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Suppression of weak ferromagnetism in small particles of Gd_2CuO_4

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Abstract. – Gd_2CuO_4 particles were synthesized by sol-gel techniques in order to study the effects of particle size d on the magnetic properties measured by dc magnetization and microwave absorption. Decreasing d reduced the intensity and temperature of onset of weak ferromagnetism, which was not detected at all in 850 Å particles. This finding is attributed to the impossibility of Cu three-dimensional antiferromagnetic ordering when d reaches a limit somewhat below the two-dimensional magnetic correlation length corresponding to bulk Gd_2CuO_4 at the Néel temperature.

The rare-earth cuprates R_2CuO_4 crystallize in tetragonal structures (La in the T phase, the others in T') in which R_2O_2 blocks are separated by CuO_2 planes [1]. The Cu moments exhibit strong antiferromagnetic (AF) coupling ($J_{Cu\text{-}Cu} \sim 1500$ K) [2], although the magnetic order is of short range over a wide temperature interval [3]. Three-dimensional (3D) order has been reported to develop in the Cu sublattice at Néel temperatures T_N in the range 250–280 K [4]. Interest in these materials has increased since the discovery that appropriate doping destroys the magnetic order in the CuO_2 planes and results in high-temperature superconductivity [5].

For R=Gd and heavier rare earths, the square Cu lattice is distorted by displacement of the oxygen atoms from their symmetric positions, giving rise to Dzyaloshinskii-Moriya interactions [6] which cause canting of the Cu moments and weak ferromagnetism (WF) [7]. The lattice constant value a = Cu—O—Cu = 3.910 Å [8], which corresponds to Eu_2CuO_4,

has been proposed as an upper limit for the existence of WF. Dc susceptibility measurements on polycrystalline R_2CuO_4 samples have shown that a characteristic feature of such WF is a difference between zero-field–cooled (ZFC) and field-cooled (FC) dc magnetizations [9]. The dependence of this irreversible behaviour on the annealing temperature used in synthesis [10] has been interpreted in terms of variation in the size of hypothetical WF clusters due to modification of the coherence of the oxygen displacements [10].

Alteration of the magnetic properties of the CuO_2 planes in R_2CuO_4 may be expected when the size of the R_2CuO_4 particle is of the order of the 2D correlation length of the copper AF ordering. To explore this, we have carried out dc magnetization and electron spin resonance (ESR) measurements of Gd_2CuO_4 powder samples with various particle sizes.

Gd_2CuO_4 samples were synthesized by sol-gel techniques, which allow the final particle size to be controlled by varying the calcination temperature. The appropriate nitrates were mixed in water, and urea was used as gelling agent [11]. The gel was decomposed by heating at 250 °C, and the resulting material was ground and heated to temperatures ranging from 600 °C to 950 °C at 50 °C intervals (table I). As reference material, a ceramic sample was also prepared by solid-state reaction of Gd_2O_3 and CuO. The polycrystalline powders were characterized analytically by inductively coupled plasma atomic-emission spectroscopy (ICP-AES) using a Perkin-Elmer 5000 spectrometer with Ar plasma. Structural characterization was carried out by X-ray powder diffraction using a Philips PW-1710 diffractometer. Room temperature lattice parameters were calculated by Rietveld refinement of the spectra. Particle size distributions were determined by photon correlation spectroscopy (PCS) and transmission electron microscopy (TEM). Dc magnetic measurements were performed on a Quantum Design SQUID magnetometer and a DMS-1660 vibrating sample magnetometer over the temperature range 4-300 K. Microwave magnetoabsorption measurements were performed at 9 GHz with a Bruker ESP 300 spectrometer between 100 K and 330 K. The C, H and N contents of the final sol-gel samples were below the detection limit of gravimetric pyrolysis measurements, showing that the urea had decomposed completely and had not contaminated the final samples. ICP measurements indicated a Gd/Cu mole ratio of 2.1 ± 0.1. X-ray diffraction data showed that the ceramic sample was a pure Gd_2CuO_4 phase and that the time required to obtain the desired phase in the sol-gel samples decreased with increasing calcination temperature. Small amounts of unreacted Gd_2O_3 and CuO were observed in the samples prepared below 750 °C but at the fields used they have minimal influence on dc magnetization, CuO being antiferromagnetic and Gd_2O_3 paramagnetic [12]; in resonance experiments they were found not to affect the

