Weak ferromagnetism and spin-glass-like behavior in the rare-earth cuprates R_2CuO_4 (R =Tb, Dy, Ho, Er, Tm, and Y)

M. Tovar
Centro Atómico Bariloche and Instituto Balseiro, 8400 San Carlos de Bariloche, Río Negro, Argentina and Instituto de Ciencia de Materiales de Barcelona, Consejo Superior de Investigaciones Científicas, Campus UAB, 08193 Bellaterra, Spain

X. Obradors and F. Pérez
Instituto de Ciencia de Materiales de Barcelona, Consejo Superior de Investigaciones Científicas, Campus UAB, 08193 Bellaterra, Spain

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

R. J. Duro and J. Rivas
Applied Physics Department, University of Santiago de Compostela, E-15706 Santiago de Compostela, Spain

D. Chateigner, P. Bordet, and J. Chenavas
Laboratoire de Cristallographie 166X, 38042 Grenoble CEDEX, France
(Received 28 June 1991; revised manuscript received 2 October 1991)

dc magnetization, ac magnetic susceptibility, and microwave magnetoabsorption measurements on rare-earth cuprates, R_2CuO_4 (R =Tb, Dy, Ho, Er, Tm, and Y), synthesized under high pressure, indicate the presence of antiferromagnetic order with a weak-ferromagnetic component below a characteristic temperature T_0. From the maximum in the amplitude of the microwave absorption, we have determined T_0=295(3) K for R=Tb. The values of T_0 decrease monotonically along the series down to T_0=260(3) K for R=Tm. For R=Y we have measured T_0=265(3). The in-phase component of the ac magnetic susceptibility $\chi'(T)$ presents a peak whose shape and intensity are dependent on both the amplitude and the frequency of excitation of the magnetic field. The simultaneous observation of a nonzero and also frequency-dependent out-of-phase term, $\chi''(T)$, suggests the presence of relaxation phenomena. The dc magnetization of Tb_2CuO_4, measured in magnetic fields up to 50 kOe, shows: (i) a linear and reversible part associated with the polarization of the rare-earth ions by the applied magnetic field, (ii) a contribution M_{Cu} related to the appearance of weak ferromagnetism and spin-glass-like features in the Cu lattice, and (iii) an effective internal field H_i acting on the Tb ions, which is linearly dependent on M_{Cu}. Both M_{Cu} and H_i present a strong dependence on the magnetothermal history of the samples, below a characteristic temperature $T_{irr}(H)$. The maximum values of M_{Cu} observed in Tb_2CuO_4 were $2.4(7)\times10^{-3}$ and $4.7(14)\times10^{-3}$ μ_B/mole Cu, for two samples prepared under different conditions. A mean-field analysis of the proportionality between H_i and M_{Cu} gives an exchange interaction $J_{Tb\text{-}Cu}$=0.19(3) meV. The frequency dependence of the ac susceptibility, a strong magnetothermal irreversibility, and the time relaxation of the dc magnetization, point to the existence of a disordered magnetic state with spin-glass-like behavior. We discuss the possible relation between microscopic structural distortions and the observation of weak ferromagnetism in the heavier rare-earth compounds. Maxima in the ac susceptibility and the dc magnetization observed at $T_L \approx 9$–10 K for Tb_2CuO_4 and Dy_2CuO_4 indicate possible spin reorientations of the Cu moments or long-range magnetic order of the rare-earth ions.

I. INTRODUCTION

The presence of long-range antiferromagnetism (AF) associated with the ordering of the magnetic moments of the Cu^{2+} ions is a common characteristic of the rare-earth cuprates R_2CuO_4, parent compounds of the electron-doped high-T_c superconductors[1] $R_{2-x}(Ce,Th)_xCuO_4$. Muon-spin-rotation[2] and neutron-diffraction experiments[3] indicate that AF order develops below room temperature for R=Pr, Nd, and Sm. The magnetic behavior is complex for the heavier rare-earth cuprates, and the presence of a weak ferromagnetic (WF) component has been reported[4–6] for R=Eu, Gd, Ho, and Y, and also for several solid solutions including heavy rare-earth ions.[5]

These cuprates form in a tetragonal (T') crystal structure[7] and can be prepared in air at atmospheric pressure for the light rare-earth elements R=Pr, Nd, Sm, Eu, and Gd. Solid solutions including heavier rare-earth elements, such as R=(Eu,Tb), (Eu,Dy), or (Nd,Tb), have also been prepared under the same experimental conditions. Recently, several new cuprates with R=Dy, Ho,

Er, Tm, and Y have been synthesized under high pressures.[8]

The WF behavior has been shown to be dependent on the magnetic history of the samples for Y_2CuO_4 and Gd-doped Eu_2CuO_4, as reported in Refs. 6 and 9, respectively. A history-dependent magnetization has also been observed[10] in La_2CuO_4, a compound with orthorhombic (T) structure in which a hidden WF behavior is present[11] with indications of magnetic disorder.[12] In this case the WF component has been suggested to arise from the antisymmetric exchange interaction[13] because of the tilting of the CuO_6 octahedra, which gives rise to an orthorhombic distortion of the structure. In the case of the tetragonal T' cuprates, the origin of the weak ferromagnetism is still unknown.

A preliminary report on the synthesis and magnetic characterization of Tb_2CuO_4 has been given in Ref. 14. We present here ac susceptibility, dc magnetization, and microwave magnetoabsorption measurements in R_2CuO_4 compounds for R=Tb, Dy, Ho, Er, Tm, and Y, all prepared by ceramic methods under high pressure. We describe in Sec. II the preparation techniques and present in Sec. III the experimental results. In Sec. IV we analyze the variation of the ordering temperature along this series of compounds and discuss the relaxation phenomena observed in these materials. We also estimate the strength of the R-Cu exchange coupling. In Sec. V we discuss the possible microscopic origin of the weak ferromagnetism in these T' cuprates, in terms of disordered static local distortions of the average tetragonal symmetry of the structure.

II. R_2CuO_4 SYNTHESIS

Polycrystalline R_2CuO_4 compounds, with R=Tb, Dy, Ho, Er, Tm, and Y, were prepared from stoichiometric mixtures of R_2O_3 and CuO oxides (99.9% and 99% purity, respectively) under high-temperature–high-pressure conditions.

The powders were mechanically mixed during approximately 10 min, then placed in platinum capsules, heated during 1 h at high temperature by means of molybdenum or graphite furnaces under very high pressure in a belt-type apparatus, and finally quenched rapidly to ambient temperature before releasing the pressure.

Typical high-temperature–high-pressure conditions were 8 GPa, 1000 °C in a molybdenum furnace for Y_2CuO_4, Er_2CuO_4, Dy_2CuO_4, and Ho_2CuO_4, and 9 GPa, 1200 °C in a graphite furnace for Tm_2CuO_4. The Tb_2CuO_4 samples were synthesized at 8.5 GPa either in a graphite furnace at 820 or 1000 °C in a molybdenum one.

