Weak ferromagnetism induced by the external field above T_N in Gd_2CuO_4

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A detailed study of the temperature and field dependence of the dc magnetization near the antiferromagnetic (AF) transition in Gd_2CuO_4 shows the presence of field-induced weak ferromagnetism (WF) well above the Néel temperature T_N. ac susceptibility measurements indicate $T_N=266(3)$ and 282(3) K, for single crystals and ceramic samples, respectively. The shift of the electron-spin-resonance line of the Gd^{3+} ions as a function of temperature T, $\delta H_r(T)$, is compared with the static internal field $H_i(T)$, which describes the coupling between the paramagnetic Gd lattice and the WF component of the Cu moments. Both $\delta H_r(T)$ and $H_i(T)$ show that the WF persists up to ≈ 50 K above T_N. The initial susceptibility (for $H<100$ G) presents a contribution in excess of the paramagnetism of Gd ions. For $T \geqslant T_N$, it decays as $K(T-T_N)^{-1}$, with $K=0.20(3)$ emu K mol. The relationship between this result and the strong two-dimensional AF correlations in these cuprates is discussed.

The R_2CuO_4 cuprates of heavy rare earths (R =Gd,Tb,... ,Tm) present weak ferromagnetism (WF) below the antiferromagnetic Néel temperature T_N due to a small canting of the Cu sublattice caused by Dzyaloshinkii–Moriya (DM) interactions.[1–3] Different experimental features characterize[4] the complex magnetic behavior of these materials around T_N: a nonzero spontaneous magnetization $M_s(T)$ linearly extrapolated from the high-field magnetization, a sharp peak of the dc and ac low-field susceptibilities, a shift of the electron-spin-resonance (ESR) spectrum of the Gd ions $\delta H_r(T)$, and the presence of a low-field microwave absorption. As was pointed out in Ref. 5, the onset of both M_s and δH_r occurs for Gd_2CuO_4 and $Gd_{2-x}Ce_xCuO_4$ at a temperature well above the T_N determined from the peak of the low-field magnetization. An observation of WF above T_N has also been recently reported[6] for Y_2CuO_4. We present here a detailed study of the WF transition in Gd_2CuO_4 through ac susceptibility, dc magnetization, and ESR measurements, analyzing the effects of magnetic coupling between the R ions and the Cu lattice.

Single crystals were grown in Pt crucibles using a flux technique.[1] All samples had the Nd_2CuO_4-type[7] crystal structure, usually identified as T'. Typical crystals were thin platelets ($2\times2\times0.1$ mm^3) oriented perpendicular to the c axis. Ceramic samples prepared from pressed pellets of the corresponding oxides were also measured when larger samples were needed. dc magnetization measurements were performed using either a vibrating sample magnetometer, a Quantum Design superconducting quantum interference device (Squid) magnetometer, or a homemade Faraday balance magnetometer. ac susceptibility measurements were carried out in a Lake Shore susceptometer and electron paramagnetic resonance in an ESP 300 Bruker spectrometer for the X band (9 GHz) and a modified Varian V4500 for the Q band (35 GHz).

The ac susceptibility $\chi_{ac}(T)$, measured with an excitation field of 1 G, presents a sharp maximum at 266(3) and 282(3) K for the single-crystal and ceramic samples, respectively.[8] The temperature of the peak is frequency independent in the measured range (10–1000 Hz) and agrees with that of the low-field dc susceptibility.[1] We define T_N as the temperature of this peak.

Well above T_N ($T>330$ K), the dc magnetization $M_{dc}(T)$ presents a paramagnetic behavior with a Curie–Weiss constant determined essentially by the Gd^{3+} moments in the $^8S_{7/2}$ ground state.[1] At lower temperatures, the high-field differential susceptibility, $\chi_{diff} \equiv \partial M_{dc}(T)/\partial H|_{H\to\infty}$ still follows a Curie–Weiss law but $M_{dc}(H,T)$ extrapolates to a finite value $M_s(T)$, associated with the WF of the system.[1,3] $M_s(T)$, determined by a linear extrapolation from the measurement of $M_{dc}(T)$ in the range between 1 and 12.5 kG, starts to develop at about 310 and 330 K for the single crystal and ceramic samples, respectively.[1,5] A comparison with the temperature dependence of the low-field measurements determines a temperature range (T_N,T_N+50 K), where the WF is strongly dependent on the applied magnetic field. We have examined in detail the field and temperature dependence of $M_{dc}(T)$ in this temperature interval.

