Weak ferromagnetism and spin-glass-like behavior in Tb_2CuO_4

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Polycrystalline Tb_2CuO_4 with tetragonal (T') structure was synthesized under high pressure. The in-phase component of the alternating-current (ac) susceptibility $\chi'(T)$ presents a peak whose onset at $T_N \approx 290$ K, we associate with antiferromagnetic ordering of the Cu moments. The shape of this peak is strongly dependent on the amplitude of the excitation field, indicating nonlinearity of the magnetization as a function of the applied magnetic field. The frequency dependence of the peak observed in $\chi'(T)$ and the nonzero out-of-phase component $\chi''(T)$ in the same temperature range indicate the existence of relaxation processes associated with the development of a weak ferromagnetic component. Below ~ 100 K, the relaxation becomes much slower than the frequency of the oscillating field and the ac susceptibility is dominated by the paramagnetic response of Tb ions, which follows a Curie–Weiss law. The direct-current (dc) magnetization presents a nonlinear dependence on the applied field for $H_a \lesssim 2$ kOe and shows thermomagnetic irreversibility below a second characteristic temperature $T_{irr} < T_N$. An additional peak at $T_L \approx 10$ K indicates a long range magnetic order of the Tb ions with a possible spin reorientation of the Cu moments. The thermal irreversibility and nonlinearity of the dc magnetization below T_{irr}, the relaxation processes revealed by the ac susceptibility, and the typical logarithmic decay of the remanent magnetization, point to the existence in this material of a weak ferromagnetic state with spin-glass-like characteristics.

I. INTRODUCTION

Rare earth cuprates, R_2CuO_4, are the parent compounds of high-T_c superconductors[1] for the lighter rare earths R = Nd, Pr, Sm, and Eu. They form in a tetragonal (T') crystal structure[2,3] an array of CuO_2 planes, where strong two-dimensional magnetic correlations exist between the Cu moments up to very high temperatures, although three-dimensional long range order only appears about room temperature,[4] possibly because of the much weaker interplanar interactions. For R = Y and the heavier rare earths R = Eu, Gd, and Ho, and for solid solutions including Tb, Dy, and Er, a complex magnetic behavior has been reported,[5,6] indicating the presence of antiferromagnetic order with a weak ferromagnetic component. The weak ferromagnetism of these materials has been shown to have a strong dependence on their magnetothermal history. Particularly, differences were observed in the electron-spin resonance (ESR) spectra[7] of Gd ions diluted into Eu_2CuO_4 and in the direct-current (dc) magnetization[6] of Cu ions in Y_2CuO_4, between samples cooled in zero magnetic field (ZFC) and in a finite field (FC).

We report here the synthesis of a new compound in this series, Tb_2CuO_4, and a study of its magnetic properties, through measurements of the ac susceptibility and dc magnetization under different cooling conditions.

II. R_2CuO_4 SYNTHESIS

Polycrystalline Tb_2CuO_4 samples were prepared from stoichiometric mixtures of Tb and Cu oxides (99.9% and 99% purity, respectively), heated under high pressure (8.5 GPa) in a belt-type apparatus. The samples were characterized by energy dispersive microanalysis and by x-ray diffraction using a Guinier camera. The Tb_2CuO_x stoichiometry was confirmed by the microanalysis measurements. Guinier films showed the Bragg peaks characteristic of the T' phase and many extra weak peaks which could be indexed as superstructure reflexions. The existence of these extra reflexions was also confirmed by electron diffraction studies. Otherwise, no impurity phase could be detected on the x-ray films. Details of the synthesis and structural studies of these compounds will be published elsewhere.[8]

III. EXPERIMENTAL RESULTS

We have measured the alternating-current (ac) susceptibility $\chi_{ac}(T) = \chi'(T) - i\chi''(T)$, and the dc magnetization $M_{dc}(T)$ of Tb_2CuO_4, using a Lake Shore susceptometer and a Quantum Design magnetometer, respectively. At room temperature, both χ_{ac} and M_{dc} indicate a paramagnetic behavior. Below ≈ 290 K, $\chi'(T)$ pre-

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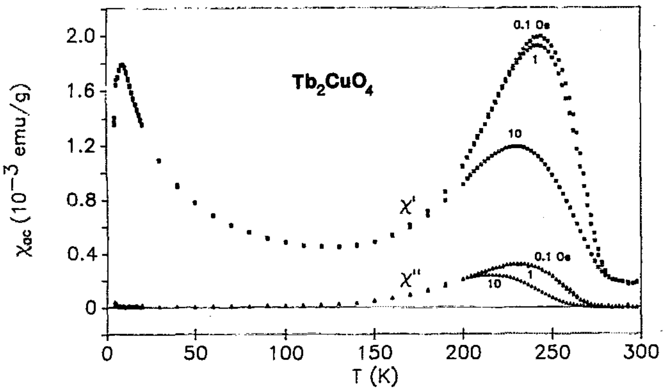

FIG. 1. Real and imaginary parts of the ac susceptibility $\chi'(T)$ and $\chi''(T)$ of Tb_2CuO_4, measured at 111 Hz with excitation magnetic fields, $H_{exc} = 0.1$, 1, and 10 Oe.