The samples obtained were characterized by energy-dispersive microanalysis and x-ray diffraction using a Guinier camera. The cationic stoichiometry of $R_2CuO_{4+\delta}$ was confirmed by microanalysis measurements. However, deviations (δ) from the correct oxygen stoichiometry could not be determined because of the small size of the samples. These materials have been found[15] to decompose when heated to about 300 °C, and this fact has made difficult the attempts to control the oxygen content through heat treatments in different atmospheres. So far, we have not found significant differences in the physical properties for samples heat treated in N_2 or O_2 below 300 °C. A detailed study of samples prepared under varying pressure and temperature conditions is presently under way. Guinier films showed the Bragg peaks characteristic of the T' phase and many extra weak peaks which could be indexed as superstructure reflections. The existence of these extra reflections 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 separately.[15]

III. EXPERIMENTAL RESULTS

The magnetic behavior of these compounds has been characterized through ac susceptibility, dc magnetization, and low-field microwave magnetoabsorption measurements. The ac susceptibility data were taken with a Lake Shore Susceptometer, the dc magnetization measurements were performed with a Quantum Design Magnetometer, and the microwave absorption experiments were done with a Varian E-109 spectrometer operating at 9 GHz.

A. ac susceptibility

We have measured the real (χ') and imaginary (χ'') parts of the ac susceptibility between 4.5 and 300 K. A maximum of χ' was found near room temperature for R=Tb, Dy, Ho, Er, and Tm, as shown in Fig. 1. For R=Y the susceptibility of the samples was too low to be determined with the susceptometer used.

The intensity of the observed anomaly was larger for Tb_2CuO_4 than for the other compounds studied. As reported earlier,[14] the shape of the maximum was found to be strongly dependent on the intensity and frequency of the excitation magnetic field H_{exc}. The susceptibility measured[14] for a sample of Tb_2CuO_4 synthesized at 820 °C, and identified here as I, is shown in Fig. 2 for H_{exc}=0.1, 1, and 10 Oe. Note that the onset temperature T_{on}=290 K for this sample is basically independent

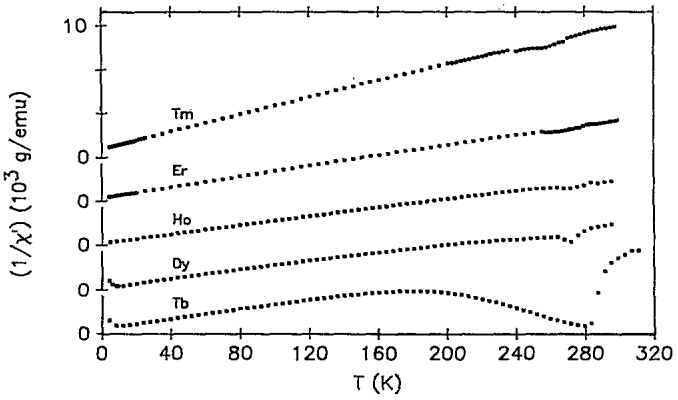

FIG. 1. Inverse of the real part of the ac magnetic susceptibility, $\chi'(T)$, for R_2CuO_4 (R=Tb, Dy, Ho, Er, and Tm) vs temperature, measured at a frequency of 111 Hz with an excitation field H_{exc}=10 Oe.

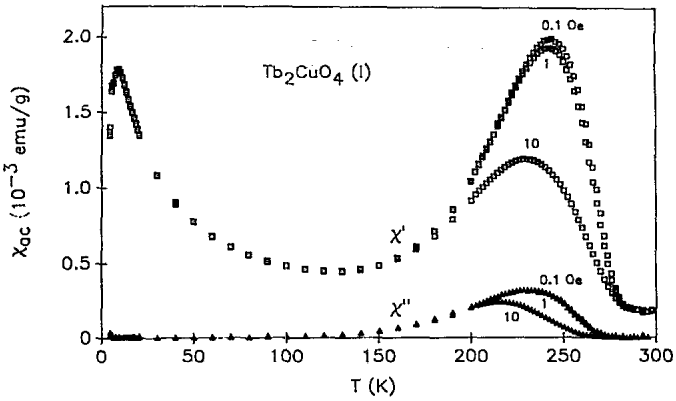

FIG. 2. Real and imaginary parts of the ac susceptibility, $\chi'(T)$ and $\chi''(T)$, of Tb_2CuO_4 (sample I), measured at a frequency of 111 Hz and excitation magnetic fields $H_{exc}=0.1$, 1, and 10 Oe.

of H_{exc}, but the temperature at which the maximum occurs is shifted to lower temperatures as the excitation field is increased, decreasing from $T_{max}=245$ K for $H_{exc}=0.1$ Oe to $T_{max}=230$ K for $H_{exc}=10$ Oe.

Besides, variations were observed between samples prepared under different conditions. In Fig. 3 we present data taken for a second sample, synthesized at 1000 °C and identified as II. Although the onset temperature $T_{on}\approx 300$ K was only slightly higher than that of sample I, the peak was more intense in this case, with its maximum at a higher temperature $T_{max}=285$ K for $H_{exc}=0.1$ Oe. The dependence on the intensity of the excitation field was found to be qualitatively similar for both samples. $\chi'(T)$ was found to be also strongly dependent on the frequency of H_{exc}, as shown in Fig. 3 for $\nu=10$, 111, and 1000 Hz.

For $R=$Dy, Ho, Er, and Tm, the maxima of $\chi'(T)$ were less intense and we were only able to observe them for $H_{exc}=10$ Oe. For this series of compounds, T_{on} was found to be only weakly dependent on the rare-earth elements, varying from $T_{on}\approx 285$ K for $R=$Dy to $T_{on}\approx 270$ K for $R=$Tm. The peak in $\chi'(T)$ for Tb_2CuO_4 has an associated anomaly in $\chi''(T)$, shown also in Figs. 2 and 3. $\chi''(T)$ presents a maximum at a temperature slightly lower than that of $\chi'(T)$, which is also dependent on the amplitude and frequency of H_{exc}. For the other compounds studied, the χ'' anomaly, if it exists, was below the sensitivity of our apparatus.

For temperatures $T \ll T_{max}$, $\chi''(T)$ goes to zero and $\chi'(T)$ approaches a Curie-Weiss law, independently of the excitation field. The effective magnetic moments and Curie-Weiss temperatures are given in Table I for the different systems studied. The measured total effective moments are close to the values expected for the free R^{3+} ions alone. This observation is in agreement with the almost two-orders-of-magnitude smaller susceptibility measured for La_2CuO_4 (Refs. 10–12) and Y_2CuO_4,[6] where the R^{3+} ions are nonmagnetic. Diamagnetic corrections, estimated[6] in $\approx 3\times 10^{-7}$ emu/g, do not affect the calculated effective moments beyond the experimental uncertainty.

For $R=$Tb and Dy, we have observed additional anomalies in χ' and χ'' at low temperatures, which are shown in Figs. 4 and 5. Broad peaks in χ' were found with their maximum values at $T_L\approx 9$–10 K for both compounds. At about 6 K smaller sharp peaks were observed in χ'', superimposed on the broader features centered at T_L. These peaks occur in coincidence with an inflection point in $\chi'(T)$ for Dy_2CuO_4 and with a small feature in the low-temperature side of the maximum for Tb_2CuO_4. For $R=$Ho, Er, and Tm, we have not observed this type of low-temperature anomalies down to 4.2 K.