The high-field dc magnetization ($H>1000$ G) may be described by a linear dependence, $M_{dc}(H,T)=M_s(T)$

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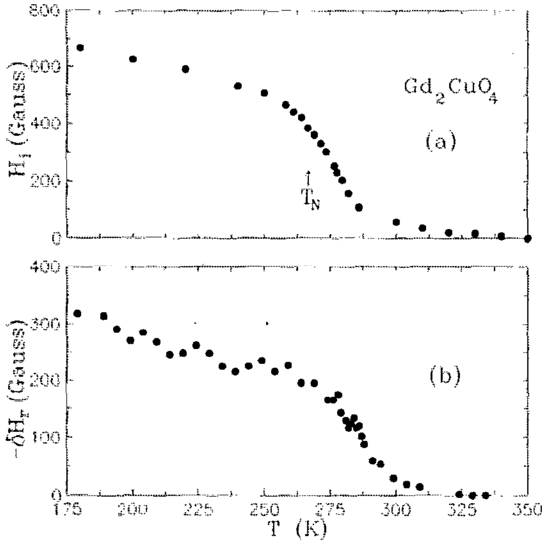

FIG. 1. (a) Static internal field $H_i(T)$ and (b) shift of the Gd^{3+} ESR line $\delta H_r(T)$ measured at 9.3 GHz for a Gd_2CuO_4 single crystal. The arrow corresponds to the Néel temperature determined from the $\chi_{dc}(T)$ peak.

$+\chi_{Gd}(T)H$. Here $M_s(T)$ has two contributions,[1] $M_s(T) = M_{Cu}(T)+\chi_{Gd}(T)H_i(T)$, arising, respectively, from the canting of the ordered Cu moments and the polarization of the paramagnetic Gd ions through an internal magnetic field. As determined in Ref. 9, $H_i(T)=\lambda' M_{Cu}(T)$, with $\lambda' = -1.8(5)\times 10^5$ G Cu atom/μ_B. We present in Fig. 1(a) values determined for $H_i(T)$ in a single crystal from data taken with applied fields larger than 1 kG. In the low-field limit, $M_{dc}(H,T)$ is linear in H above T_N with a slope that increases strongly as T_N is approached, as shown in Fig. 2. Below T_N a small remanent magnetization develops. We have measured the initial susceptibility $\chi_i(T)=dM_{dc}(H,T)/dH|_{H\to 0}$ in a 144 mg ceramic sample, which shows a peak in the ac susceptibility at $T_N=282(3)$ K. For applied fields up to 100 G we found a linear behavior for $T>T_N$. In Fig. 3 we compare $\chi_i(T)$ with the free-ion susceptibility of the Gd^{3+} moments $\chi_{Gd}(T)$. The excess susceptibility $[\chi_i(T)-\chi_{Gd}(T)]$, tends to diverge near

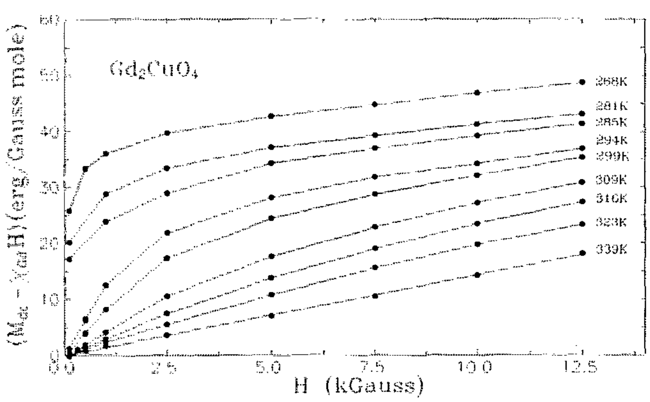

FIG. 2. Magnetic-field dependence of $[M_{dc}(H,T)-2\chi_{Gd}(T)H]$ measured for a Gd_2CuO_4 ceramic sample.

