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Magnetic-Field–Induced Weak Ferromagnetic Order in Y_2CuO_4.

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Abstract. – D.c. magnetization measurements in the weak ferromagnetic (WF) cuprate Y_2CuO_4 are reported. A strong peak in the low-field susceptibility is observed at $T_N = 257\,K$, associated with the development of 3-dimensional antiferromagnetic (AF) order. The field dependence of this peak signals the existence of WF order, arising from antisymmetric exchange interactions. An external magnetic field induces a WF component which saturates at a value $M_s(0) \simeq \simeq 9 \cdot 10^{-3} \mu_B/Cu$ atom. We observe that the saturation regime extends up to temperatures as high as $(40 \div 50)$ K above T_N, which is a completely new phenomenon. This behaviour is discussed in terms of a simple thermodynamic potential and the intensity of the peak is related to the strong 2D AF correlations within the CuO_2 planes above T_N.

High-temperature superconductivity is observed in several families of Cu oxides when these compounds are hole- or electron-doped through heterovalent substitution or oxygen nonstoichiometry [1, 2]. Otherwise, the pure compounds are insulating and present antiferromagnetic order of the Cu lattice [3], which is sometimes accompanied by a weak ferromagnetic component, $M_s \approx 10^{-3} \mu_B/Cu$ atom. This is for instance the case of R_2CuO_4 compounds, with R = La, Y, Gd, and other heavy rare earths [4-7], which form in crystal structures where the Cu atoms are arranged in CuO_2 layers with square planar coordination, separated by R_2O_2 blocks.

La_2CuO_4 has the K_2NiF_4-type tetragonal (T) structure and has been extensively studied as a p-type high-temperature superconductor, when doped by excess oxygen or by substitution of a divalent cation for La. It presents 3D antiferromagnetism below $T_N \simeq 250\,K$, with strong 2D correlations, ξ_{2D}, in the paramagnetic phase. The size of ξ_{2D} has been demonstrated to correspond to a 2D spin-(1/2) Heisenberg system [8] with a large nearest-neighbour Cu-Cu superexchange coupling, $J_{NN} \simeq 1300\,K$. Deviations from the Heisenberg Hamiltonian are related to antisymmetric exchange terms arising from a small rotation of the oxygen octahedra that surround each Cu atom. Due to these interactions, the Cu moments are slightly canted out of the CuO_2 layers in the AF state, giving rise to a weak ferromagnetic

(WF) component in each CuO_2 plane. However, this WF is «hidden» in La_2CuO_4 because neighbouring planes order AF below T_N [4].

For smaller rare earths, a different tetragonal structure (T′), Nd_2CuO_4-type [9], is stable. In this case, the apical oxygen is no longer present and no out-of-plane displacements of the oxygen atoms of the CuO_2 layers have been observed. However, for R = Gd and heavier rare earths, in-plane distortions of the Cu lattice have been suggested [10, 11]. This may be the origin of the also in-plane WF component measured in Gd_2CuO_4, $EuTbCuO_4$ and other solid solutions [5]. The observed WF component is believed to be originated in a canting of the Cu moments away from a perfect AF alignment, which in turn polarizes the rare-earth paramagnetic lattice through an internal field, H_i, arising from an exchange coupling between the R ions and the Cu atoms. Y_2CuO_4 is unique within this T′ series, since the Y ions are diamagnetic and thus the magnetic properties arise solely from the Cu lattice, providing an excellent opportunity to study its magnetic behaviour separately.

We have measured the d.c. magnetization of polycrystalline Y_2CuO_4 samples, prepared at high temperature under high pressure (80 kbar) using a belt-type apparatus. Energy dispersive microanalysis has confirmed the cationic stoichiometry for the whole series of heavy-rare-earth cuprates, R_2CuO_4, with R = Tb, Dy, Ho, Er, Tm and Y, and X-ray diffraction indicates that the average structure corresponds in all cases to the tetragonal T′ structure [11]. For Y_2CuO_4, the lattice parameters are: $a = 3.860$ Å and $c = 11.72$ Å, although several superstructures have been observed using electron microscopy, often simultaneously in the same samples, in different grains. The most common lattice superstructure observed for Y_2CuO_4 corresponds to $2\sqrt{2}a \times \sqrt{2}a \times c$. Details of the preparation techniques and crystallographic analysis will be given separately.