TABLE I. – *Characteristic of the different samples.*

Sol-gel samples	Calcination temperature (°C)	Gd_2CuO_4 (%)	a (Å)	size (Å)
A	950	> 95	3.894(1)	3500 ± 600
B	900	> 95	3.894(1)	2800 ± 500
C	850	> 95	3.894(1)	2700 ± 400
D	800	> 95	3.895(1)	2000 ± 300
E	750	95	3.895(1)	1600 ± 300
F	700	92	3.896(1)	1300 ± 200
G	650	90	3.896(1)	1100 ± 200
H	600	85	3.896(1)	850 ± 200
ceramic	1080	> 95	3.894(1)	> 10000

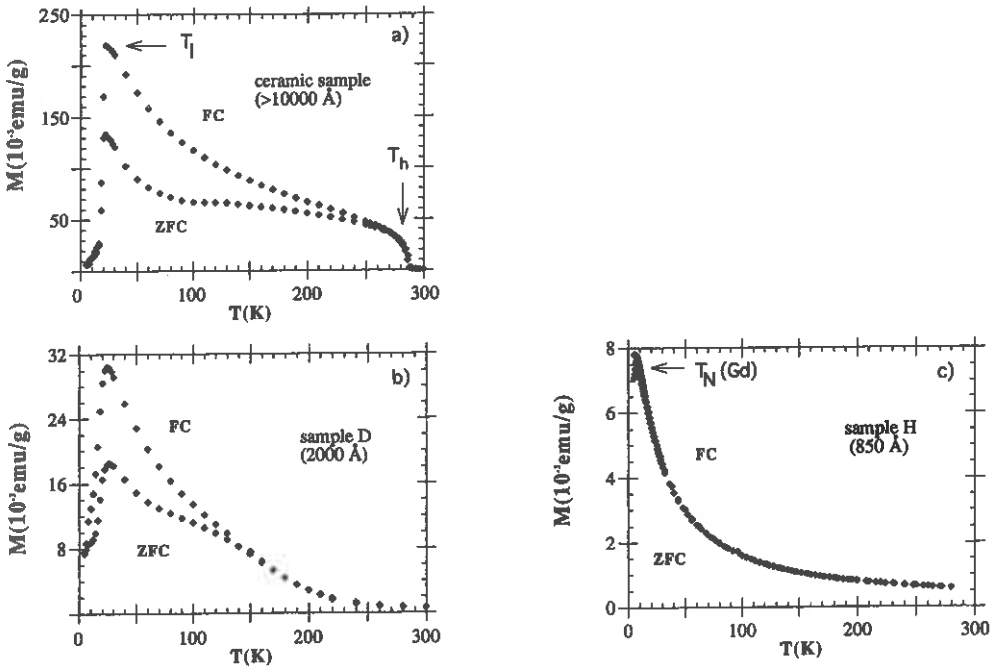

Fig. 1. – Magnetization of Gd_2CuO_4 samples *vs.* temperature, measured at a field of 5 Oe: *a*) ceramic, *b*) sol-gel calcinated at 800 °C (D), *c*) sol-gel calcinated at 600 °C (H). See text for the definition of T_h, T_l and T_N(Gd). Particle sizes are indicated in parentheses.

measured resonance lines. Rietveld refinement of the spectra indicated a slight increase in the lattice parameter a as calcination temperature decreased (table I). The average particle size of the samples, as measured by TEM, increased with calcination temperature (table I); PCS data showed the same trend.

