Weak ferromagnetic resonance of Gd_2CuO_4 small particles[a)]

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(Received 4 December 1995; accepted for publication 21 February 1996)

Microwave-absorption measurements have been performed in Gd_2CuO_4 particles of controlled size. We have measured the microwave absorption associated with a magnetic resonance of the weak-ferromagnetic component of the magnetization. The onset temperature of this signal, related to the appearance of weak ferromagnetism, is depressed when the particle size is decreased. A simultaneous depression of the Néel temperature is suggested as the origin of the observed dependence, due to the limitation on the two-dimensional correlation length imposed by the particle size. © *1996 American Institute of Physics.* [S0021-8979(96)00211-2]

I. INTRODUCTION

The presence of CuO_2 planes is a constant in almost all the high-T_c superconductors. The compounds RE_2CuO_4 (RE=rare earth), which crystallize in the tetragonal T' phase,[1] are the basis of the n-type superconductors $RE_{2-x}(Th,Ce)_xCuO_4$ (RE=Nd, Pr, Sm, Eu).[2] The Cu^{2+} moments are antiferromagnetically (AF) coupled with an in-plane exchange constant[3] $J \approx 1500$ K. At high temperatures strong two-dimensional AF correlations are present.[4] When the temperature is lowered a crossover to a 3D AF order takes place[5] at $T_N \approx 260-290$ K. For Gd and heavier rare earths the small RE^{3+} size leads to a distortion of the square array of oxygen ions in the CuO_2 planes, with a displacement of the O(1) in a direction perpendicular to the Cu–O(1)—Cu bond.[6] This allows an antisymmetric exchange interaction between the Cu moments leading to weak ferromagnetism (WF).[7,8]

The presence of WF in the distorted cuprates causes the appearance of a low field absorption line in the microwave spectrum that has been identified as a low-energy WF resonance mode.[9] This signal has been extensively used to study the WF behavior of the cuprates. In this work we present a magnetic resonance study in small particles of Gd_2CuO_4 in order to analyze how the changes in particle size affect weak ferromagnetism.

II. EXPERIMENTAL DETAILS

The samples were synthesized by a sol-gel method described elsewhere[10] in order to control particle size. They were characterized by gravimetric pyrolisis. X-ray diffraction showed the presence of small amounts of unreacted Gd_2O_3 and CuO for the smaller particle sizes. A Rietveld refinement of the spectra indicated a slight increase of the lattice parameters[11] when the particle size decreases. In Table I the a lattice parameter is shown. The sizes were characterized by photon correlation spectroscopy and transmission electron microscopy with the results given in Table I. A ceramic sample, used as a reference, was also synthesized by a conventional solid-state reaction at 1080 °C.

The magnetic resonance experiments were performed in L, X, and Q bands, corresponding to frequencies of 1.17, 9.5, and 35 GHz, respectively, in a Bruker ESP 300 spectrometer between 100 and 330 K for X band, and between 150 and 310 K for L and Q bands.

III. RESULTS

In Fig. 1(a) we show a typical X-band microwave spectrum for the ceramic sample below $T_N \sim 288$ K. The low field absorption (LFA) corresponds to the narrow WF resonance.[7] The other signal, very broad, centered at a resonance field $H_r \sim 3300$ Oe, corresponds to the paramagnetic (PM) resonance of the Gd^{3+} ions.[7] This signal shows a displacement δH_r from $g=2$ because of the dynamical coupling of the PM Gd sublattice with the WF component in the CuO_2 planes.[12] These two effects have been taken as the signatures of WF. The LFA decreases abruptly as the temperature approaches T_N and disappears at $T=295$ K. The shift of the Gd^{3+} resonance field also decreases, although it does not disappear at the same temperature as the LFA, being observed up to about 330 K. The LFA resonance field H_r^L varies from 300 Oe at 100 K to a minimum of 40 Oe at 285 K, increasing again up to 170 Oe at 295 K. In L band the LFA is at about 10 Oe and can be observed only up to 288 K. In Q band the LFA is observed at $H_r^L \approx 300$ Oe and was found up to ≈ 310 K.

In Fig. 1(b), an X-band spectrum for the largest size sol-gel sample, S1, measured at $T=280$ K is shown. The behavior is similar to that of the ceramic one. The onset

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 0021-8979/96/79(11)/8612/3/$10.00

TABLE I. Percentage of right-hand phase from x rays, a lattice parameter, and average size of the synthesized sol-gel samples.