The d.c. magnetization has been measured in magnetic fields up to 5 T in the temperature range from 6 K to 340 K, using a quantum design SQUID magnetometer. Figure 1 shows an overall picture of the temperature and magnetic-field dependence of the measured magnetization, after corrections for core diamagnetism have been made, $\chi_{dia}(SI) = -2.8 \cdot 10^{-5}$.

For the highest temperature used in the experiments (340 K), the magnetization $M(H)$ was linear in the whole magnetic-field range, with a paramagnetic slope, $\chi_p(SI) = +7(1) \cdot 10^{-5}$. On lowering the temperature, the magnetization showed a significant

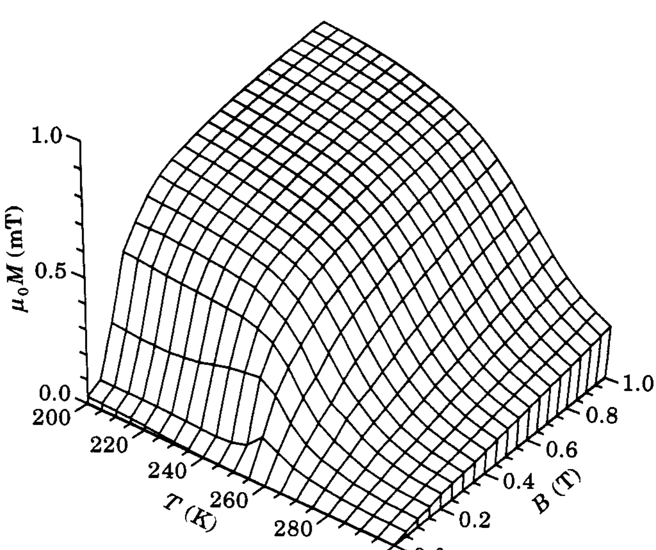

Fig. 1. – Magnetization for Y_2CuO_4 as a function of T and B.

departure from linearity at high fields. The initial susceptibility, $\chi_i(T) \equiv dM(H)/dH|_{H\to 0}$, was rapidly increasing with decreasing temperatures. It presents a divergent behaviour down to a characteristic temperature where a sharp maximum is observed. As we will discuss below, this temperature has been identified as the Néel temperature of the system, T_N. Below T_N, and for applied magnetic fields smaller than about 50 mT, $\chi_i(T)$ decreases again, while a small spontaneous magnetization, $\sigma_1(T)$, is observed, whose absolute magnitude depends on the magnetic history of the sample. For samples cooled in zero field (ZFC) from 340 K, we have found $\sigma_1(T) \approx 0$ within experimental accuracy. On the other hand, finite values for $\sigma_1(T)$ have been measured for samples cooled in a magnetic field (FC) from 340 K. However, the initial slope, $\chi_i(T)$, remained the same in both cases. In fig. 2 we show the experimental data measured for $H = 6$ mT for FC and ZFC samples. The difference between both curves below T_N corresponds to $\sigma_1(T) \simeq 2 \cdot 10^{-5} \mu_B$/Cu atom.

For larger applied fields, the observed behaviour varies considerably depending on the temperature range of the experiments. For $T > T_N$, the d.c. magnetization deviates from the low-field linear behaviour as seen in fig. 3, where we present a set of typical cycles in the $\pm$ 5 T range. These loops are fully reversible and no coercive fields were observed. With increasing magnetic fields the magnetization approaches a saturation behaviour, described by

$$M(H, T) = M_s(T) + \chi_d(T) H, \tag{1}$$

where $\chi_d(T)$ is approximately constant except near $T_c \simeq T_N + 50$ K, where a small and broad maximum is observed as indicated in fig. 4. $M_s(T)$ varies with temperature, as also shown in fig. 4, becoming smaller than the experimental uncertainty at about T_c. For temperatures larger than T_c, the magnetization remained linear up to 5 T, thus indicating that the system was far from saturation. It is worth mentioning that the observation of a saturation regime at temperatures well above the AF Néel temperature is a very unusual phenomenon, which will be further addressed below.