Figure 1*a*) shows the temperature dependence of the dc magnetization $M_{dc}(T)$ of the ceramic sample at an applied field of 5 Oe. The onset of WF is signalled by the rapid increase in $M_{dc}(T)$ below a temperature $T_h \approx 290$ K which coincides with T_N, the 3D ordering temperature of the copper sublattice [13]. The peak around $T_l \approx 20$ K, which is due to a spin reorientation of the Cu moments [13], [14], is another signature of WF, as is the difference between FC and ZFC curves [9]. The behaviour of $\mathbf{M}_{dc}(H,T)$ is well described [13] by

$$\mathbf{M}_{dc}(H,T) = \mathbf{m}_{WF} + \chi_{Gd}(T)\mathbf{H}_0 = \frac{D}{2J_{Cu\text{-}Cu}}\mathbf{M}_0 + \chi_{Gd}(T)\mathbf{H}_{int} + \chi_{Gd}(T)\mathbf{H}_0\,, \qquad (1)$$

where $\mathbf{m}_{WF}$ is the WF component, $J_{Cu\text{-}Cu}$ is the value of the super-exchange integral between the copper moments $\mathbf{M}_0$, D is the modulus of the Dzyaloshinskii-Moriya vector, $\chi_{Gd}(T)$ the magnetic susceptibility of Gd^{3+} ions and $\mathbf{H}_{int}$, the average effective internal field at Gd sites is given [8] by $\mathbf{H}_{int} = \lambda_{Cu\text{-}Gd}\frac{D}{2J_{Cu\text{-}Cu}}\mathbf{M}_0$, $\lambda_{Cu\text{-}Gd}$ being the coupling constant for interaction between the Gd and Cu lattices.

Among the sol-gel samples calcinated below 850 °C (fig. 1*b*) and *c*)), $\mathbf{m}_{WF}$ decreased with calcination temperature. For sample H (fig. 1*c*)), the measured magnetization may be attributed to the paramagnetic free-ion Gd lattice; there was no indication of ferromagnetic polarization, neither T_h nor T_l nor differences between the ZFC and FC loops having been detected. The peak at $T_N(Gd) = 7$ K reflects the AF ordering of the Gd moments [15], whose

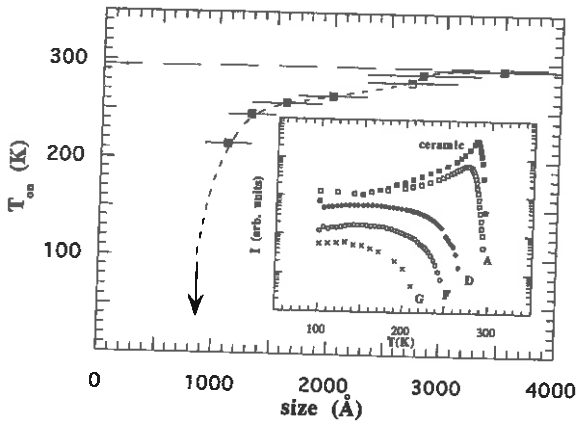

Fig. 2. – T_{on} for the WF resonance mode *vs.* particle size for the sol-gel samples. The dashed line shows the value for the ceramic sample. The arrow indicates the absence of T_{on} for sample H. The inset shows the temperature dependence of the intensity of the WF signal, normalized to the Gd^{3+} EPR resonance line, for selected samples.

AF ordering temperature remains the same as for bulk Gd_2CuO_4. T_h was the same for the largest particle size (sample A) as for the ceramic sample, ≈ 290 K, but decreased significantly for the other samples.

Microwave absorption has been found to be the most sensitive technique for measurement of the onset of WF [7]. The normal mode of this resonance, derived by Pincus [16], has been identified in Gd_2CuO_4 [17], as occurring, for X-band radiation (9 GHz), at a field of ≈ 100 Oe. For ceramic samples the resonance line is observed below an onset temperature $T_{on} \approx 295$ K. For the sol-gel sample with the largest particle size (sample A), T_{on} was similar to that of ceramic samples. Among the other samples, T_{on} and the signal intensity fell with calcination temperature, as shown in fig. 2. No WF resonance signal was observed for sample H.

