Boundary for weak ferromagnetism in $Sm_{2-x}Gd_xCuO_4$ solid solutions

L. B. Steren
Centro Atómico Bariloche and Instituto Balseiro, 8400 San Carlos de Bariloche, Río Negro, Argentina

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

S. B. Oseroff
San Diego State University, San Diego, California 92182
(Received 2 December 1991; revised manuscript received 18 March 1992)

dc-magnetization and electron-spin-resonance measurements in the solid solutions $Sm_{2-x}Gd_xCuO_4$ have shown weak ferromagnetism for $1<x\leq 2$. Low-temperature values for the extrapolated spontaneous magnetization associated with a spin canting of the Cu moments, M_{Cu}, and the internal magnetic field, H_i^{Gd}, that polarizes the rare-earth ions have been determined. An exchange coupling constant $J_{Gd\text{-}Cu}=1.0(4)$ meV has been estimated from the ratio between these two parameters. Hysteresis loops show a small coercive field and differences in the remanent magnetization between field-cooled and zero-field-cooled samples. The possible relation of the boundary for weak ferromagnetism in the series of R_2CuO_4 cuprates with the existence of local static distortions of the lattice is discussed in terms of Dzyaloshinski-Moriya exchange interactions between the Cu ions.

I. INTRODUCTION

The rare-earth cuprates, R_2CuO_4, with $R=$Pr, Nd, and Sm, are parent compounds of the electron-doped high-T_c superconductors,[1,2] $R_{2-x}(Ce,Th)_xCuO_4$. The Cu spins order in these materials at about 250–280 K in a simple antiferromagnetic configuration.[3,4] Other members of the series, with $R=$Gd, Tb, and heavier rare earths, also present a weak ferromagnetic component[5–7] and do not show superconductivity when doped with Ce or Th. Thus, superconductivity (SC) and weak ferromagnetism (WF) seem to be mutually exclusive in these materials. An extensive investigation[6] of the magnetic properties of several $(R,R')_2CuO_4$ solid solutions suggests a boundary for WF in the cuprates associated with the size of the planar CuO_2 lattice. Eu_2CuO_4, with $a\approx 3.910(1)$ Å (Ref. 8), lies on this boundary, presenting extremely weak indications of ferromagnetism[6,9,10] in the pure compound and difficulties to achieve superconductivity in Ce-doped samples.[2] Both the WF and SC properties of Eu_2CuO_4 have been found to be extremely sensitive to the preparation procedures and annealing conditions.[9] Sm_2CuO_4 and Gd_2CuO_4 are located at either side of this boundary. Both compounds order antiferromagnetically[4,5] at $T_N\approx 270$–280 K but, while $Sm_{1.85}Ce_{0.15}CuO_4$ is a superconductor[1,2] with $T_c\approx 20$ K, $Gd_{2-x}Ce_xCuO_4$ presents WF up to the Ce solubility limit[11] at $x\approx 0.16$ with no indication of superconductivity above 4 K. We present here a study of the evolution of WF in the series of solid solutions $Sm_{2-x}Gd_xCuO_4$ through dc magnetic susceptibility and electron-spin-resonance (ESR) measurements.

II. EXPERIMENTAL DETAILS

Ceramic samples of $Sm_{2-x}Gd_xCuO_4$, with $0\leq x\leq 2$, were prepared in a solid-state reaction from stoichiometric amounts of Gd_2O_3, Sm_2O_3, and CuO. The oxides were pressed into pellets and allowed to react in air at 950 °C for 24 h. In a second treatment the samples were ground again, pressed and sintered at 1100 °C. X-ray diffraction measurements showed a single phase with the tetragonal Nd_2CuO_4-type[1] (T') structure in the whole composition range studied. The measured lattice parameters for the intermediate concentrations followed a Vegard's rule between those of the pure compounds: $a(Sm_2CuO_4)=3.921(3)$ Å and $a(Gd_2CuO_4)=3.887(3)$ Å. These values are in agreement with previously reported x-ray-diffraction analysis.[8]

Magnetization measurements were performed using a Faraday Balance Magnetometer with applied fields $0.2\leq H_a\leq 12.5$ kG, in the temperature range 60–360 K. Hysteresis loops were measured with a vibrating sample magnetometer at 77 K.

