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# Thermal treatment dependence of the dynamic magnetic behavior of $Gd_2CuO_4$

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dc and ac magnetization measurements in $Gd_2CuO_4$ ceramic samples synthesized at different annealing temperatures show that their magnetic properties are influenced by the thermal treatment. The changes consist of variations of the onset point for differences between zero field cooled and field cooled dc magnetizations, in the coercive fields, and in the position and frequency dependence of a maximum in the real part of ac susceptibility. An explanation suggesting a temperature-dependent homogeneity of the oxygen distortions causing weak ferromagnetism in the $CuO_2$ planes is given. © *1996 American Institute of Physics.* [S0021-8979(96)08215-1]

## I. INTRODUCTION

The interest on the properties of the rare earth cuprates $RE_2CuO_4$ (RE=rare earth) has been high since the discovery of the superconductors $R_{2-x}(Th,Ce)_xCuO_4$ (R=Pr, Nd, Sm, Eu).[1] They all are characterized by the presence of $CuO_2$ planes with long range ordering of the magnetic moments of the $Cu^{+2}$ ions.[2] The AF ordering shows a three-/two-dimensional transition at a Néel temperature, $T_N$, between 260 and 290 K.[3] All of them, but $La_2CuO_4$, crystallize in the tetragonal $T'$ phase.[4] For R=Gd and heavier rare earths, a distortion of the oxygen atoms in the $CuO_2$ planes, O(1), takes place in a direction perpendicular to the Cu–O(1)–Cu bond.[5] This leads to an antisymmetric exchange interaction which generates a weak ferromagnetic behavior (WF).[6] The fact that the usual electron doping with Th or Ce does not lead to superconductivity in the WF cuprates has been recognized by several authors.[7,8]

The presence of WF makes the magnetic behavior of these compounds very complex. Among other features, the presence of large differences between field cooled (FC) and zero field cooled (ZFC) dc magnetizations has been reported in ceramic samples of $Gd_2CuO_4$,[9] as well as, in the high pressure obtained $R_2CuO_4$ (for Tb and heavier rare earths).[10]

In a previous work,[11] we found differences in the dynamic behavior of two ceramic $Gd_2CuO_4$ samples, depending on the final annealing temperature at which they were synthesized. The changes consist of variations of the temperature of splitting between FC and ZFC curves, equal to $T_N$ in the sample annealed at the highest temperature. Our aim in this work is to go deeper in the cause leading to the changes in their magnetic properties. For this purpose, we have synthesized five ceramic samples at different annealing temperatures, $T_{an}$, and observed their dc and ac magnetic behavior. This serves in the search for the origin of magnetic irreversibilities in these WF cuprates.

## II. EXPERIMENTAL DETAILS

The samples were synthesized by conventional solid state reaction, using $Gd_2O_3$ and CuO oxides as starting materials, at several temperatures. Stoichiometric amounts of the oxides were ground for several hours and, for sample C1, thermally treated at 850 °C with frequent intermediate grindings. Around 400 h were required to obtain the pure phase. Other ceramic samples, C2, C3, C4, and C5, were prepared, in several steps with intermediate grindings, at different synthesis temperatures, 950, 1000, 1040, and 1080 °C, respectively.

The polycrystalline powders were characterized analytically by inductively 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 (Cu $K\alpha$ radiation of $\lambda=1.541\,86$ Å). X-ray diffraction measurements were performed at room temperature, showing the characteristic pattern of the $T'$ phase.[4] The dc magnetic measurements were carried out using a Quantum Design SQUID and a Digital Measurement Systems-1660 vibrating sample magnetometer in the temperature range $4<T<300$ K. The real and imaginary part components $\chi'$ and $\chi''$ of the external complex ac susceptibility were measured as functions of temperature using a mutual inductance technique described elsewhere.[11] The

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calibration was performed using a $Gd_2(SO_4)_3 \cdot 8H_2O$ 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 to 300 K, after zero field cooling of the sample. For each run of measurements, the ac field was applied with a fixed amplitude of $H_{ac}=300$ A/m (3.75 Oe) at fixed frequencies $f$, ranging from 5 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.

## III. EXPERIMENTAL RESULTS

In Fig. 1, we show dc magnetization, $M_{dc}$, measurements for all the samples. They were first zero-field cooled from 300 to 77 K and subsequently measured at increasing temperatures with an applied field $H_a=0.5$ Oe. After that, they were field cooled under the same $H_a$ from a temperature above $T_N$ (marked by an abrupt change in $M_{dc}$ due to the presence of WF),[7] measuring while cooling. It is clear from the difference between FC and ZFC that the temperature at which they split, $T_B$, changes from sample to sample, being equal to $T_N$ for C5 and decreasing monotonically with a decreasing $T_{an}$. In Fig. 2, we show hysteresis loops for samples C1 and C5 framed in $M_{dc}$ vs $T$ curves at $H_a=5$ Oe. In the case of sample C1, three regimes are seen: (a) WF with magnetic irreversibilities, where measurable coercive fields, $H_c$, are present, (b) WF without magnetic irreversibilities, where hysteresis loops show the typical rare earth WF polarization,[8] and (c) paramagnetic state, once $T_N$ is passed. For C5 only, cases (a) and (c) are present. In Fig. 3, the evolution of $H_c$ for samples C1 and C5 is shown and the above mentioned differences are more clearly seen.