That the observed variation in WF among the sol-gel samples was not the result of a direct effect of calcination temperature is shown by the fact that T_{on} was the same for all the members of a series of ceramic samples synthesized at various calcination temperatures, which is in keeping with our earlier finding that annealing temperature affects only the magnetothermal properties of ceramic samples [10]. Nor may the fall in WF with decreasing size be attributed to the non-contribution of the increasing proportion of atoms on the particle surface, since surface atoms made up less than 3% even in the smallest particles used. Attribution of the WF variation to differences in the lattice parameter a may also be ruled out: although the observed increase in a with decreasing calcination temperature must certainly tend to reduce distortion, canting angle and WF ($\mathbf{D}$ is dependent on the canting angle [18], and hence $\mathbf{m}_{WF}$ is too according to eq. (1)), it is too small to account for the observed variation in the latter. Moreover, sample H exhibited no WF in spite of its value of a, 3.896 Å, being far below the limit for WF, 3.910 Å [8]. Even if the variation in a were capable of accounting for the fall on M_{dc}, it could not explain the shifts of T_{on} and T_h; greater variation in a among bulk R_2CuO_4 cuprates without any great variation in their ordering temperatures [4] supports this idea.

We suggest that the observed variation in WF can be explained by hypothesizing that $\xi_{2D}(T)$, the function representing the temperature dependence of the 2D spin correlation length in the CuO_2 planes, is affected by particle size, d. Since in these materials the temperature of the transition to 3D order, which we identify with T_{on}, is the temperature at which coupling between planes is of the order of k_BT [19], the above hypothesis implies that T_{on} is a function

of d, $T_{on} = T_{on}(d)$, in keeping with fig. 2. For Gd_2CuO_4 sol-gel samples larger than 2700 Å, T_{on} is the same as in bulk samples, implying that $\xi_{2D}(T)$ is also the same; the fall in T_{on} when d falls below 2700 Å suggests that below this limit the reduction of particle size reduces $\xi_{2D}(T)$, until a point is reached at which $\xi_{2D}(T)$ can be reduced no further and the transition to 3D order becomes impossible. Assuming that at this point d is actually almost identical to the limiting value $\xi_{2D}(T_{on})_{min}$, and taking it about half-way between the sizes of samples G and H, implies that $\xi_{2D}(T_{on})_{min}$ is about 250 times the lattice parameter a. For Gd_2CuO_4 there are no measured values of ξ_{2D} with which to compare this prediction, but the factor of 250 is of the same order as values of about 290, 130 and 60 obtained for $\xi_{2D}(T_N)/a$ for bulk La_2CuO_4, Nd_2CuO_4 and Pr_2CuO_4, respectively [20], using a 2D $S = 1/2$ Heisenberg model [21] and available neutron diffraction data [3], [22].

In the mean-field theory the 3D ordering temperature can be estimated [20] from

$$J_\perp S^2 \left(\frac{M_S}{M_0}\right)^2 \left(\frac{\xi_{2D}(T_N)}{a}\right)^2 \sim k_B T_N, \tag{2}$$

where $J_\perp$ is the coupling constant for interaction between planes, M_S is the sublattice magnetization and $M_0 = g\mu_B$. If $\xi_{2D}(T_N)$ is identified with particle size and T_N with T_{on}, eq. (2) successfully predicts that T_{on} falls with d, but fails to predict a lower limit for $\xi_{2D}(T_N)$. Equation (2) also fails to predict the observed dependence of $\xi_{2D}(T_N)$ on T_N among T' cuprates [20], which has led to the suggestion that a 2D XY anisotropy term be added to the Hamiltonian [23]. Inclusion of this term leads to a logarithmic relationship between the correlation length and the ordering temperature, which implies a rapid fall in the ordering temperature as the particle size approaches a lower limit for ξ_{2D}, as in fig. 2.

To sum up, we have strongly modified the magnetic properties of Gd_2CuO_4 through particle size reduction. WF is suppressed, which is interpreted as showing the impossibility of a 3D AF transition of the Cu moments below a certain particle size.

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