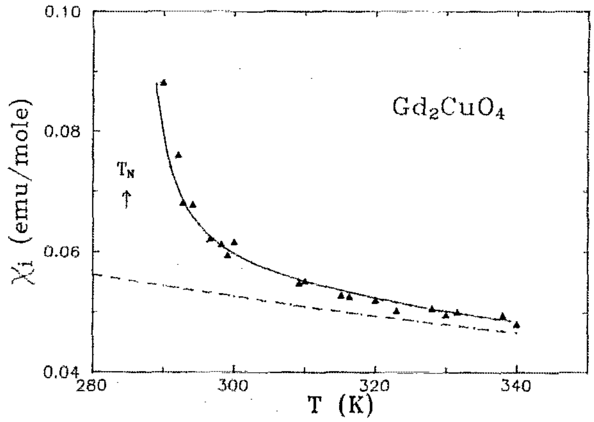

FIG. 3. Initial susceptibility $\chi_i(T)=dM_{dc}(T)/dH|_{H\to 0}$, measured for a Gd_2CuO_4 ceramic sample with applied fields up to 100 G. ▲ correspond to ac susceptibility measurements. The dashed line is the paramagnetic contribution $(\chi_0+2\chi_{Gd})$, and the solid line represents the fitting including the $K/(T-T_N)$ term.

T_N and may be described by a $K(T-T_N)^{-1}$ law, with $K=0.20(2)$ emu K/mol.

As we approach T_N, the field for resonance H_r of the Gd^{3+} ESR spectrum shifts[4] from its high-temperature value, which corresponds to the free-ion gyromagnetic factor, $g=1.99$. The onset of this shift has been observed[5] at temperatures higher than T_N. Since our ESR experiments require the use of magnetic fields larger than 1 kG ($H_r=3.3$ kG for the X band and $H_r=13.2$ kG for the Q band, when $g=2$), significant amounts of field-induced WF are expected to be present in these experiments, which results in the observation of the ESR shift $\delta H_r(T)$ up to temperatures much higher than T_N. Our measurements indicate that $\delta H_r(T)$ presents a similar temperature dependence for X and Q bands. In Fig. 1 we compare the results for the X band with the internal field $H_i(T)$, determined from $M_{dc}(T)$ measurements for 1 kG $<H<$ 12.5 kG. The difference in magnitude (a factor ≈ 2) has been associated[10] with the dynamic coupling between the Gd and Cu moments.

The field-induced WF above T_N may be analyzed in terms of a free energy for the coupled system,

$$\mathcal{F} = \left(\frac{A(T)}{2}\right)|\mathbf{l}|^2 + \left(\frac{1}{2\chi_0}\right)|\mathbf{m}|^2 + \boldsymbol{\beta}\cdot(\mathbf{l}\times\mathbf{m}) + \left(\frac{C}{4}\right)|\mathbf{l}|^4 + \left(\frac{1}{4\chi_{Gd}}\right)|\mathbf{M}_{Gd}|^2 + \lambda'\mathbf{M}_{Gd}\cdot\mathbf{m} - (\mathbf{m}+\mathbf{M}_{Gd})\cdot\mathbf{H}, \quad (1)$$

where $\mathbf{m}=(\mathbf{M}_1+\mathbf{M}_2)/2$ and $\mathbf{l}=(\mathbf{M}_1-\mathbf{M}_2)/2$ are the uniform and staggered magnetizations of the Cu lattice, respectively. $\mathbf{M}_1$ and $\mathbf{M}_2$ are the two antiferromagnetic sublattices of the Cu system. The third term, $\boldsymbol{\beta}\cdot(\mathbf{l}\times\mathbf{m})$, represents the antisymmetric exchange interaction within the Cu planes. The Gd sublattice is coupled to the uniform Cu magnetization through the term $\lambda'\mathbf{M}_{Gd}\cdot\mathbf{m}$. For $\lambda'=0$ this corresponds to the two-sublattice description of a canted antiferromagnet.[11] When $\mathbf{H}\perp\boldsymbol{\beta}$, $\mathbf{m}$ is parallel to $\mathbf{H}$

and represents a WF component. In this case $\boldsymbol{\beta}$, $\mathbf{l}$, and $\mathbf{H}$ are mutually perpendicular. We may define then a reference frame such that $\mathbf{m}=m\hat{x}$, $\mathbf{l}=l\hat{y}$, and $\boldsymbol{\beta}=\beta\hat{z}$. The equilibrium conditions are given by

$$\frac{\partial \mathscr{F}}{\partial m_x}=\left(\frac{1}{\chi_0}\right)m-H+\lambda' M_{\mathrm{Gd}}-\beta l=0,$$
$$\frac{\partial \mathscr{F}}{\partial M_{\mathrm{Gd},x}}=\left(\frac{1}{2\chi_{\mathrm{Gd}}}\right)M_{\mathrm{Gd},x}-H+\lambda' m=0, \quad (2)$$
$$\frac{\partial \mathscr{F}}{\partial l_x}=A(T)l+Cl^3-\beta m=0.$$