Samples	%Gd_2CuO_4	a (Å)	Average size (Å)
Ceramic	>95	3.894(1)	5000–10000
Sol gel:			
S1	>95	3.894(1)	3500±600
S2	>95	3.894(1)	2800±500
S3	>95	3.894(1)	2700±400
S4	>95	3.895(1)	2000±300
S5	95	3.895(1)	1600±300
S6	92	3.896(1)	1300±200
S7	90	3.896(1)	1100±200
S8	85	3.896(1)	850±200

temperature for the LFA, $T_{on} \approx 295$ K does not change, and the shift of the Gd^{3+} resonance is similarly temperature dependent; however, the intensity of the LFA is smaller. When going to smaller particle sizes T_{on} begins to decrease, as we can see in Figs. 1(c) and 1(d), which show the X-band spectra for samples S3 and S4 at the same temperature. For S4 T_{on} is 267 K.

As in the case of the ceramic sample there are small variations when the microwave frequency is changed. We have found that for the L band $T_{on} \approx 260$ K, with a resonance field $H_r^L \approx 10$ Oe, while for Q band $T_{on} \approx 280$ K with $H_r^L \approx 400$ Oe.

The Gd shift is also affected by the particle size. For instance, at 200 K δH_r decreases with decreasing size: from $\delta H_r \approx 230$ Oe for S1 to $\delta H_r \approx 100$ Oe for S7. For the smallest particle size (S8) we did not observe any WF signatures. In Fig. 2 we present the intensity of the LFA, normalized to the Gd^{3+} electron-paramagnetic-resonance line, as a function

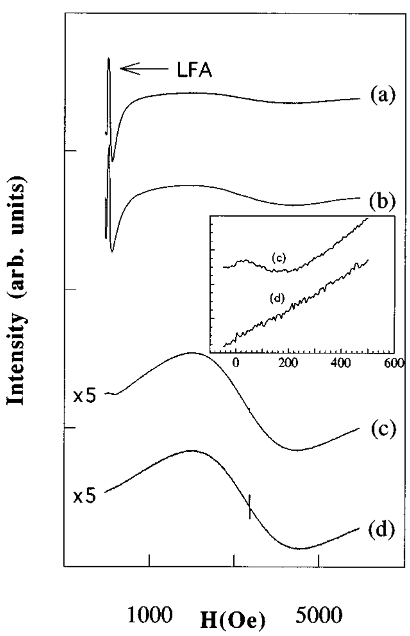

FIG. 1. Gd_2CuO_4 X-band microwave spectra measured at $T = 280$ K for (a) ceramic sample, (b) sol-gel S1 sample, (c) sol-gel S3 sample, (d) sol-gel S4 sample. The inset shows the detail of the LFA zone for samples S3 and S4.

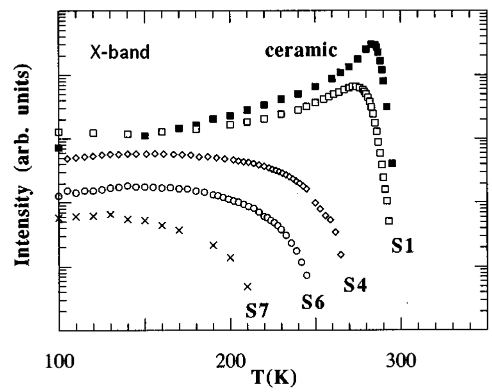

FIG. 2. Intensity of the LFA line vs temperature for the ceramic and several sol-gel samples, normalized to the intensity of the PM Gd^{3+} line.

of temperature, for different particle sizes. The depression of T_{on} can be clearly seen.

IV. DISCUSSION

Using the simple image that a WF is a canted AF structure, we have that when LFA is present, AF ordering exists. We have seen that the temperature for the onset of the LFA, T_{on}, is larger than T_N and varies with the frequency used in the experiment, although we would expect that T_{on} be coincident with T_N. A similar behavior is observed for the displacement of the Gd^{3+} resonance line. This fact has already been interpreted in terms of the induction of WF above T_N due to the external applied magnetic field.[13] When the microwave frequency is increased the field required for resonance increases as well, so the effect of WF induction is enhanced and the LFA and the shift of the Gd^{3+} line are detected up to higher temperatures.

We have found that when the grain size becomes smaller than ≈2500 Å, T_{on} is depressed with respect to the ceramic sample used as a reference, and for sizes lower than 1000 Å no evidence of WF was observed. We may try to explain this effect through the increase of the a lattice parameter, which defines the degree of the structural distortion that produces WF; however, the variations for a are very small (less than 0.1%) and the values measured, even for S8, are far away from the boundary for WF ($a = 3.910$ Å as determined in Refs. 6 and 7). A different approach is to consider the size effects on the AF transition. The two-dimensional (2D) correlation length may be limited by the particle size, thus affecting the crossover to a 3D AF behavior[14] and giving rise to a simultaneous decrease of T_N and T_{on}.

ACKNOWLEDGMENTS

We wish to acknowledge finantial support from the DGICYT, PB93-0540; Fundación Ramón Areces; NSF-DMR-91172122; and NATO, CRG920255. J.M. and C.V. also thank Fundacion Segundo Gil Dávila and Xunta de Galicia for its financial support.

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