Below T_N, the $\pm$ 5 T cycles are reversible down to about 220 K. At high magnetic fields the $M(H, T)$ dependence is still given by eq. (1) with $M_s(T)$ slowly increasing with decreasing temperature as shown in fig. 4, without presenting any particular feature on crossing T_N.

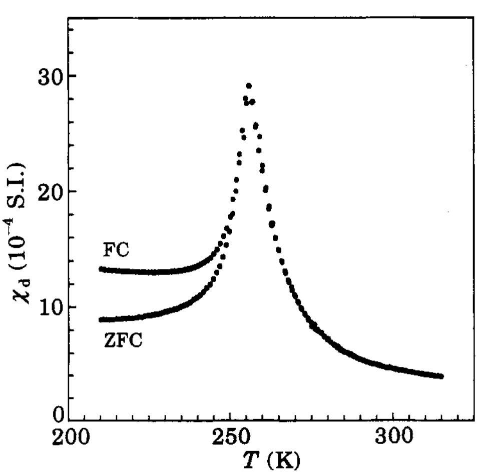

Fig. 2.

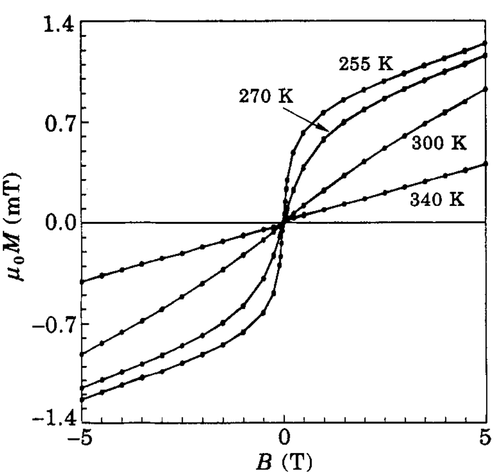

Fig. 3.

Fig. 2. – Differential susceptibility measured for Y_2CuO_4 with $B = 6$ mT in field-cooled (FC) and zero-field-cooled (ZFC) samples.

Fig. 3. – Magnetization cycles measured for Y_2CuO_4 above T_N.

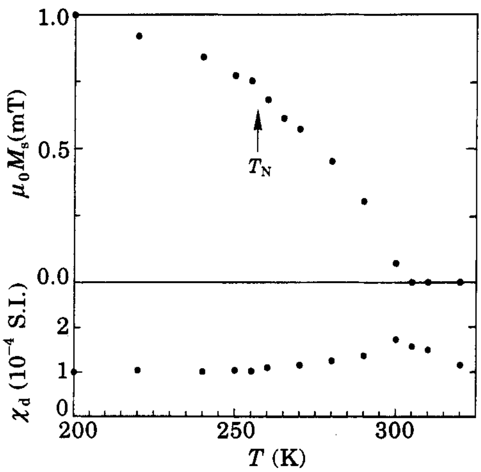

Fig. 4.

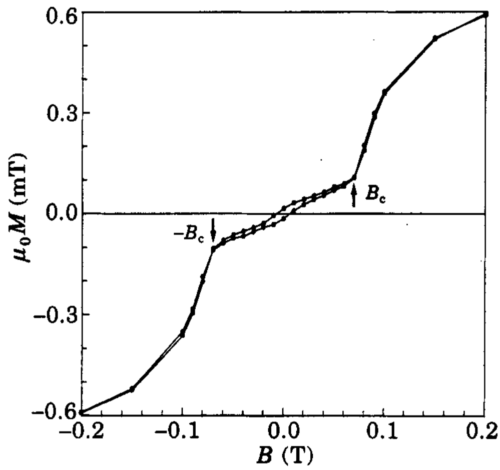

Fig. 5.

Fig. 4. – Spontaneous magnetization and differential susceptibility measured for Y_2CuO_4.