Magnetic resonance experiments were done in a Bruker ESP 300 Spectrometer and a Varian V4500, operating in the X band (9 GHz). The samples were powdered and mixed with KCl (in a 1:3 ratio) for the ESR experiments in order to minimize texture effects.

III. RESULTS AND ANALYSIS

A. dc magnetization

As reported in Refs. 5 and 6, Gd_2CuO_4 presents a magnetization linear in the applied field H_a for $T>320$ K.

The magnetic susceptibility follows a Curie-Weiss (CW) law, $\chi(T)=C_{Gd}/(T+\Theta)$, with a Curie constant, C_{Gd}, in good agreement with the expected value for the free Gd^{3+} ($4f^7;{}^8S_{7/2}$) ion, corresponding to an effective magnetic moment, $\mu_{eff}=7.94\mu_B$/Gd atom. The paramagnetic contribution from the Cu lattice is negligible, as expected from a comparison with the magnetic susceptibility of La_2CuO_4 (Ref. 12) and Y_2CuO_4 (Ref. 13), where the R ions are nonmagnetic. Below a characteristic temperature, $T_0\simeq 320$ K, the magnetization exhibits nonlinearity as a function of the applied field, associated with the onset of weak ferromagnetism. However, for applied magnetic fields larger than a few hundred gauss, the magnetization approaches a linear regime well described by[5]

$$M_{dc}(T)=M_{Cu}(T)+\chi_d(T)[H_a+H_i^{Gd}(T)] , \quad (1)$$

where $\chi_d(T)\equiv dM_{dc}(T)/dH_a|_{Ha\to\infty}$ corresponds closely to the paramagnetic susceptibility of the Gd ions, as shown in Fig. 1. From the data in the temperature range $60\le T\le 360$ K, we have determined $\mu_{eff}=7.99(1)\mu_B$/Gd atom and a CW temperature, $\Theta=14(2)$ K. $M_{Cu}(T)$ is associated with the net magnetization of the CuO_2 planes due to the canting of the Cu moments and $H_i^{Gd}(T)$ represents an internal field that polarizes the rare-earth paramagnetic moments, which results from their magnetic coupling to the ordered copper lattice.

As in Ref. 7, Eq. (1) may be rewritten as

$$\chi_d^{-1}(T)[M_{dc}(T)-\chi_d(T)Ha] = H_i^{Gd}(T)+C_{Gd}^{-1}(T+\Theta)M_{Cu}(T) \quad (2)$$

and for temperature-independent values of both M_{Cu} and H_i^{Gd} this expression results in a linear function of T, whose slope is proportional to M_{Cu}. The internal field, H_i^{Gd}, may be determined from its extrapolated value for $T=-\Theta$. In our case, the experimental data approach this linear dependence for $T<140$ K, and from this low-temperature asymptotic behavior, we have determined $M_{Cu}(0)=3.5(15)\times 10^{-3}\mu_B$/Cu atom and $H_i^{Gd}(0)=550(80)$ G.

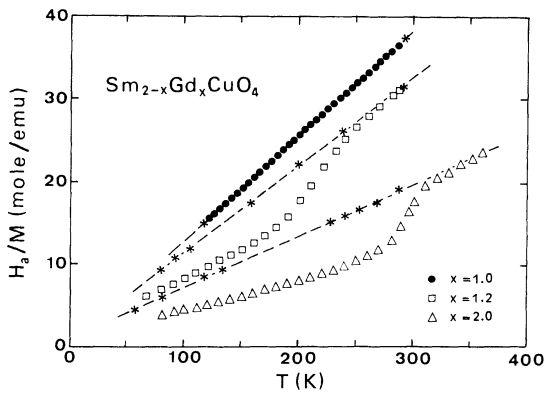

FIG. 1. Inverse of the apparent magnetic susceptibility of the Gd sublattice, H_a/M, as determined for $Sm_{2-x}Gd_xCuO_4$ with an applied field $H_a=1000$ G. The magnetization M was derived from the measured data after subtracting the Sm paramagnetic contribution and the diamagnetic corrections. The * symbols correspond to the inverse of the measured high-field derivative, dM/dH_a, and the dashed lines to a CW fit of these data, from where $\mu_{eff}=7.99(1)$, 7.91(1), and $7.93(1)\mu_B$/Gd atom and $\Theta=14(2)$ K, 8(2) K, and 2(2) K have been determined for $x=2.0$, 1.2, and 1.0, respectively.