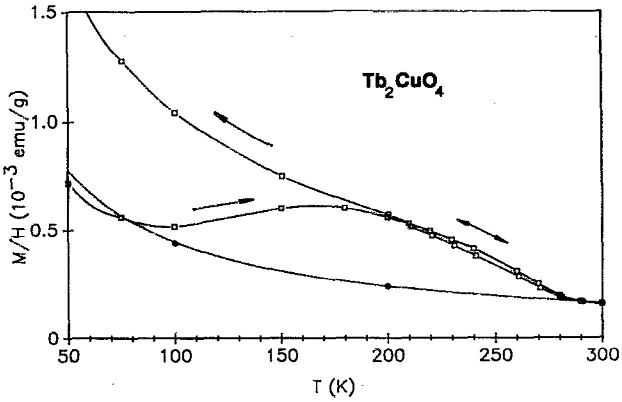

FIG. 2. FC and ZFC dc magnetization of Tb_2CuO_4 vs temperature, measured with an applied field of 100 G. Also shown (full circles) are the values of the differential susceptibility $\chi_d = dM_{dc}/dH_a$ measured at 100, 200, and 300 K, for applied fields up to 30 kOe.

sents a broad peak whose shape was found to be strongly dependent on the excitation magnetic field H_{exc} as shown in Fig. 1. The temperature at which the maximum of the peak occurs is shifted to lower temperatures as H_{exc} is increased, varying from $T_{max} \approx 245$ K for $H_{exc} = 0.1$ Oe to $T_{max} \approx 230$ K for $H_{exc} = 10$ Oe. The onset temperature $T_{on} \approx 290$ K is basically independent of H_{exc}.

The peak in $\chi'(T)$ has an associated anomaly in the out-of-phase component $\chi''(T)$, which is also shown in Fig. 1. $\chi''(T)$ is negligible at T_{on} and presents a maximum at a temperature slightly below the maximum of $\chi'(T)$. The shape of the maximum is also dependent on the amplitude of H_{exc}.

For temperatures $T \ll T_{max}$, $\chi''(T)$ decreases with decreasing temperature, reaching values below the experimental uncertainty for $T \approx 100$ K. Below this temperature $\chi'(T)$ approaches a Curie–Weiss (CW) law, independently of H_{exc}. The effective moment is $\mu_{eff} = 9.7\ \mu_B$/Tb atom, close to the value for free Tb^{3+} ions in the ground state $(4f^8;{}^7F_6)$. The CW temperature, $\Theta = 18$ K, indicates antiferromagnetic coupling between the Tb ions.

A broad maximum of $\chi'(T)$ at $T_L \approx 10$ K and nonzero values of $\chi''(T)$ around this temperature, indicate magnetic ordering of the Tb ions, with a possible reorientation of the Cu moments. The dc magnetization was measured with applied fields H_a up to 50 kOe. The differential susceptibility $\chi_d \equiv dM_{dc}/dH_a$ was found to be independent of the applied field H_a, in the high field limit. It follows a Curie–Weiss law, with $\mu_{eff} = 9.62(8)\ \mu_B$/Tb atom and $\Theta = 18(1)$ K, in agreement with the ac measurements at low temperatures. For $H_a < 1$ kOe, the dc magnetization is strongly dependent on the magnetic field H_c applied when cooling the samples from temperatures above T_{on}. In Fig. 2 we show the values of $M_{dc}(T)$ measured for: (a) ZFC case, where the sample was cooled down from 300 to 2 K in zero field ($H_c < 1$ Oe) and measured subsequently at increasing temperatures with an applied field, $H_a = 100$ Oe, and (b) FC case, where the sample was cooled with the measuring field already applied, $H_a = H_c = 100$ Oe. The ZFC magnetization approaches a paramagnetic regime at low temperatures ($10 < T < 80$ K), showing a linear dependence of the magnetization on the applied field and a Curie–Weiss behavior for the differential susceptibility: $M_{dc}(T) \approx \chi_d(T)\, H_a \approx C_{Tb}/(T + \Theta)\, H_a$. At higher temperatures the ZFC magnetization is larger than predicted by this linear relation. This is also the case for FC samples, but in the whole temperature range $10 < T < 300$ K. The observed behavior can be described in both cases in terms of an internal effective field H_i acting on the Tb ions. It is strongly dependent on the thermomagnetic history of the sample and increases with decreasing temperature for FC samples, saturating at low temperatures. The value of H_i is a function of the field for cooling. For $H_c = 100$ Oe, the internal field is ≈ 100 Oe and reaches a limiting value of about 120 Oe for samples cooled in $H_c > 500$ Oe. For ZFC samples the internal field is negligible at low temperatures but it increases as the temperature is raised, reaching a maximum at ≈ 200 K. Above this temperature the magnetization curves are thermally reversible and there is little difference between the FC and ZFC magnetizations.

