprates R<sub>2</sub>CuO<sub>4</sub> are characterized by the presence of long-range-order antiferromagnetism (AF) associated with the ordering of the magnetic moments of the Cu<sup>+2</sup> ions. This AF ordering presents a three-dimensional/ two-dimensional (3D/2D) transition at a temperature  $(T_N)$ between 250-280 K. The study of the magnetic properties of these compounds has initially led to their classification into two groups:<sup>1</sup> the first one with R=Pr, Nd, Sm, Eu, and the second with R=Gd and heavier rare earths. Both groups crystallize in the tetragonal T' structure, but, in the second group, a distortion of the oxygen in the CuO<sub>2</sub> planes in a direction perpendicular to the Cu-O-Cu bond<sup>2,3</sup> leads to an antisymmetric superexchange interaction that generates a weak ferromagnetic behavior.<sup>4,5</sup> Whereas for the former group superconductivity (SC) is achieved with Th or Ce doping,<sup>6</sup> for the latter superconductivity has not been observed.<sup>7</sup> The exclusion of weak ferromagnetism (WF) and SC has been recognized by several authors.<sup>1</sup>

A subdivision in the second group, revealing differences between  $Gd_2CuO_4$  and the  $R_2CuO_4$  (R=Tb, Dy, Ho, Er, and Tm) obtained at high pressure<sup>8</sup> (PO) has been suggested.<sup>9</sup> A difference is encountered in the temperature dependence of the ac magnetic susceptibility,<sup>9</sup> where  $Gd_2CuO_4$  presents a double peak structure in the real part of the susceptibility at low temperatures, from  $T \approx 1-20$  K; while for the PO compounds only one peak, associated to the ordering of the R ions, appears in that range. The explanation of this difference has been sought in comparison between the R–R and R–Cu sublattice interactions. Differences have also been reported in the dynamic behavior of these compounds.<sup>10</sup> The mechanism leading to the observed dynamical behavior remains unclear, although spin-glass-like effects have been claimed.<sup>10</sup> The aim of the present work is to perform a detailed study of the ac magnetic susceptibility of polycrystalline  $Gd_2CuO_4$  in the temperature range 10 < T(K) < 300. A comparison with ac magnetic susceptibility measurements of other weak ferromagnets of the  $R_2CuO_4$  series is also presented.

#### **II. EXPERIMENTAL TECHNIQUES**

 $Gd_2O_3$  and CuO oxides were used as starting materials for the ceramic synthesis of  $Gd_2CuO_4$ . Two methods were used to obtain the samples: (a) Stoichiometric amounts of the starting materials were milled for several hours and thermal treatments at 850 °C, with frequent intermediate millings were subsequently carried out. Around 400 h were required in order to obtain the pure  $Gd_2CuO_4$  phase. We call this sample, sample I. (b) In the second method, the starting materials were sintered at 950 °C for 12 h. The product was milled again and resintered at 1000 °C for 20 h. Finally, it was sintered at 1080 °C for 24 h and slow cooled. The sample thus obtained is called sample II.

The structural characterization of the samples was performed by means of x-ray diffraction using a Philips PW-1710 diffractometer with Cu anode (Cu $K_{\alpha 1}$  radiation,  $\lambda = 1.540$  60 A). The x-ray patterns showed a single phase with the same tetragonal structure for both samples. The analytic characterization was derived using inductively coupled plasma atomic emission spectroscopy (ICP-AES) with Ar plasma ICP (Perkin-Elmer 5000). The dc magnetic measurements were performed using a SQUID magnetometer (Quantum Design) in the 4 < T(K) < 300 temperature range. The real and imaginary parts  $\chi'$  and  $\chi''$ , of the external complex ac susceptibility were measured during warming from T=13-300 K using a system with a concentric assembly consisting of a primary solenoid and two oppositely wound



FIG. 1. FC and ZFC dc magnetization of the  $Gd_2CuO_4$  sample I vs temperature, measured with an applied field of  $H_{appl}$ =400 A/m. The inset shows the dc magnetization for sample II.

sensing coils connected in series. A phase-sensitive detector is used to measure the output voltage that is proportional to the sample susceptibility. High sensitivity is obtained by moving the sample between the two sensing coils with high precision. The calibration was performed using a Gd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. 8H<sub>2</sub>O 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. For each run of measurements, the ac field was applied with a fixed amplitude of  $H_{ac}$ =300 A/m and fixed frequencies f, ranging from 5 to 1000 Hz. A dc field,  $H_{dc}$  from 0 to 800 A/m, 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.