Fig. 5. – Magnetization cycle measured for Y_2CuO_4. at $T = 240$ K. B_c corresponds to a critical field as described in the text.

For $T = 6$ K, $M_s(T)$ reaches a value of $9(2) \cdot 10^{-3} \mu_B$/Cu atom. An enlargement of the central zone of the hysteresis loops shows the small remanent magnetization $\sigma_1(T) \ll M_s(T)$ and the low-field linear behaviour previously described. Figure 5 corresponds to a sample cooled in a field (FC) of 5 T, which presents values of $\sigma_1(220\,\mathrm{K}) \approx 2 \cdot 10^{-4} \mu_B$/Cu atom and $M_s(0\,\mathrm{K}) = 7 \cdot 10^{-3} \mu_B$/Cu atom.

Another interesting feature of these cycles is the field-induced, metamagneticlike transition observed at a critical magnetic field, B_c, where the magnetization of the system increases faster as a function of the applied magnetic field until it reaches a saturation regime as described by eq. (1). The critical field increases from $B_c \approx 0$ near T_N up to $B_c \approx 80$ mT at $T = 220$ K. Below this temperature magnetic hysteresis is first observed at the metamagnetic transition and the isothermal magnetization measured in the $\pm$ 5 T cycles presents two separated hysteresis loops centred at $\pm B_c$. The hysteresis increases when the temperature is lowered and finally the width of the hysteresis loops becomes larger than B_c and a single and very wide loop is observed centred at $B = 0$. At $T = 6$ K the coercive field reaches a value of 800 mT, which is much larger than the extrapolated value of the critical field, $B_c(0) \approx 100$ mT. A full analysis of these low-temperature magnetic properties will be reported separately.

The temperature dependence of the magnetization around T_N may be analysed in terms of the thermodynamical theory developed by Dzyaloshinskii [12] for weak ferromagnetism in antiferromagnetic materials. According to the subsequent work by Borovick-Romanov and Ozhogin [13], the sharp anomaly observed can be understood in terms of WF ordering induced above T_N by the external magnetic field.

The thermodynamical potential that we may write in order to describe an antiferromagnetic system including weak ferromagnetic interactions [12], for temperatures close to T_N is

$$\mathcal{F} = (1/2)A|\boldsymbol{l}|^2 + (1/2\chi_0)|\boldsymbol{m}|^2 + \boldsymbol{\beta}\cdot(\boldsymbol{l} \times \boldsymbol{m}) + (C/4)|\boldsymbol{l}|^4 - \boldsymbol{m}\cdot\boldsymbol{H}, \tag{2}$$

where $\boldsymbol{m}$ is the uniform magnetization and $\boldsymbol{l}$ represents a staggered magnetization of the system, which describes the AF order below T_N. If the system presents four magnetic sublattices, as may be expected by analogy with other cuprates of the series [3], $\boldsymbol{l}$ corresponds to the staggered magnetization whose coefficient changes sign at the highest temperature [12]. Equation (2) couples $\boldsymbol{m}$ to $\boldsymbol{l}$ through the antisymmetric exchange term $\boldsymbol{\beta}\cdot(\boldsymbol{l}\times\boldsymbol{m})$, where the orientation of $\boldsymbol{\beta}$ depends on the symmetry of the Cu-Cu exchange bonds. For instance, in the case of Gd_2CuO_4, $\boldsymbol{\beta}$ would be restricted to the c-axis [14], according to the in-plane local distortions of the average T′ structure proposed from X-ray diffraction measurements [10, 11].

The equilibrium conditions $\partial\mathcal{F}/\partial\boldsymbol{m} = \partial\mathcal{F}/\partial\boldsymbol{l} = 0$ indicate that for $\boldsymbol{H}\perp\boldsymbol{\beta}$, $\boldsymbol{m}$, $\boldsymbol{l}$ and $\boldsymbol{\beta}$ result mutually perpendicular with $\boldsymbol{m}$ pointing parallel to $\boldsymbol{H}$. The magnitudes $m = |\boldsymbol{m}|$ and $l = |\boldsymbol{l}|$ satisfy the following equations:

$$m = \chi_0(H+\beta l), \qquad Cl^3 + [A(T)-\chi_0\beta^2]\,l - \chi_0\beta H = 0. \tag{3}$$