B. dc magnetization

We have measured the dc magnetization of Tb_2CuO_4, $M_{dc}(T)$, in the temperature range $2\le T\le 300$ K with applied magnetic fields H_a up to 50 kOe. For H_a larger than ≈ 2 kOe and up to the larger applied fields, $M_{dc}(T)$ has been found[14] to be linear in H_a. The differential susceptibility $\chi_d(T)\equiv dM_{dc}(T)/dH_a$ follows a Curie-Weiss law $\chi_d(T)=C_{Tb}/(T+\Theta)$, with $\mu_{eff}=9.62(8)\mu_B$/mol Tb and $\Theta=18(1)$ K. The measured susceptibility did not

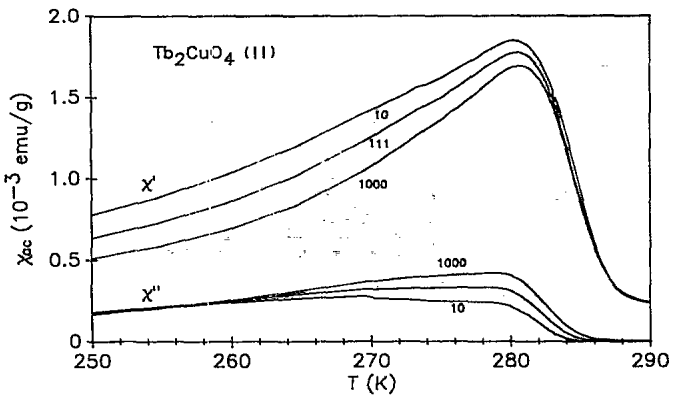

FIG. 3. Real and imaginary parts of the ac susceptibility, $\chi'(T)$ and $\chi''(T)$ of Tb_2CuO_4 (sample II), measured at frequencies of 10, 111, and 1000 Hz with an excitation magnetic field $H_{exc}=10$ Oe.

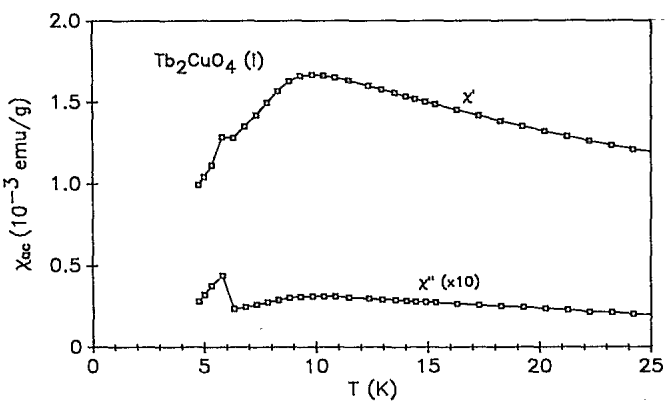

FIG. 4. Low-temperature anomalies observed in the ac susceptibility of Tb_2CuO_4(I), measured at 111 Hz with $H_{exc}=10$ Oe.

TABLE I. Effective moments and Curie-Weiss temperatures determined from the differential magnetic dc susceptibility $\chi_d(T)\equiv dM_{dc}(T)/dH_a = C/(T+\Theta)$ and the low-temperature ac susceptibility $\chi_{ac}(T)$. Bracketed values are taken from Ref. 6.

R_2CuO_4	μ_{eff} (μ_B/R atom)			Θ (K)	
	χ'_{ac}	χ_d	free ion	χ'_{ac}	χ_d
Tb_2CuO_4	9.70(10)	9.6(1)	9.72	18(2)	18(2)
Dy_2CuO_4	10.70(25)	10.7(2)	10.64	17(5)	22(2)
		[10.60]			[22.1]
Ho_2CuO_4	10.40(15)	[10.43]	10.60	7(2)	[12.2]
Er_2CuO_4	9.60(15)	[9.64]	9.58	10(2)	[23.9]
Tm_2CuO_4	7.55(15)	[7.49]	7.56	20(2)	[20.6]

show any significant deviation that could be ascribed to crystal-field effects, down to temperatures close to $T_L \approx 9$ K, where the maximum of $\chi'(T)$ was observed. This high-field linear magnetization extrapolates, for $H_a = 0$, to a nonzero spontaneous magnetization $M_0(T)$. As found for Gd_2CuO_4 (Ref. 4) and other WF compounds such as $CoCO_9$ (Ref. 16) and $GdCrO_3$,[17] $M_{dc}(T)$ may be described at high fields by

$$M_{dc}(T) \simeq M_0(T) + \chi_d(T) H_a \ . \tag{1}$$

For $H_a < 1$ kOe, the dc magnetization is nonlinear and strongly dependent[14] on the magnetic field applied during the cooling of the samples, H_c. This effect is illustrated in Fig. 6 where we show the values of $M_{dc}(T)$ measured in sample I when (a) zero-field cooled (ZFC) from 300 to 2 K ($H_c < 1$ Oe) and measured subsequently at increasing temperatures with an applied field $H_a = 100$ Oe and (b) field cooled (FC), i.e., measured while cooling down from 300 K with the same applied field ($H_a = H_c = 100$ Oe). For comparison, the paramagnetic linear contribution $\chi_d(T)H_a$ is also shown. At low temperatures ($10 < T < 80$ K) and for ZFC samples, a very small value of $M_0(T)$ was measured and thus $M_{dc}(T) \approx \chi_d(T)H_a$. At higher temperatures the ZFC magnetization becomes nonlinear and develops a larger $M_0(T)$, as is also the case for FC samples, where $M_0(T) \neq 0$ in the whole temperature range $10 < T < 300$ K.

We found that, for $20 < T < 120$ K, the temperature dependence of $M_0(T)$ can be reasonably described, as in the case of Gd_2CuO_4 (Ref. 4) and $GdCrO_9$,[17] by the relation

$$M_0(T) = M_{Cu} + \chi_d(T) H_i \ , \tag{2}$$

where M_{Cu} and H_i are temperature-independent parameters. In this description[4,17] M_{Cu} has been associated with a contribution arising from the ordered Cu lattice and H_i represents an effective internal field polarizing the paramagnetic rare-earth ions. For Tb_2CuO_4 we have found that both parameters are strongly dependent on the magnetothermal history of the samples, i.e., the magnetic field applied while they are cooled from temperatures above T_{on}.