We may solve this set of nonlinear equations in the vicinity of the magnetic transition by taking into account that $|\mathbf{m}|$, $|\mathbf{l}|$, and $|\mathbf{M}_{\mathrm{Gd}}|$ are all small quantities and thus making a series expansion in powers of the applied field H. The Néel temperature T_N is determined by the zero of the determinant of the linearized equations,

$$\Delta(T_N)=A(T_N)(1-2\lambda'^2\chi_0\chi_{\mathrm{Gd}})-\beta^2\chi_0=0, \quad (3)$$

where we may write, as usual, $\Delta(T)\cong\nu(T-T_N)$ for $T\approx T_N$. For $T>T_N$, the resulting total magnetization is given by

$$\begin{aligned}m+M_{\mathrm{Gd}}\cong[&\chi_0+2\chi_{\mathrm{Gd}}(T)+2\lambda'\chi_0\chi_{\mathrm{Gd}}\\&\times(\lambda'\chi_0+2\lambda'\chi_{\mathrm{Gd}}-2)/(1-2\lambda'^2\chi_0\chi_{\mathrm{Gd}})\\&+\beta^2\chi_0^2(1-2\lambda\chi_{\mathrm{Gd}})^2/\nu(1-2\lambda'^2\chi_0\chi_{\mathrm{Gd}})\\&\times(T-T_N)]H. \quad (4)\end{aligned}$$

The first two terms correspond to the susceptibility of the uncoupled Cu and Gd lattices, respectively. The third term describes their magnetic coupling, and is expected to contribute less than 3% of $\chi_{\mathrm{Gd}}(T_N)$. The last term gives a field-induced weak ferromagnetic component arising from the DM interaction. Notice that this last term varies as $K(T-T_N)^{-1}$, in the same way as the excess contribution measured for $M_{\mathrm{dc}}(T)$. This kind of contribution was originally reported by Borovick-Romanov and Ozhogin[11] for $MnCO_3$ and also found[6] recently for Y_2CuO_4.

In the case of Y_2CuO_4, only the Cu lattice contributes to the WF and $K=\beta^2\chi_0^2/\nu=0.055(6)$ emu K/mol. The main difference in Gd_2CuO_4 is the enhancement factor $[1-2\lambda'\chi_{\mathrm{Gd}}(T_N)]^2\approx 7$, that appears due to the coupling to the paramagnetic lattice. The factor $[1-2\lambda'^2\chi_0\chi_{\mathrm{Gd}}(T_N)]$ is very close to unity for $T\approx T_N$. Values for $\beta\chi_0$ may be derived[11] from the low-temperature value $M_{\mathrm{Cu}}(0)=\beta\chi_0 M_0$, where $M_0\approx 0.4\mu_B$/Cu atom is the Cu magnetic moment in the antiferromagnetic lattice. In the case of Y_2CuO_4, a value of $\beta\chi_0=0.025(4)$ has been reported.[6] For Gd_2CuO_4, we estimate $\beta\chi_0=0.009(4)$ from the Cu magnetization,[9] $M_{\mathrm{Cu}}(0)=(3.5\pm 1.5)\times 10^{-3}\,\mu_B$/Cu atom. However, the smaller WF in Gd_2CuO_4 is enhanced in the expression for K by the Gd-Cu coupling. Using these values we have estimated $\nu^{-1}(Gd_2CuO_4)\approx 350$ emu K/mol, although with a large uncertainty due to the experimental error in the determination of M_{Cu}.

This value for ν^{-1} is of the same order of magnitude as that found[6] for Y_2CuO_4 ($\nu^{-1}\approx 100$ emu K/mol). As mentioned in Refs. 6 and 11, ν^{-1} is related to the staggered susceptibility of the system, which in a mean-field approximation would be given by $\nu^{-1}=C_m$, where C_m is the Curie constant of the antiferromagnetic species. If the values for ν^{-1} were analyzed in such a way, they would correspond to large effective moments (30–$50\mu_B$). This large staggered susceptibility may be related to the strong 2D magnetic correlations present in the CuO_2 planes near T_N, as was discussed in Ref. 12 for La_2CuO_4. This large staggered magnetization would also be responsible for the saturation of the WF component above T_N for moderate magnetic fields, as shown in Fig. 2.

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