Ac magnetization vs temperature measurements in this compound show several WF signatures, specially one peak in the real part of the complex susceptibility at high temperatures, which we will call $T_M$, associated with the beginning of magnetic irreversibilities. This peak is located at $T_N$ and is independent of the frequency of the ac field, $H_{ac}$ for sample C5, the same as for single crystals.[7] For the other samples, $T_M$ is at lower temperatures than $T_N$, similar to $T_B$ in dc magnetization. The peak amplitude becomes larger as $T_{an}$ decreases and it is frequency dependent. This dependence is also enhanced for lower $T_{an}$. We have represented the dependence in the form of an Arrhenius plot for all the samples in Fig. 4.

## IV. DISCUSSION

We have already stated that the dynamic phenomena studied here only happen for the WF $R_2CuO_4$. Although, we have seen that in the case of all the samples, except C5, WF can coexist with the absence of magnetic irreversibilities. The effect of the magnitude of the applied field does not seem to be the cause of the elimination of metastabilities, although these metastabilities are very sensitive to small fields (note for sample C5 in Fig. 2 that, at 5 Oe, FC, and ZFC split at a temperature 20 K lower than at 0.5 Oe). We

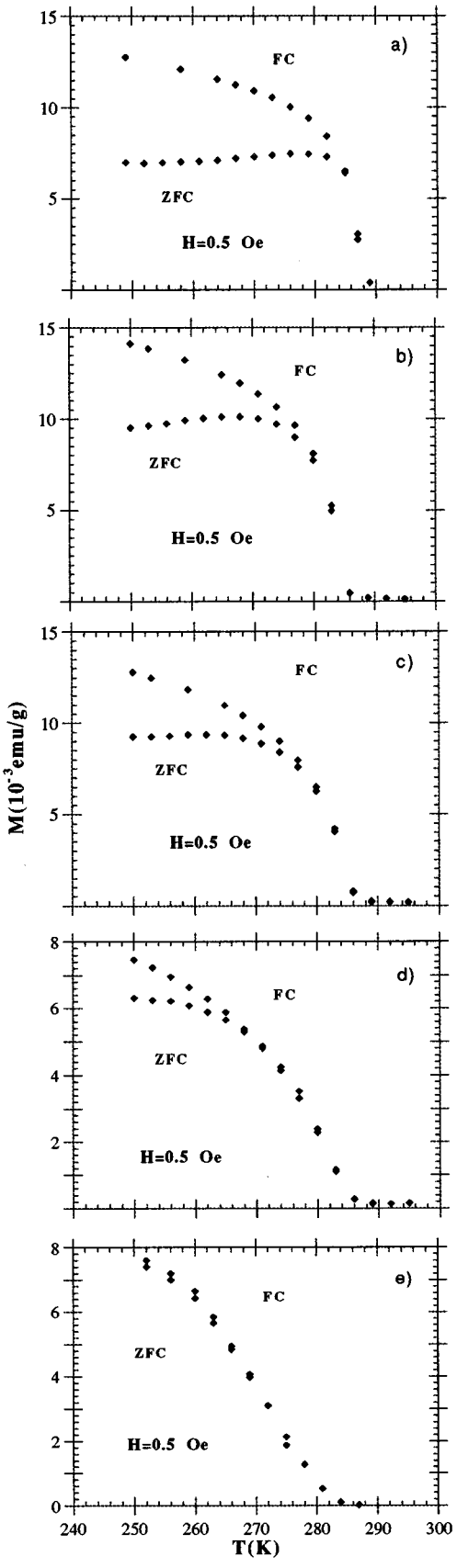


FIG. 1. $M_{dc}$ vs $T$ at $H_a=0.5$ Oe for $Gd_2CuO_4$ annealed at (a) 1080 °C (C5), (b) 1040 °C (C4), (c) 1000 °C (C3), (d) 950 °C (C2), and (e) 850 °C (C1).