For $T > 120$ K, $M_0(T)$ deviates from the linear dependence on $\chi_d(T)$ of Eq. (2) and eventually goes to zero at T_{on}. Since the high-field linear magnetization is still well described by $\chi_d(T)H_a$, we have found it convenient to keep the same functional form given by Eqs. (1) and (2) in order to describe the experimental data, but allowing a temperature dependence for $M_{Cu}(T)$ and $H_i(T)$. Thus we write

$$M_{dc}(T) = M_{Cu}(T) + \chi_d(T)[H_a + H_i(T)] \ , \tag{3}$$

which has the correct limits for both high fields and low temperatures. This equation may be rewritten as

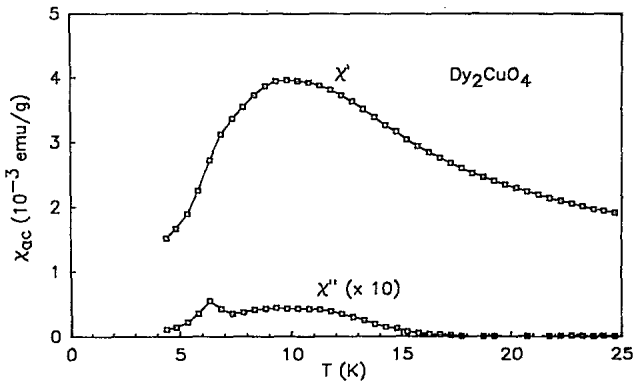

FIG. 5. Low-temperature anomalies observed in the ac susceptibility of Dy_2CuO_4, measured at 111 Hz with $H_{exc} = 10$ Oe.

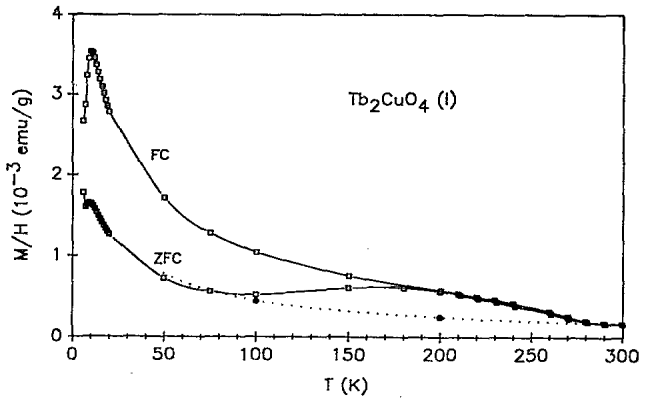

FIG. 6. FC and ZFC dc magnetization of Tb_2CuO_4(I) vs temperature, measured with an applied field of 100 G. Also shown (solid circles) are the values of the differential susceptibility $\chi_d \equiv dM_{dc}/dH_a$, measured at 100, 200, and 300 K, for applied fields up to 30 kOe. The dotted line corresponds to a fit of $\chi_d(T)$ to a Curie-Weiss law.

$$\chi_d^{-1}(T)[M_{dc}(T)-\chi_d(T)H_a] = H_i(T)+C_{Tb}^{-1}(T+\Theta)M_{Cu}(T) . \quad (4)$$

When the contribution of the Cu lattice to the total magnetization is negligible, Eq. (4) gives directly the internal field $H_i(T)$. For temperature-independent values of both M_{Cu} and H_i, it results in a linear function of T, whose slope is proportional to M_{Cu}. In this case the internal field H_i may be determined from the value of Eq. (4) extrapolated to $T=-\Theta$.

In Fig. 7(a) we have represented the data of Fig. 6, obtained for sample Tb_2CuO_4(I), but plotted as indicated by Eq. (4). From the low-temperature linear asymptotic behavior, we have determined $M_{Cu}(0)=2.0(6)\times10^{-3}\mu_B$/(Cu atom) and $H_i(0)=85(10)$ Oe for FC in $H_c=100$ Oe. Both the internal field and Cu magnetization were found to be almost negligible for the ZFC case at low temperatures (the small negative value observed is due to the residual magnetic field of the magnetometer present, while zero-field-cooling the sample). As the temperature is increased above ≈120 K, the ZFC magnetization increases and presents a maximum at ≈200 K. At about the same temperature, the system reaches a reversible regime where the differences between ZFC and FC cases are minimal. Thus we identify this characteristic temperature, which is dependent on the measuring field H_a, as $T_{irr}(H_a)$, emphasizing the irreversibility observed below

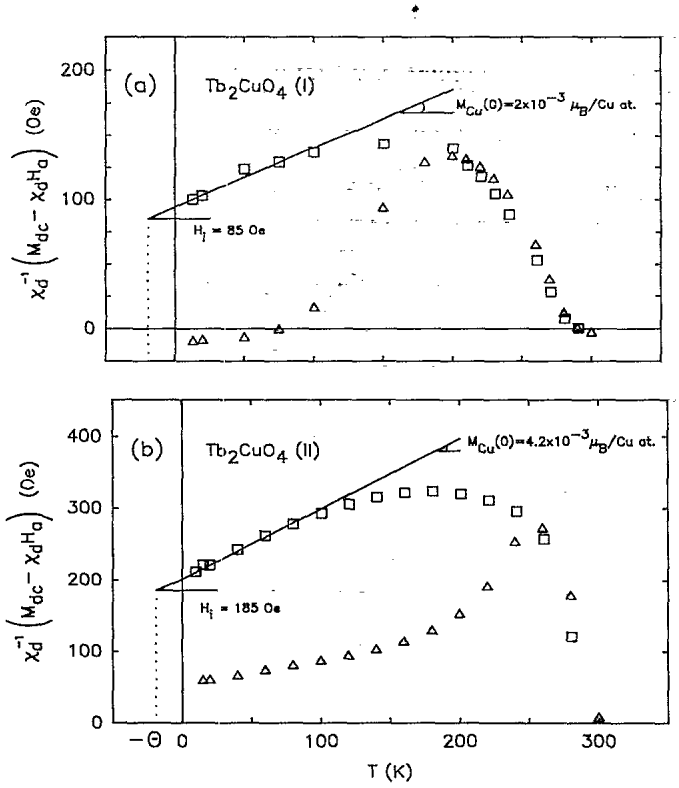

FIG. 7. $[M_{dc}(T)-\chi_d(T)H_a]/\chi_d(T)$ vs T, measured for samples Tb_2CuO_4(I) and Tb_2CuO_4(II). The triangles correspond to ZFC samples and the squares to samples FC in 100 Oe. The straight lines correspond to the asymptotic low-temperature linear dependence from which we have determined $M_{Cu}(0)$ and $H_i(0)$.

it. Cooling in a field of 500 Oe increases the value of $M_{Cu}(0)$ to $2.4(7)\times10^{-3}\mu_B$/(Cu atom) and $H_i(0)$ to 115(15) Oe. The maximum of the ZFC magnetization is shifted to $T_{irr}\approx190$ K. Further increasing of the field for cooling does not appreciably change the values of $M_{Cu}(0)$ and $H_i(0)$.

Measurements of $M_0(T)$ in sample Tb_2CuO_4(II) showed larger values than in sample I in the whole temperature range. In terms of Eqs. (3) and (4), this observation implies larger values for both the internal field and cooper magnetization in this sample for the same cooling conditions. For comparison we present in Fig. 7(b) the results obtained for $H_a=100$ Oe after field-cooling the sample in $H_c=100$ Oe or in a residual field (ZFC) of ≈0.2 Oe. Note that even this small field creates a measurable internal field. As in the case of sample I, both $M_{Cu}(0)$ and $H_i(0)$ increase as a function of H_c and reach saturation values (for H_c larger than ≈1 kOe) of $M_{Cu}(0)=4.7(14)\times10^{-3}\mu_B$/(Cu atom) and $H_i(0)=235(25)$ Oe, which are about twice the maximum values measured for sample I. It should also be noted that there is a narrower temperature range where the dc magnetization is reversible for this sample: $T_{irr}\approx250$ K for $H_a=100$ Oe.