Previous measurements in single crystals[6] have shown that the internal field follows a $H_i^{Gd}(\theta,T)=H_i^{Gd}(\pi/2,T)\sin\theta$ law, as a function of the angle, θ, between H_a and the c axis. Assuming random orientation of the microcrystals in polycrystalline ceramic samples, the angular average for the internal field is given[11] by

$$\langle H_i^{Gd}(\theta,T)\rangle=(\pi/4)H_i^{Gd}(\pi/2,T) .$$

Thus, the value for the internal field derived in Ref. 6 from single-crystal measurements has been multiplied by a factor $(\pi/4)$ in order to compare it in Fig. 3 with our results in ceramic samples.

At the other end of the series, Sm_2CuO_4 presents a dc magnetization[14] linear in H_a for the whole temperature range, showing no indication of WF. The temperature dependence of the susceptibility, $\chi_{Sm}(T)$, contains (after diamagnetic corrections) two contributions from the Sm^{3+} ions:[14,15] a Curie-Weiss component arising from the ground-state multiplet ($4f^5;{}^6H_{5/2}$) and a Van Vleck term mainly due to the first excited ${}^6H_{7/2}$ multiplet. Antiferromagnetic order of the Cu lattice at $T_N\simeq 280$ K has been reported from neutron-diffraction experiments.[4] However, no specific feature associated with this transition has been observed in the dc magnetization.

For the samples with intermediate concentrations, $Sm_{2-x}Gd_xCuO_4$, we have found a CW behavior at high temperatures, with the onset of weak ferromagnetism occurring at a temperature T_0, which varies very little from $T_0\approx 320$ K for $x>1.4$. For $x<1.4$, T_0 decreases reaching a value of ≈ 250 K for $x=1.1$, as shown in Fig. 2. In analogy with the case of Gd_2CuO_4, the measured magnetization below T_0 may be written as

$$M_{dc}(T)=M_{Cu}(T)+x\chi_{Gd}(T)(H_a+H_i^{Gd}) +(2-x)\chi_{Sm}(T)(H_a+H_i^{Sm}) . \quad (3)$$

The high-field differential susceptibility is given, within experimental accuracy, by

$$\chi_d(T)=x\chi_{Gd}(T)+(2-x)\chi_{Sm}(T) ,$$

with an average value for the Gd^{3+} moments, $\mu_{eff}=7.9(1)\mu_B$/Gd atom, and using for χ_{Sm} the values derived from the measured susceptibility of Sm_2CuO_4. We have assumed identical diamagnetic corrections throughout the series and neglected any contribution from the Cu lattice. The CW temperatures decrease with Gd dilution, down to $\Theta=2(2)$ K for $x=1$.

We have found weak ferromagnetism only for samples with $1<x\le 2$. The measured internal field is in this case a weighted average of those acting on the Gd and Sm ions, respectively. However, since $\chi_{Gd}\gg\chi_{Sm}$, the relative weighting factor for H_i^{Sm} is expected to be small within the entire composition range of interest:

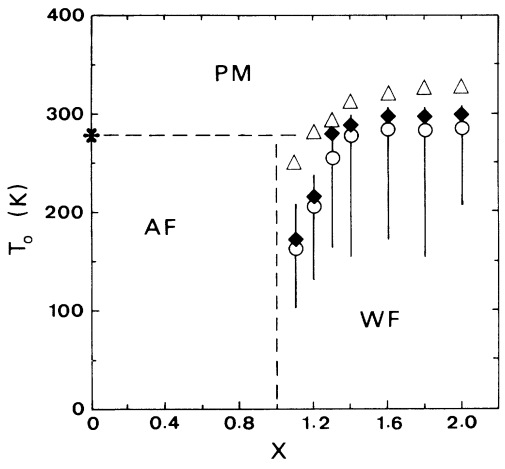

FIG. 2. Characteristic temperatures in $Sm_{2-x}Gd_xCuO_4$ vs x: (△) Onset of deviations from Curie-Weiss behavior in the magnetic susceptibility, T_0. (○) temperatures where $H_i^{Gd}(T)$ reaches 50% of its maximum value $H_i^{Gd}(0)$. The vertical bars indicate the temperature interval where $H_i^{Gd}(T)$ varies from 10 to 90%. (◆) Onset of the low-field microwave absorption lines associated with a resonance of the CuO_2 planes (T_{ESR}). For comparison, the Néel temperature T_N for Sm_2CuO_4, as determined in Ref. 4 from neutron-diffraction data, is also shown as (*). The dashed lines indicate approximate boundaries separating the paramagnetic (PM), antiferromagnetic (AF), and weak-ferromagnetic (WF) regions in the magnetic phase diagram.

$(2-x)\chi_{Sm}/(x\chi_{Gd})<0.04$ and thus its contribution to Eq. (3) has been neglected. Within this approximation we have determined $H_i^{Gd}(0)$ for different Gd concentrations and the values obtained are given in Fig. 3.

For the highest concentrations, $1.6\leq x\leq 2$, its powder average remains nearly constant at $H_i^{Gd}(0)\cong 550$ G. For lower Gd concentrations, the internal field decreases rapidly, becoming negligible for $x\approx 1$. The measured values of $M_{Cu}(0)$ also decrease with x and a linear relation has been found between $H_i^{Gd}(0)$ and $M_{Cu}(0)$ along the series of solid solutions. The proportionality constant is $1.8(5)\times 10^5$ G-Cu atom/μ_B.

We have measured hysteresis loops at 77 K that show small coercive field (10–25 G) which are slightly larger than those reported[5,6] for Gd_2CuO_4 and $EuTbCuO_4$ single crystals. A remanent magnetization, M_r, has been measured which is dependent on the magnetic history of the samples. M_r presents small values in zero-field-cooled (ZFC) samples but, after cycling the samples up to a finite magnetic field at constant temperature, it increases as a function of the maximum field reached during the cycle. However, the high-field dc magnetization

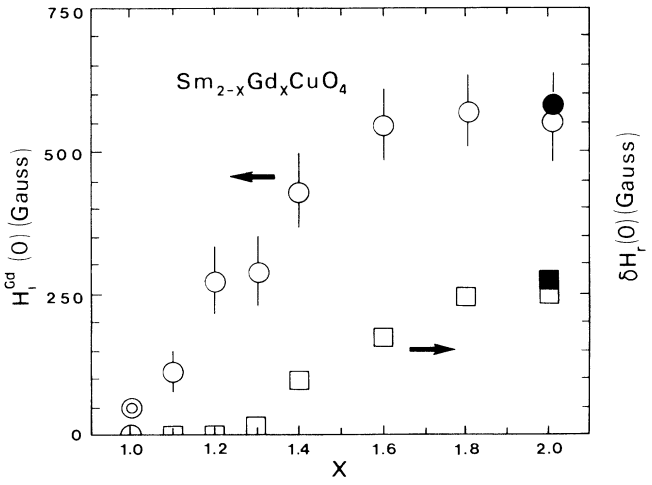

FIG. 3. Gd concentration dependence of (○) the powder average of the internal field $H_i^{Gd}(0)$, as determined from the dc magnetization of ceramic samples and (□) the powder average low-temperature shift of the Gd^{3+} ESR line, $\delta H_r(0)$. All the data correspond to ZFC samples, except for $x=1.0$, where (⊙) indicates a value measured in a FC sample. For comparison, numerically calculated values from single-crystal data of Ref. 6 are also shown with solid symbols.