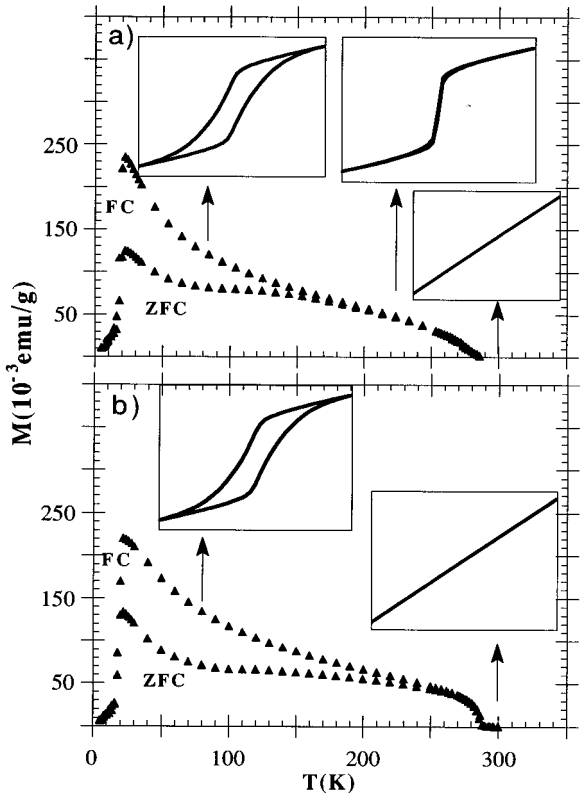


FIG. 2. $M_{dc}$ vs $T$ at $H_a = 5$ Oe for samples (a) C1 and (b) C5, showing hysteresis loops in several regimes. The hysteresis loops were measured between $\pm 100$ Oe.

had previously pointed out the possibility of the existence of domains or large clusters[11] to explain the variations of the dynamic behavior. If we consider $T_B$ as a blocking temperature of these domains, their size should increase with increasing $T_{an}$, to explain the increase of $T_B$. By neutron diffraction studies,[12] it has been observed that the oxygen distortion forms a superstructure described by the Acam space group. In our hypothesis, an increasing $T_{an}$ would cause a larger homogenization of the oxygen distortion tending to an unique superstructure. Such homogeneously-distorted regions would mark an unique direction for the local WF component, leading to the aforementioned domains or clusters. This situation would cause a similar behavior to that of fine

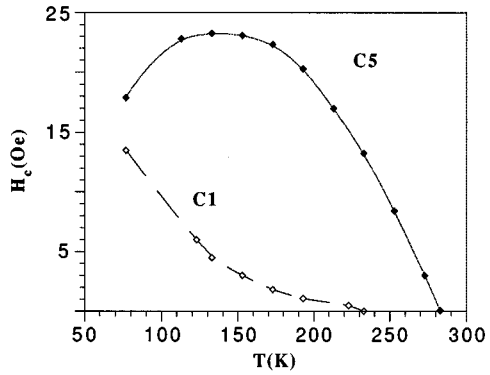


FIG. 3. $H_c$ vs $T$ for samples C1 and C5 for applied fields of $\pm 100$ Oe.

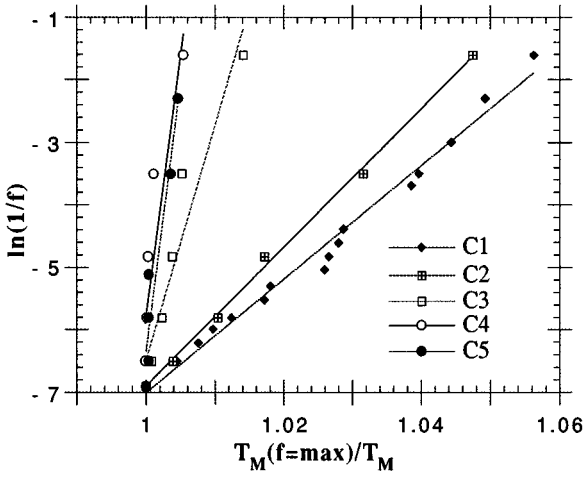


FIG. 4. Frequency dependence of $T_M$, in an Arrhenius plot form, for all the $Gd_2CuO_4$ samples.

ferromagnetic particles,[13] with measurable coercive fields under a given blocking temperature. The fact of the growth of the WF clusters with $T_{an}$ is suggested by the data reported in Fig. 4. There, the dependence of $T_M$ is plotted in an Arrhenius law form. Although the observed pre-exponential values are nonphysical, indicating the nonindependent character of the clusters (an Arrhenius law is expected for isolated superparamagnetic particles), we can deduce that their activation energy (proportional to the slope) increases for increasing $T_{an}$. Assuming a certain proportionality of these activation energies with the WF domain or cluster volume, we conclude that they do actually grow with $T_{an}$.

## V. CONCLUSIONS

Dc and ac magnetic susceptibility measurements give evidence of effects of the thermal treatment on the magnetic behavior of $Gd_2CuO_4$ ceramic samples. It is proposed that, with increasing the synthesis temperature, the extension of WF domains in the $CuO_2$ planes increases, due to the enlargement of the regions in which the O(1) distortions allow a unique WF component. This is supported by a higher irreversibility temperature in dc curves and by a lower frequency dependence of the temperature at which the associated maximum in ac curves is located, when increasing the synthesis temperature.

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