We have performed hysteresis loops for FC samples in a magnetic field of 50 kOe. After subtracting the reversible part associated with the polarization of the Tb ions, $\chi_d(T)H_a$, we have found rather large coercive fields for Tb_2CuO_4: 270 and 1100 Oe for samples I and II, respectively. Instead, a coercivity of less than 1 Oe has been reported in Gd_2CuO_4 single crystals.[4,5] We have measured the relaxation of the remanent magnetization M_r and found that it decays logarithmically as a function of time,[14] as shown in Fig. 8.

At low temperatures the magnetization presents a maximum at $T_L\approx9$ K for a measuring field $H_a=10$ kOe, showing little thermal hysteresis, as seen in Fig. 9. At lower fields the behavior is more complex since additional features are present at temperatures below T_L.

We have also measured the dc magnetization of Dy_2CuO_4 for $H_a=100$ Oe and found that there is only a small anomaly at high temperatures, peaked at

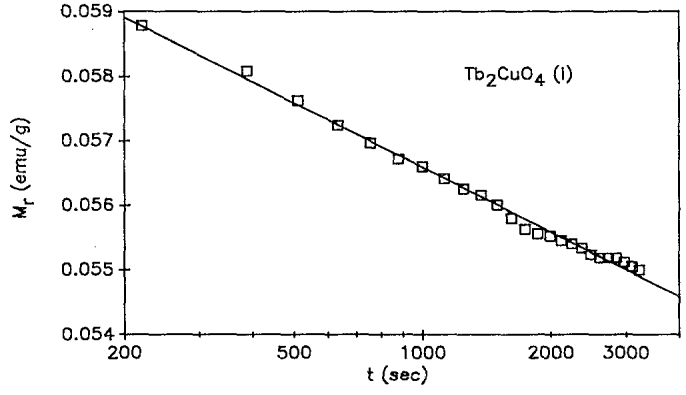

FIG. 8. Logarithmic time decay of the remanent magnetization for Tb_2CuO_4(I), measured at $T=100$ K after field cooling in a field $H_c=500$ Oe.

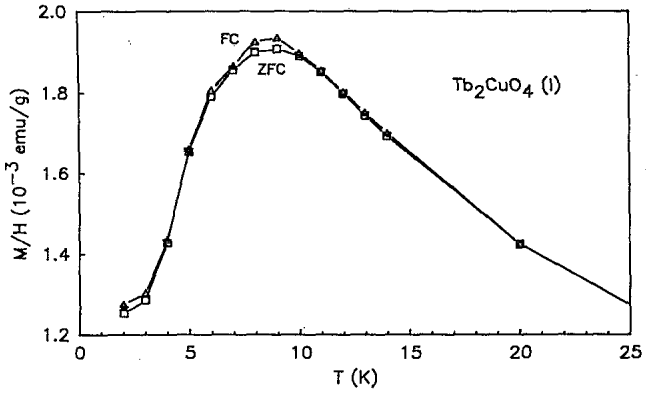

FIG. 9. ZFC and FC low-temperature dc magnetization of Tb_2CuO_4(I), measured in a field of 10 kOe.

$T_{max}=260(10)$ K. The internal field, as defined by Eq. (3), was $H_i<10$ Oe. At lower temperatures the magnetization follows a Curie-Weiss law with $\mu_{eff}=10.7(2)\mu_B$/atom Dy and $\Theta=22(2)$ K. Deviations from this law (probably due to crystal-field effects) are observed below ≈ 120 K. $M_{dc}(T)$ presents a rounded maximum at $T_L \approx 9-10$ K, resembling that found for $\chi'(T)$. Thermal hysteresis effects are observed around this maximum and down to $T^*=6.3$ K. This is also the temperature where $\chi'_{ac}(T)$ shows an inflection point and $\chi''_{ac}(T)$ presents a sharp peak.

C. Microwave magnetoabsorption

We have observed a microwave-magnetoabsorption signal in all the samples studied, including Y_2CuO_4. The absorption line, measured as a function of magnetic field, was broad and asymmetrical in all cases. The amplitude of the signal was monitored as a function of temperature, and the onset of the microwave absorption was observed in coincidence with (or a few degrees higher than) the appearance of the described anomalies in both χ_{ac} and M_{dc}. A maximum of the amplitude (not integrated) was reached at a characteristic temperature T_0 about 10 K below the onset temperature, and a fast decrease was observed on further cooling, as shown in Fig. 10. These changes in the signal amplitude were accompanied by variations in the width and shape of the signals, with the minimum linewidth being measured in coincidence with the maximum amplitude. This minimum linewidth increases along the series from $\Delta H_{p.p.}<200$ Oe for $R=$Tb to $\Delta H_{p.p.}>3000$ Oe for $R=$Tm. For $R=$Y and Ho, we found $\Delta H_{p.p.}\approx 1500$ Oe. The maximum absorption, indicated by the zero of the field derivative, always occurred at low magnetic fields $H_r(T)$, as compared to the field for resonance for $g=2$. However, a large variation of $H_r(T)$ was observed as a function of temperature with a minimum in correspondence with the minimum linewidth.

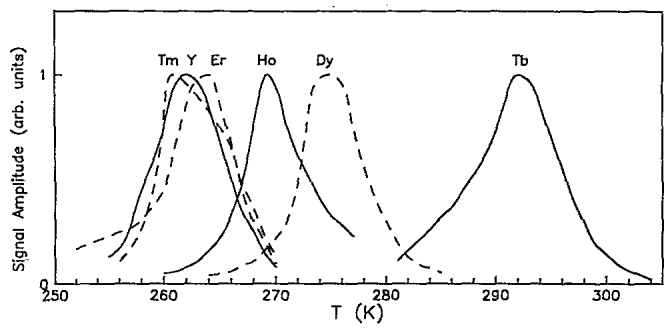

FIG. 10. Relative amplitude (not integrated) of the microwave-magnetoabsorption line vs temperature for R_2CuO_4 ($R=$Tb, Dy, Ho, Er, Tm, and Y).

IV. DISCUSSION

The magnetic measurements indicate that the rare-earth and Cu moments behave as weakly coupled independent magnetic systems over a large temperature range. The response of the system to dc and ac external fields characterizes different temperature regions.

A. Néel temperature of the Cu sublattice

At $T>T_0$ all the systems studied present a dc magnetization linear in the applied magnetic field and an ac susceptibility $\chi_{ac}\simeq\chi_d\equiv dM_{dc}/dH_a$, independent of the amplitude and frequency of the excitation field, and with no measurable imaginary component.