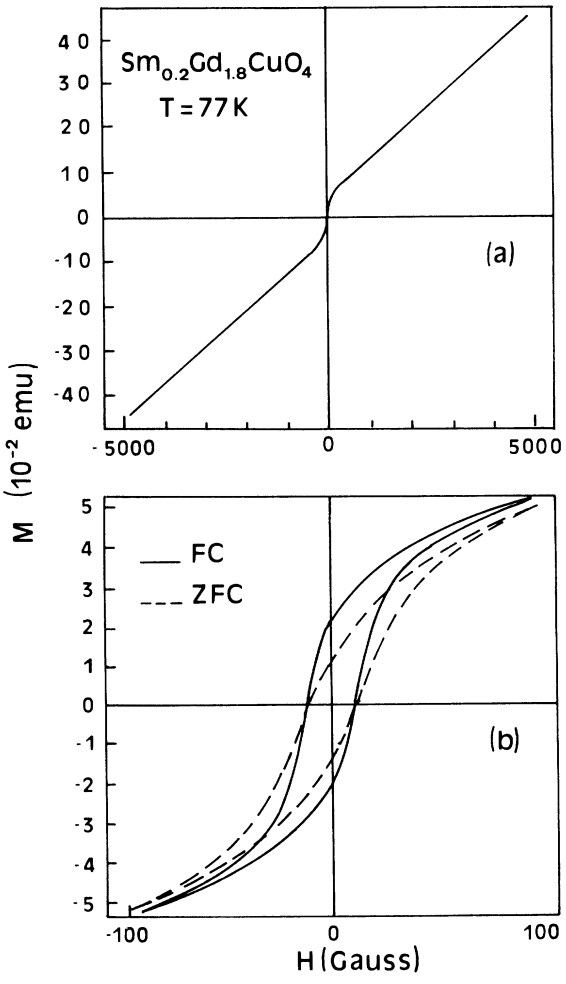

FIG. 4. Hysteresis loops measured at 77 K for a 250-mg sample of $Sm_{0.2}Gd_{1.8}CuO_4$. Data were taken for (a) a ±5-kG cycle and (b) a ±100-G cycle. A remanent magnetization is observed which depends on the magnetic history of the sample as explained in the text. The two curves shown in (b) correspond to cycles in the ±100-G interval for the sample cooled either in zero field (ZFC) or in 10 kG (FC). The small coercive field remains almost unchanged.

remains unaffected, including the extrapolated spontaneous magnetization, M_s. After applying fields above ≈ 1 kG, M_r begins to saturate and reaches values ≈ 30–$40\,\%$ of M_s. The coercive field is not affected by the cycling. In Fig. 4 we show typical loops. Field-cooling (FC) the samples in a magnetic field produces similar effects on the hysteresis loops leaving almost unchanged the high-field behavior. In the particular case of $x \approx 1.0$, where no weak ferromagnetism was observed for ZFC samples, a small WF component was induced by cooling the sample in a magnetic field of 10 kG. An estimated value of $H_i^{Gd} \approx 50$ G was obtained for the internal field in this case. A rotation of the ceramic samples with respect to the measuring coils showed that M_r remains fixed and parallel to the direction of the magnetic field applied while cooling the sample.

B. Electron spin resonance

The ESR spectrum presents a broad line ($\Delta H_{pp} \approx 2.5$ kG) associated with the paramagnetic resonance of the Gd^{3+} ions. For $T > 320$ K, the field for resonance corresponds to $g \approx 2$, as expected for the $^8S_{7/2}$ ground state. For pure Gd_2CuO_4 a shift of the resonance from the high-temperature value, $\delta H_r(T)$, has been measured[6] in single crystals for $T \leq T_0$ and H_a applied parallel to the CuO_2 planes. This shift saturates at $\delta H_r(0) = 500(150)$ G, which is significantly smaller than the static internal field, $H_i^{Gd}(0)$, determined from dc-magnetization measurements. The difference found between $\delta H_r(0)$ and $H_i^{Gd}(0)$ has been related to the dynamic coupling between the paramagnetic Gd moments and the WF Cu lattice.[16] In this case, it is more difficult to estimate the powder average due to the anomaly observed[6] in the angular dependence for H_a oriented very close to the c axis. We have calculated numerically a value $\langle \delta H_r(0) \rangle \approx 275$ G for a powder average from the single-crystal data of Ref. 6, which is in agreement with the results measured for ceramic samples.[11] For $x < 2$, $\delta H_r(0)$ decreases as a function of x, as shown in Fig. 3. This shift remains smaller than $H_i^{Gd}(0)$, but follows a similar dependence on the Gd concentration x, becoming negligible for $x \approx 1$.