We have performed hysteresis loops for samples FC in a magnetic field of 50 kOe. In Fig. 3 we present our results after subtracting the reversible part associated to the polarization of the Tb ions, $\chi_d(T)H_a$. At variance with the little or no coercivity observed for Gd_2CuO_4 single crystals,[9] we have found a coercive field of ≈ 280 Oe for Tb_2CuO_4. The remanent magnetization M_r shows a logarithmic time decay, which reflects the relaxation process of the magnetic system. This effect is illustrated in Fig. 4, where we present the evolution of M_r for a sample FC in 500 Oe, after removing the applied field.

IV. DISCUSSION

Our results indicate that Tb_2CuO_4 presents a weak ferromagnetic component, but showing also typical characteristics of canonical spin glasses: (i) a maximum of the in-phase component of the ac susceptibility and a nonzero out-of-phase component, whose shapes depend on the amplitude and frequency of the excitation magnetic field, (ii)

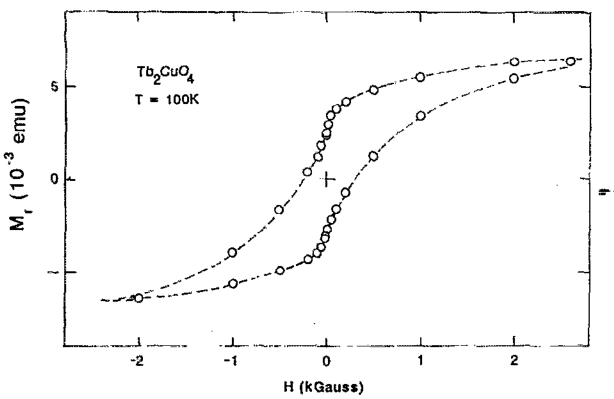

FIG. 3. Hysteresis loop of the dc magnetization of a 60 mg sample of Tb_2CuO_4 measured at 100 K after FC in 50 kOe. The magnetization has been plotted after subtracting the paramagnetic contribution $\chi_d(T)H_a$.

large differences between the ZFC and the FC dc magnetizations, and (iii) the presence of very slow relaxation processes characterized by a logarithmic time decay of the remanent magnetization.

The microscopic origin of the weak ferromagnetism remains still unknown in these T' compounds, although it has been suggested[9] that Dzyaloshinsky–Moriya (DM) interactions[10,11] between neighboring Cu moments may be responsible for this behavior. These are not allowed in tetragonal symmetry and crystal distortions are required in order to have a nonzero interaction. Indications of the actual existence of these distortions have been given by unusually large anisotropic temperature factors[2] in the positions for the oxygen ions in the CuO_2 planes,[12] when refining the structure of Gd_2CuO_4 from single crystal x-ray diffraction data. Also the ESR spectrum[7] of Gd ions diluted in Eu_2CuO_4 have shown evidence of local distortions around the R sites. The proposed displacements of the oxygen ions[12] eliminates partially the symmetry

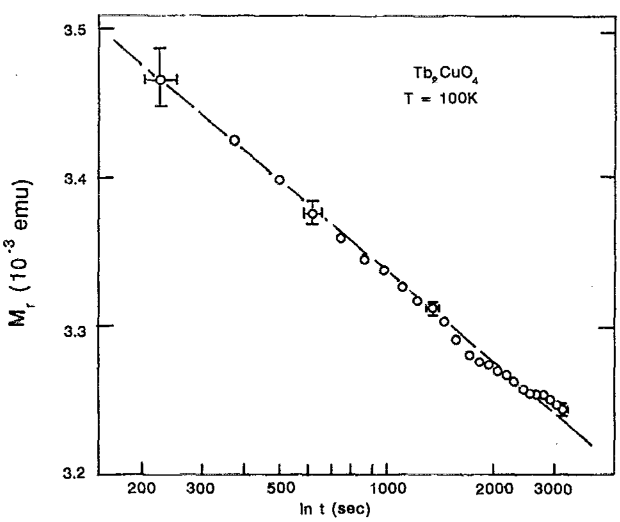

FIG. 4. Logarithmic time relaxation of the remanent magnetization for a 60 mg sample of Tb_2CuO_4, measured at $T = 100$ K after FC in a field of 500 Oe.

restrictions[11] for the DM interaction and allow energy terms of the type $D_{ij}\cdot[M^{(i)}_{Cu}\times M^{(j)}_{Cu}]$, with $D_{ij}\|c$ axis. This interaction favors a canting of the Cu moments in the *ab* plane giving rise to a weak ferromagnetic component. The assumed disorder associated with the oxygen displacements would originate a random variation of D_{ij} from site to site, introducing frustration into the magnetic system if energy minimization cannot be achieved simultaneously for all Cu pairs. Thus, a large number of metastable states would be present, as required for the formation of a glassy magnetic phase. Further work is in progress in order to analyze the spin dynamics of the magnetic system around T_N and the time relaxation of the magnetic remanence, which may help to clarify the microscopic origin of the glassy features presented here.

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