The onset of the anomalies in the dc and ac susceptibilities and the simultaneous appearance of a microwave-magnetoabsorption line at T_{on} suggest that the Cu lattice orders antiferromagnetically around this temperature, as it does for the lighter rare-earth cuprates.[2,9] The Néel temperature estimated in this way, $T_N\approx T_{on}$, varies across the series of compounds studied, decreasing monotonically with the atomic number of the R ions from $T_N\approx 290-300$ K for $R=$Tb to $T_N\approx 270$ K for $R=$Tm. For Y_2CuO_4 we have determined $T_N\approx 270$ K from the onset of the microwave absorption, in agreement with a previous determination[6] from dc magnetization measurements. However, in the case of $R=$Ho and Er, our ac susceptibility and microwave-absorption measurements indicate values of T_N higher than those reported in Ref. 6.

As discussed in Ref. 18, strong two-dimensional (2D) magnetic correlations are present at high temperatures in these kind of planar cuprates, as a result of the large intraplane magnetic coupling. However, the crossover to three-dimensional (3D) magnetic behavior only occurs at much lower temperatures because of a weaker interplanar interaction. This argument leads to values of the 3D Néel temperature T_N given by[18]

$$k_B T_N \approx J'[\xi_{2D}(T_N)/a]^2 ,$$

where J' is the exchange coupling between Cu planes and $\xi_{2D}(T_N)$ is the 2D correlation length at T_N in the absence of 3D coupling. $\xi_{2D}(T)$ has been determined experimentally for lighter rare-earth elements[18] and may be adequately described by the expression proposed by Chakravarty, Halperin, and Nelson[19] for a 2D Heisenberg model,

$$\xi_{2D}/T=\xi_0\exp(2\pi\rho_s/k_BT)\ ,$$

where $2\pi\rho_s$ is proportional to the intraplane coupling. The corresponding coupling constant J has been determined from two-magnon Raman-scattering measurements[20] and found to be of the order of 1000 K for Nd_2CuO_4, Pr_2CuO_4, and Sm_2CuO_4, showing a monotonous increase with the decrease of the size of the planar lattice. In this context a continuous increase of the correlation length would be expected along the rare-earth series with a subsequent tendency for larger T_N, unless the interplane coupling given by J' presents a faster decrease, which is unexpected because of the shorter distance between CuO_2 planes.

Attempts[18] to compare the measured T_N for the T compound La_2CuO_4 and the T' materials Pr_2CuO_4 and Nd_2CuO_4 have shown the inadequacy of the simple arguments given above, and certainly, the identification of the mechanisms that determine T_N will require further investigation. In this context it is interesting to note the depression of T_N reported here along the R_2CuO_4 series.

B. Weak ferromagnetism and spin-glass-like behavior

Below this temperature the dc magnetization becomes nonlinear in the applied magnetic field H_a, but it may be adequately described by Eq. (3) for $H_a<1$ kOe. Here we can identify a field-independent WF component and a linear paramagnetic contribution that we associate with the rare-earth system. This behavior presents strong similarities with the cases Gd_2CuO_4, Y_2CuO_4, (EuTb)CuO_4, and other cuprates including heavy rare-earth elements.[4–6] However, typical features of disordered magnetic systems have also been observed,[14] as we discuss below. The weak ferromagnetism, characterized by the nonzero values of $M_{Cu}(T)$ and $H_i(T)$, has been found to be strongly dependent on the magnetic history of the samples. We also note that the absolute magnitude of these WF parameters varies not only with the rare-earth element R, but is also affected by the preparation procedure of the samples, as has been discussed for the case of Tb_2CuO_4.

At low fields the dc magnetization departs from the linear behavior indicated by Eq. (3) and the real part of the ac susceptibility $\chi'(T)$ presents a significant increase, reflecting the buildup of weak ferromagnetism in the sample. The simultaneous observation of an imaginary component $\chi''(T)$ indicates that this process involves relaxation phenomena.

At the onset of the weak ferromagnetism, a negligible dependence on the frequency of the excitation field was observed in the range of our experiments (10–1000 Hz), as shown in Fig. 3. At these temperatures the dc magnetization is thermally reversible within experimental accuracy. On lowering the temperature, both $\chi'(T)$ and $\chi''(T)$ show a marked frequency dependence. $\chi'(T,\omega)$ was found to decrease for increasing ω at all temperatures. On the other hand, $\chi''(T,\omega)$ is an increasing function of ω above $T\approx250$–260 K, but a decreasing one for lower temperatures. This qualitative behavior[21] of $\chi''(T,\omega)$ suggests that above 250–260 K the distribution of relaxation times is peaked at shorter values than the time domain corresponding to our frequency window (10^{-2}–10^{-4} sec), becoming longer at lower temperatures. This process is correlated with the appearance of thermal irreversibility in the dc magnetization below $T_{irr}(H)$, the temperature at which the dominant relaxation times reach the observation window of the experiment, i.e., a few minutes.

For $T<120$ K the response of the system to an external dc field is reversible for $H_a>2$ kOe and the differential susceptibility $\chi_d(T)$ follows a Curie-Weiss (CW) law. Simultaneously, $\chi''(T)$ becomes negligible and $\chi'(T)$ is independent of the excitation field and decreases with decreasing temperatures, and approaches the same CW temperature dependence of $\chi_d(T)$. The effective moments determined from either $\chi'(T)$ or $\chi_d(T)$, given in Table I, are very close to those expected for the free R^{3+} ions, in agreement with the data reported in Ref. 6 for R=Dy, Ho, Er, and Tm. We note that this is evidence for the weakness of the R-Cu magnetic interaction, as compared to the coupling R-Ni in the series of nickelates R_2NiO_4. For these materials the effective paramagnetic moment of the R ions is enhanced[22] because of the exchange interaction with the Ni moments.

The observed behavior of the magnetic susceptibility indicates that at low temperatures the frequency of the excitation field is much higher than the inverse of the dominant relaxation times involved, and neither M_{Cu} or H_i are able to follow the oscillating ac field. Thus a frozen magnetic state has been formed and the logarithmic evolution[14] of the remanent magnetization observed at 100 K suggests the existence of metastable states, as occurs in spin glasses or superparamagnetic systems.

C. Low-temperature anomalies

The regime described in the previous section extends down to a second characteristic temperature $T_L\approx9$–10 K, where a maximum was found for the measured susceptibility of both Tb_2CuO_4 and Dy_2CuO_4. Instead, for R=Ho, Er, and Tm, a Curie-Weiss dependence has been observed down to 4.5 K. Although T_L is only slightly dependent on the measuring field, additional features observed at lower temperatures present a complex behavior. A detailed study of this transition, associated with either a reorientation of the Cu moments or magnetic order of the rare-earth elements, is currently under way and is planned to be reported separately.