An additional microwave absorption line, also a signature[6] of WF, was observed at low magnetic fields for $x \geq 1.2$, in either FC or ZFC samples. For $x = 1.1$ we were able to observe this absorption line only for samples FC in applied fields of 10 kG, although with a very small intensity. The intensity of this absorption line decreases rapidly with increasing T at temperatures near T_0. The intensity becomes smaller than the experimental resolution at about 20 K below T_0.

IV. DISCUSSION

Our results show that the strength of the weak ferromagnetism in the $Gd_{1-x}Sm_xCuO_4$ system, as measured by the magnitude of $M_{Cu}(0)$ and $H_i^{Gd}(0)$, decreases with x, becoming negligible for $x \simeq 1$. A comparison with other solid solutions in the T' cuprate series shows that a qualitatively similar boundary for weak ferromagnetism in $Eu_{2-x}Gd_xCuO_4$ (Ref. 5) for $x \approx 0$ and 1.4 in $Nd_{2-x}Gd_xCuO_4$ (Ref. 17). Assuming Vegard's rule for the lattice parameters in the $R_{2-x}Gd_xCuO_4$ series of solid solutions, the limit for WF results in $a \approx 3.910$ Å for $R = $ Eu, $a \approx 3.905$ Å for $R = $ Sm, and $a \approx 3.913$ Å for $R = $ Nd.

The existence of a boundary for WF associated with the size of the crystal lattice may be associated with a misfit of the RO fluoride-type planes between the CuO_2 planar square sheets. Gd_2CuO_4, with $a = 3.893(1)$ Å (Ref. 8), is the last member of the series that can be obtained under normal pressures, and x-ray-diffraction measurements[8,18] have shown anomalously large thermal parameters for the O(1) ions in the CuO_2 planes. This observation has been interpreted[18] in terms of static disordered local distortion, involving average displacements of 0.18 Å for the O(1) ions in the basal plane. Even larger effects have been reported[19] for Tm_2CuO_4, which is the compound with smallest lattice parameter that has been synthesized under hydrostatic pressure.[20] Different superstructures have been observed for this compound[19] and also for Gd_2CuO_4, involving small deformations of the tetragonal structure. When the crystal structure is refined in an average tetragonal lattice (with $a = 3.837$ Å), oxygen displacements within the planes as large as 0.36 Å have been estimated[20] for Tm_2CuO_4. Independent indications of this kind of local distortion have been derived from the ESR spectrum[10] of dilute Gd^{3+} ions in Eu_2CuO_4 and from Raman scattering experiments[21] in Gd_2CuO_4.

Antisymmetric exchange interactions of the Dzyaloshinski-Moriya[22] (DM) type between the Cu ions have been suggested[5] as a possible source of the observed WF. This suggestion implies that the CuO_2 lattice is not exactly square planar in the heavier rare-earth cuprates because the symmetry of the Cu—O—Cu bonds has to be reduced from that in the perfect T' structure in order to allow nonzero DM interactions. From this point of view, a magnetic phase boundary for WF associated with the size of the R ions seems reasonable. In this case the magnetic measurements indicate a limit for WF at about $a = 3.910(5)$ Å, which also signals the appearance of microstructural distortions of the tetragonal structure.

From our results we have also estimated the magnitude of the magnetic coupling between Gd and Cu ions. Assuming a Heisenberg exchange coupling between Gd and Cu moments of the form

$$\mathcal{H} = \sum_{i,j} J_{ij} \mathbf{S}_{Gd}^{(i)} \cdot \mathbf{S}_{Cu}^{(j)} \cong \sum_{NN} J_{Gd\text{-}Cu} \mathbf{S}_{Gd} \cdot \mathbf{S}_{Cu}^{(NN)}$$

and limiting the sum to the $z = 4$ nearest Cu neighbors, the ratio between the internal field polarizing the Gd moments and the magnetization of the Cu lattice is given in a mean-field approximation by