#### **III. EXPERIMENTAL RESULTS**

In Fig. 1, we display dc magnetization measurements for both Gd<sub>2</sub>CuO<sub>4</sub> samples when they were (a) zero field cooled (ZFC) from 300 to 4 K ( $H_{cool}$ <80 A/m), and subsequently measured at increasing temperatures with an applied field,  $H_{appl}$ =400 A/m; and (b) field cooled (FC), i.e., measured at an applied field while cooling down from 300 K at  $H_{cool}$ = $H_{appl}$ =400 A/m. The difference between the ZFC and FC curves indicates the onset of irreversibility for this field at a temperature  $T_{irr}$ ≈210 K for sample I and  $T_{irr}$ ≈280 K for sample II.

In Fig. 2, we show the temperature dependence of  $\chi'$  at two different frequencies. We observe for both samples, two well-defined peaks. For sample I, one peak is centered at  $\approx 210 \text{ K} (T_{M1})$  and the other at  $\approx 20 \text{ K} (T_{M2})$ . The high temperature peak is frequency dependent (it shifts to a higher temperature with an increasing frequency, as shown in Fig. 3). Instead, the low temperature peak is frequency independent. For sample II, the position and behavior of  $T_{M2}$  is similar to sample I. But  $T_{M1}$  is found at  $\approx 280 \text{ K}$ , and it is frequency independent.

Figure 4 shows the temperature dependence of  $\chi'$  for sample I measured at the same ac field  $(H_{ac})$  for different



FIG. 2. The real part of the ac susceptibility,  $\chi'$  of sample I, measured at frequencies of 10 and 1000 Hz in an ac magnetic field of  $H_{\rm ac}$ =300 A/m. The inset shows the curve for sample II in the high temperature range.

superposed dc fields  $(H_{dc})$ . We observe that the amplitude of the 210 K maximum decreases with increasing field and disappears for a dc field of about  $H_{dc}$ =800 A/m. The maximum onset temperature (~280 K) and the position of the maximum remains constant. For the 20 K peak, the dependence on the dc field is much weaker. It shifts slightly toward lower temperatures and decreases in amplitude with increasing field.

## **IV. DISCUSSION**

The existence of WF in the R<sub>2</sub>CuO<sub>4</sub> series is accompanied by the presence of irreversibility effects.<sup>10,11</sup> Differences are observed in the irreversible behavior of Gd<sub>2</sub>CuO<sub>4</sub>, depending on the thermal treatment. For the sample annealed at high temperature, sample II, the irreversibility appears at a temperature of the order of the AF 3D/2D ordering of the Cu<sup>+2</sup> ions,  $T_N \approx 270$  K. Instead, for the sample annealed at a low temperature, sample I,  $T_{irr}$  and the temperature of the maxima of the real and imaginary parts of the susceptibility



FIG. 3. Frequency dependence of the high temperature peak  $T_{M1}$  for sample I.



FIG. 4. Temperature dependence of  $\chi'$  of sample I measured at the same ac magnetic field ( $H_{ac}$ =300 A/m) for different superposed dc fields ( $H_{dc}$ ).

are located at  $T \approx 210$  K, which is much lower than  $T_N$ . Another difference is that for sample I the position of the high temperature  $\chi'$  maximum is frequency dependent. This dependence is not observed for sample II, as in the case of other weak ferromagnetic compounds treated at high temperature.<sup>1</sup>

The low temperature peak observed for both samples may be interpreted as due to a phase transition. Below this temperature, both the WF and the dynamic effects disappear, as seen in Fig. 5. This figure shows several isotherms of  $\chi'$ versus the frequency. As we decrease the temperature below 20 K, the isotherms become frequency independent. The ori-