D. Exchange coupling between the Cu and R moments

In the low-temperature limit (but still above T_L), both $M_{Cu}(T)$ and $H_i(T)$ approach, for Tb_2CuO_4, the temperature-independent values $M_{Cu}(0)$ and $H_i(0)$. The measured values, although strongly dependent on the cooling conditions and varying between the two samples studied, showed in all cases a proportionality between the internal field "seen" by the rare-earth system, $H_i(0)$, and the net magnetization of the Cu lattice, $M_{Cu}(0)$. We have determined $H_i(0)/M_{Cu}(0)=4.3(5)\times10^4$ Oe Cu atom/μ_B. If we consider the internal field as arising

from a Heisenberg type of coupling between the rare-earth ions and Cu sublattices,

$$\mathcal{H}=\sum_{i,j} J_{ij}\mathbf{S}_{\mathrm{Tb}}^{(i)}\cdot\mathbf{S}_{\mathrm{Cu}}^{(j)}\ , \tag{5}$$

and the sum is carried out over the $z=4$ nearest Cu neighbors, the ratio of the internal field to the magnetization of the Cu sublattice is constant and given by

$$H_i(T)=-\sum_{\mathrm{NN}}(J_{\mathrm{NN}}/g_{\mathrm{Cu}}g_{\mathrm{Tb}}\mu_B^2)M_{\mathrm{Cu}}^{(\mathrm{NN})}(T)$$
$$=-(zJ_{\text{Tb-Cu}}/g_{\mathrm{Cu}}g_{\mathrm{Tb}}\mu_B^2)M_{\mathrm{Cu}}(T)\ . \tag{6}$$

Taking for the gyromagnetic factors the free-ion value for Tb^{3+}, $g_{\mathrm{Tb}}=\frac{3}{2}$, appropriate for the ground state $(4f^8;{}^7F_6)$ and a free-electron value $g=2$ for the Cu moments, a value of $J_{\text{Tb-Cu}}=0.19(3)$ meV is obtained for the exchange-coupling constant between the two magnetic systems. We have not attempted to project this Hamiltonian onto the crystal-field levels since the crystal-field splitting is unknown for this compound, and we have not observed significant deviations of the magnetic susceptibility from CW behavior in the temperature region of interest. The measured value of $H_i(0)$ corresponds to an average over the microcrystals of the powder samples,[23] but since the measured value for $M_{\mathrm{Cu}}(0)$ is affected by the same averaging process, the assumed proportionality will still give the correct exchange-coupling constant. The exchange coupling here determined for Tb_2CuO_4 is smaller than for the case of nickelates, where values of $J_{R\text{-Ni}}=0.8$ and 0.6 meV have been obtained[22] for Nd_2NiO_4 and Pr_2NiO_4, respectively. The extra oxygen superexchange paths present in the T structure of the nickelates may be the origin of the differences found.

For a temperature-independent $J_{\text{Tb-Cu}}$, the same proportionality factor is expected between $H_i(T)$ and $M_{\mathrm{Cu}}(T)$ in the whole temperature range. Thus Figs. 7(a) and 7(b) closely reflect (except for a prefactor slowly varying with temperature) the temperature variation of $M_{\mathrm{Cu}}(T)$ and also its dependence on the magnetic history of the samples. A comparison with the results reported for Y_2CuO_4 in Ref. 6 indicates a completely analogous behavior.

V. CONCLUSIONS

Our results indicate that the R_2CuO_4 compounds studied here (with R = heavy-earth elements or Y) present a weak-ferromagnetic component and features typical of magnetic systems with metastable states[14] very close to energy: (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) large differences between the ZFC and FC dc magnetizations, and (iii) the presence of very slow relaxation processes characterized by a logarithmic time decay of the remanent magnetization.

Although the microscopic origin of the weak ferromagnetism remains still unknown in the T' compounds, it has been suggested[4] that Dzyaloshinsky-Moriya (DM) interactions[13] between neighboring Cu moments may be responsible for this behavior. This interaction is not allowed in the tetragonal (T') structure, and local crystal distortions are required in order to have a nonzero interaction. Indications of the actual existence of these distortions for the heavier rare-earth cuprates of the series have been given by the presence of unusually large anisotropic temperature factors in the analysis of single-crystal x-ray-diffraction data,[7,15,24] which may be interpreted in terms of static disorder in the positions of the oxygen ions in the CuO_2 planes. Average displacements of 0.18 Å for Gd_2CuO_4 and 0.36 Å for Tm_2CuO_4 have been estimated in Refs. 24 and 15, respectively. On the other hand, these effects have not been observed for the lighter rare-earth compounds, such as Nd_2CuO_4.[15] The splitting of the electron-spin-resonance (EPR) spectrum of Gd^{3+} ions diluted in Eu_2CuO_4 (Ref. 9) is also an indication of local distortions around the Gd sites. However, this splitting has not been observed for the lighter Pr_2CuO_4.[25] It has to be emphasized that experimental indications of local distortions have been observed only for the heavier R_2CuO_4 compounds, which also present signatures of weak ferromagnetism.[5,9,14]

The displacements of the oxygen ions within the CuO_2 planes would lift the symmetry restrictions[13] for the DM interaction and allow energy terms of the type $D_{ij}M_{\mathrm{Cu}}^{i}M_{\mathrm{Cu}}^{j}$ with $D_{ij}\|c$ axis. This type of interaction would favor a local canting of the Cu moments in the *ab* plane, giving rise to a weak-ferromagnetic component. The assumed disorder associated with oxygen displacements could 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 may be present, as required for the formation of a glassy magnetic phase. The fact that the magnitudes of the WF components found in Tb_2CuO_4 are so strongly dependent on the preparation techniques suggests that the WF properties may be very sensitive to the presence of lattice defects, either structural distortions, oxygen disorder, or variations in the oxygen stoichiometry. This dependence may be correlated with the observation of several coexisting superlattice structures[15] in single-crystal studies of Tm_2CuO_4 and Y_2CuO_4. Another observation that supports the close relation between WF and changes in the crystal structure is the large depression of the internal magnetic field found[26] for the also WF compound $Gd_{1.85}Th_{0.15}CuO_4$ under static hydrostatic pressure. From $H_i=324$ Oe at normal pressure, a decrease of $\approx 30\%$ has been measured[26] for an applied pressure of 10 kbar.

So far, the large thermal parameters (or evidence of random static distortions) have been found only[7,15,24] in the T' compounds that present WF, but not in the parent compounds of the superconducting ones.[24] Thus a detailed study of the crystal structure, particularly focused on the proposed static disorder and existence of different sublattices, should be carried out in order to determine its dependence on the rare-earth ion's size, oxygen content of the materials, preparation techniques, and subsequent thermal treatments in controlled atmospheres.

Also, the correlation of these variables with the superconducting properties for the lighter rare-earth compounds must be elucidated.

Finally, the phenomena of low-temperature spin reorientations or rare-earth magnetic ordering along the R_2CuO_4 series, reported in Ref. 4 for Gd_2CuO_4 and shown here to be also present for Tb_2CuO_4 and Dy_2CuO_4, need further investigation in order to fully understand the magnetic behavior of these cuprates.

ACKNOWLEDGMENTS

This research has been partially supported at the Instituto de Ciencia de Materiales de Barcelona by the Dirección General de Investigación en Ciencia y Tecnología (DGICYT) through Program No. PB89-71, by the Programme International de Cooperation Scientifique CNRS/CSIC and the MIDAS program, at the University of Santiago de Compostela by the Comisión Interministerial de Ciencia y Tecnología through Grant No. MAT89-0425-C03, at San Diego State University under National Science Foundation Grant Nos. NSF-DMR-88-01317 and NSF-INT-89-00851. The authors would like to thank M. Perroux and Th. Fournier for their experimental assistance. One of the authors (M.T.) also acknowledges partial support from DGICYT, the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (RA), and the Fundación Antorchas (RA).