$$H_i^{Gd}(T) = -(zJ_{Gd\text{-}Cu}/g_{Gd}g_{Cu}\mu_B^2) M_{Cu}(T) \ .$$

Taking for the gyromagnetic factors the free-ion value for Gd^{3+}, $g_{Gd} = 1.991$, and a free-electron value for the Cu moments, $g_{Cu} = 2.0$, a value $J_{Gd\text{-}Cu} = 1.0(4)$ meV was obtained. This is an order of magnitude larger than the value estimated[7] for the coupling between Tb and Cu moments in Tb_2CuO_4, $J_{Tb\text{-}Cu} = 0.15(5)$ meV.

ACKNOWLEDGMENTS

We acknowledge partial support from the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (R.A.), the National Science Foundation (U.S.A.) under Grant Nos. DMR-88-01317 and INT-89-00851, the Fundación Antorchas (R.A.), the Center for Magnetic Recording (U.S.A.), and the Cooperation Program with the Kernforschungzentrum Karlsruhe (Germany).

[1]Y. Tokura, H. Takagi, and S. Uchida, Nature **337**, 345 (1989).

[2]J. T. Markert, E. A. Early, T. Bjørnholm, S. Ghamaty, B. W. Lee, J. J. Neumeier, R. D. Price, C. L. Seaman, and M. B. Maple, Physica C **158**, 178 (1989).

[3]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. Sleigh, M. A. Subramanian, S. Uchida, H. Takagi, and Y. Tokura, Nature **338**, 49 (1989).

[4]S. Skanthakumar, J. W. Lynn, J. L. Peng, and Z. Y. Li, J. Appl. Phys. **69**, 4866 (1991).

[5]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).

[6]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).

[7]M. Tovar, X. Obradors, F. Pérez, S. B. Oseroff, R. J. Duro, J. Rivas, D. Chateigner, P. Bordet, and J. Chenavas, Phys. Rev. B **45**, 4729 (1992).

[8]For lattice parameters of R_2CuO_4 compounds with T' structure, see, for instance, Kimberly A. Kubat-Martin, Z. Fisk, and R. R. Ryan, Acta Crystallogr. C **44**, 1518 (1988), for R=Gd; K. A. Kubat-Martin and R. R. Ryan [(unpublished), quoted in M. Tovar *et al.*, Phys. Rev. B **39**, 2661 (1989)], for R=Eu; Ref. 4 for R=Sm; and M. Matsuda *et al.*, Phys. Rev. B **42**, 10 098 (1990), for R=Nd. See also Ref. 18.

[9]D. C. Vier, S. Schultz, C. Rettori, D. Rao, S. B. Oseroff, M. Tovar, Z. Fisk, and S-W. Cheong, J. Appl. Phys. **69**, 4872 (1991).

[10]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).

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

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

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

[14]C. L. Seaman, N. Y. Ayoub, T. Bjørnholm, E. A. Early, S. Ghamaty, B. W. Lee, J. T. Markert, J. J. Neumeier, P. K. Tsai, and M. B. Maple, Physica C **159**, 391 (1989).

[15]J. H. Van Vleck, in *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), pp. 245–249.

[16]A. Fainstein, M. Tovar, S. B. Oseroff, and Z. Fisk (unpublished).

[17]M. B. Maple, N. Y. Ayoub, J. Beille, T. Bjørnholm, Y. Dalichaouch, E. A. Early, S. Ghamathy, B. W. Lee, J. T. Markert, J. J. Neumeier, G. Nieva, L. M. Paulius, I. K. Schuller, C. L. Seaman, and P. K. Tsai, in *Progress in High Temperature Superconductivity,* edited by R. Nicolsky (World Scientific, Singapore, 1990), Vol. 25, p. 536.

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

[19]P. Bordet, J. J. Capponi, C. Chaillout, D. Chateigner, J. Chenavas, Th. Fournier, J. L. Houdeau, M. Marezio, M. Perroux, G. Thomas, and A. Varela, Physica C **185-189**, 539 (1991).

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

[21]M. L. Laguna, M. L. Sanjuán, M. Tovar, Z. Fisk and P. Canfield (unpublished).

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