FIG. 5.  $\chi'$  vs frequency at selected temperatures.

gin of this transition has been associated to the competition between the Gd–Gd and Gd–Cu interactions.<sup>3</sup>

To analyze the frequency dependence of the high temperature maximum, we have plotted the data in an Arrhenius law form (Fig. 3). In the examined temperature range the relationship is linear. We have found that the Arrhenius law, predicted for independent fine particles or isolated clusters does not describe the observed dynamic properties, as a nonphysical value was obtained for the pre-exponential factor  $\tau_0$ ( $\tau_0 \approx 10^{-50}$  s). The observed frequency dependence could be associated to the existence of different magnetic domains (or large clusters). The domain size should be related to the coherence length of the oxygen distortion. This coherence length seems to be strongly dependent on the thermal treatment.

Finally, we discuss the effect of the superposition of a dc field on the ac measurements. The broadening of the 210 K maximum, and the decrease of its amplitude with increasing  $H_{\rm dc}$  shows the effect of the field on the resulting WF and on the dynamical behavior of the magnetic domains. The small shift of the 20 K maximum to lower temperatures with the superposition of a dc field is consistent with the H–T phase diagram for Gd<sub>2</sub>CuO<sub>4</sub> presented in Ref. 3.

### ACKNOWLEDGMENTS

We wish to acknowledge financial support from the DGICYT, PB92-1086; Fundación Ramón Areces; NSF-DMR-01172122, and NATO, CRG920255. J. M. and C. V. also thank the Fundacion Segundo Gil Dávila and Xunta de Galicia for its financial support.

- <sup>1</sup>S. B. Oseroff, D. Rao, F. Wright, D. C. Vier, S. Schultz, J. D. Thompson, Z. Fisk, S.-W. Cheong, M. F. Hundley, and M. Tovar, Phys. Rev. B **41**, 1934 (1990).
- <sup>2</sup>T. Adelmann, R. Ahrens, G. Czjzek, G. Roth, H. Schmidt, and C. Steinleitner, Phys. Rev. B 46, 3619 (1992).
- <sup>3</sup>A. A. Stepanov, P. Wyder, T. Chattopadhyay, P. J. Brown, G. Filion, I. M. Vitebsky, A. Deville, G. Gaillard, S. N. Barilo, and D. I. Zhigunov, Phys. Rev. B 48, 12 979 (1993).
- <sup>4</sup>I. Dyzaloshinskii, J. Phys. Chem. Phys. Solids 4, 241 (1958).
- <sup>5</sup>T. Moriya, Phys. Rev. 120, 91 (1960).
- <sup>6</sup>Y. Tokura, H. Takagi, and S. Uchida, Nature **337**, 345 (1989); J. T. Markert, E. A. Early, T. Bjornholm, S. Ghamaty, B. W. Lee, J. J. Nuemeier, R.
- D. Price, C. L. Seaman, and M. B. Maple, Physica C 158, 178 (1989).
- <sup>7</sup>E. Moran, A. I. Nazzal, T. C. Huang, and J. B. Torrance, Physica C 160, 30 (1989).
- <sup>8</sup>P. Bordet, J. J. Capponi, C. Chaillout, D. Chateigner, J. Chenavas, T. Fournier, J. L. Hodeau, M. Marezio, M. Perroux, G. Thomas, and A. Varela, Physica C 185, 539 (1991).
- <sup>9</sup>X. Obradors, P. Visani, M. A. De la Torre, M. B. Maple, M. Tovar, F. Pérez, P. Bordet, J. Chenavas, and D. Chateigner, Physica C 213, 81 (1993).
- <sup>10</sup> M. Tovar, X. Obradors, F. Prez, S. B. Oseroff, R. J. Duro, J. Rivas, D. Chateigner, P. Bordet, and J. Chenevas, Phys. Rev. B 45, 4729 (1992).
- <sup>11</sup> J. Mira, J. Castro, J. Mahía, C. Vázquez-Vázquez, M. A. López-Quintela, J. Rivas, and S. B. Oseroff, J. Non-Cryst. Solids (in press).

[This anticle is copyrighted as indicated in the anticle. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to ]