[1]Y. Tokura, H. Takagi, and S. Uchida, Nature **337**, 345 (1989); H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989); J. T. Markert and M. B. Maple, Solid State Commun. **70**, 145 (1989); J. T. Markert, E. A. Early, T. Bjornholm, S. Ghamathy, B. W. Lee, J. J. Neumeier, R. D. Price, C. L. Seaman, and M. B. Maple, Physica C **158**, 178 (1989); J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, G. Liang, and M. Croft, Nature **337**, 720 (1989).

[2]G. M. Luke, B.J. Sternlieb, Y. J. Uemura, J. H. Brewer, R. Kadono, R. F. Kiefl, S. R. Kritzman, T. M. Riseman, J. Gopalakrishnan, A. W. Sleight, M. A. Subramanian, S. Uchida, H. Takagiana, and Y. Tokura, Nature **338**, 49 (1989).

[3]P. Allenspach, S.-W. Cheong, A. Dommann, P. Fischer, Z. Fisk, A. Furrer, H. R. Ott, and B. Rupp, Z. Phys. B **77**, 185 (1989); H. Yoshizawa, S. Mitsuda, H. Mori, Y. Yamada, T. Kobayashi, H. Sawa, and J. Akimitsu, J. Phys. Soc. Jpn. **59**, 428 (1990); J. Akimitsu, H. Sawa, T. Kobayashi, H. Fujiki, and Y. Yamada, *ibid.* **58**, 2646 (1989); Y. Endoh, M. Matsuda, K. Yamada, K. Kakurai, Y. Hidaka, G. Shirane, and R. J. Birgeneau, Phys. Rev. B **40**, 7023 (1989); D. C. Cox, A. I. Goldman, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, *ibid.* **40**, 6998 (1989); S. Skanthakumar, J. W. Lynn, J. L. Peng, and Z. Y. Li (unpublished).

[4]J. D. Thompson, S.-W. Cheong, S. E. Brown, Z. Fisk, S. B. Oseroff, M. Tovar, D. C. Vier, and S. Schultz, Phys. Rev. B **39**, 6660 (1989).

[5]S. B. Oseroff, D. Rao, F. Wright, M. Tovar, D. C. Vier, S. Schultz, J. D. Thompson, Z. Fisk, and S.-W. Cheong, Solid State Commun. **70**, 1159 (1989); 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).

[6]H. Okada, M. Takano, and Y. Takeda, Phys. Rev. B **42**, 6813 (1990).

[7]Hk. Müller-Buschbaum and W. Wollschläger, Z. Anorg. Allg. Chem. **414**, 76 (1975); B. Grande, Hk. Müller-Buschbaum, and M. Suhweizer, *ibid.* **428**, 120 (1977); Kimberly A. Kubat-Martin, Z. Fisk, and R. R. Ryan, Acta Crystallogr. C **44**, 1518 (1988).

[8]H. Okada, M. Takano, and Y. Takeda, Physica C **166**, 111 (1990).

[9]R. D. Zysler, M. Tovar, C. Rettori, D. Rao, H. Shore, S. B. Oseroff, D. C. Vier, S. Schultz, Z. Fisk, and S-W. Cheong, Phys. Rev. B **44**, 9467 (1991).

[10]M. Tokumoto, Y. Nishihara, K. Oka, and H. Unoki, Nature **330**, 48 (1987).

[11]S.-W. Cheong, J. D. Thompson, and Z. Fisk, Phys. Rev. B **39**, 4395 (1989).

[12]G. W. Crabtree, U. Welp, W. K. Kwok, K. G. Vandervoort, J. Z. Liu, and A. Umezawa, Physica C **162-164**, 1299 (1989).

[13]I. Dzyaloshinski, J. Phys. Chem. Solids **4**, 241 (1958); T. Moriya, Phys. Rev. **120**, 91 (1960).

[14]M. Tovar, X. Obradors, F. Pérez, S. B. Oseroff, R. J. Duro, J. Rivas, D. Chateigner, P. Bordet, and J. Chenavas, J. Applied Phys. **70**, 6095 (1991).

[15]P. Bordet, J. J. Capponi, C. Chaillout, D. Chateigner, J. Chenavas, Th. Fournier, J. L. Hodeau, M. Marezio, M. Perroux, G. Thomas, and A. Varela-Losada, in Proceedings of the *M²S-HTSC* Conference, Kanazawa, Japan, 22–26 July 1991 (in press).

[16]A. S. Borovik-Romanov and V. I. Ozhogin, Zh. Eksp. Teor. Fiz. **39**, 27 (1960) [Sov. Phys.—JETP **12**, 18 (1961)].

[17]A. H. Cooke, D. M. Martin, and M. R. Wells, J. Phys. C **7**, 3133 (1974).

[18]M. Matsuda, K. Yamada, K. Kakurai, H. Kadowaki, T. R. Thurston, Y. Endoh, Y. Hidaka, R. J. Birgeneau, M. A. Kastner, P. M. Gehring, A. H. Moudden, and G. Shirane, Phys. Rev. B **42**, 10 098 (1990), and references cited therein.

[19]S. Chakravarty, B. I. Halperin, and D. R. Nelson, Phys. Rev. Lett. **60**, 1057 (1988).

[20]I. Tomeno, M. Yoshida, K. Ikeda, K. Tai, K. Takamuku, N. Koshizuka, S. Tanaka, K. Oka, and H. Unoki, Phys. Rev. B **43**, 3009 (1991).

[21]D. Fiorani, in *The Time Domain in Surface and Structural Dynamics*, edited by G. J. Long and F. Grandjean (Kluwer Academic, Dordrecht, 1988), Chap. 24, pp. 391–428.

[22]X. Obradors, B. Martinez, X. Batlle, J. Rodríguez-Carvajal, M. T. Fernández-Díaz, J. L. Martínez, and P. Odier, J. Appl. Phys. **70**, 6329 (1991); X. Batlle, X. Obradors, and B. Martínez, Phys. Rev. B **45**, 2830 (1992).

[23]A. Butera, A. Caneiro, M. T. Causa, L. B. Steren, R. Zysler, and M. Tovar, Physica C **160**, 341 (1989).

[24]Ph. Galez, P. Schweiss, G. Collin, and R. Bellissent, J. Less-Common Met. **164&165**, 784 (1990).

[25]C. Rettori, D. Rao, S. Oseroff, R. D. Zysler, M. Tovar, Z. Fisk, S-W. Cheong, S. Schultz, and D. C. Vier, Phys. Rev. B **44**, 826 (1991).

[26]J. Beille, G. Fillion, B. Barbara, Th. Grenet, M. Cyrot, A. Gerber, and J. L. Martínez, in Proceedings of the International Conference of Magnetism, Edinburgh (U.K.), 2–6 September 1991 (in press).