In the absence of an external field, the cubic equation only presents a nontrivial solution ($l \neq 0$) for $[A(T)-\chi_0\beta^2] < 0$. This condition determines the Néel temperature, T_N, below which magnetic order exists for $H = 0$. We may write then, as usual for temperatures close to T_N,

$$A(T)-\chi_0\beta^2 = \nu(T-T_N). \tag{4}$$

Equation (3) may be solved for $H \neq 0$ using a perturbation approach

$$l(H,T) = l_0(T) + a_1(T)H + a_3(T)H^3 + \ldots, \tag{5}$$

where $l_0(T) = (\nu/C)^{1/2}(T_N-T)^{1/2}$ corresponds to the solution for $H = 0$ and $T < T_N$. It then results

$$m = \chi_0 H + \chi_0\beta(l_0 + a_1 H + a_3 H^3 + \ldots), \tag{6}$$

$$m = \begin{cases} \chi_0[1+\beta^2\chi_0/\nu(T-T_N)]H + O(H^3), & T > T_N \\ \chi_0\beta l_0(T) + \chi_0[1+\beta^2\chi_0/2\nu(T_N-T)]H + O(H^3), & T < T_N\,. \end{cases} \tag{7}$$

A comparison with eq. (1) indicates that $M_s(T) = \chi_0\beta l_0(T)$ and $\chi_d(T) = \chi_0 + (\beta\chi_0)^2/\nu(T-T_N)$.

We have determined $T_N = 257(1)$ K from the peak of the low-field susceptibility. From the data taken at high magnetic fields and well above T_N we have estimated $\chi_0(\mathrm{SI}) = 7(1)\cdot 10^{-5}$ and, from the saturation magnetization extrapolated to $T = 0$, $M_s(0) = \beta\chi_0 l_0(0) = 9(1)\cdot 10^{-3}\mu_B/\mathrm{Cu}$ atom, and assuming $l_0(0) \simeq 0.4(1)\mu_B/\mathrm{Cu}$ atom as found in other rare-earth cuprates [3], we obtained $\chi_0\beta \simeq 0.025(5)$. This last number is associated with the canting angle, α, of the Cu sublattice, *i.e.* $\mathrm{tg}\,\alpha = \chi_0\beta$. The measured value indicates $\alpha \approx 1.4°$. From the divergent contribution to the initial slope of the magnetization near T_N (approaching T_N from above) we have determined $\nu(\mathrm{SI}) = 1.5(5)\cdot 10^{-4}\,\mathrm{K}^{-1}$.

When we compare the results obtained for Y_2CuO_4 with measurements in classical weak ferromagnets such as $CoCO_3$ or $MnCO_3$ [13, 15], the intensity of the susceptibility peak around T_N calls our attention, especially because the factor $(\beta\chi_0)^2$ in eq. (7) is a relatively small number. The large intensity should then arise from the small value of ν determined from the measurements.

In the case of La_2CuO_4 a similar behaviour is observed [16], although with a much smaller peak intensity. In this case the strength of the peak has been associated [16] with a very large, staggered susceptibility arising from the strong 2D antiferromagnetic correlations, ξ_{2D}, present in this kind of planar cuprates as a result of the large intraplane magnetic coupling ($J_{NN} \simeq 1300$ K).

We believe that this is also the origin of the peak observed in Y_2CuO_4, since we expect similar values for ξ_{2D} due to the small dependence found for J_{NN} the rare-earth atomic number [17]. The difference in intensity between the peaks in La_2CuO_4 and Y_2CuO_4 may be explained by the much larger value for $(\beta\chi_0)^2$ in Y_2CuO_4, due to a stronger DM interaction evidenced by the larger value found for $M_s(0)$.

Finally, the surprising phenomenon of a magnetic-field–induced weak ferromagnetic moment well above T_N, showing a saturation regime for magnetic fields of only a few tesla, may be understood as a consequence of the combined effects of a very large staggered susceptibility (due to a strong 2D antiferromagnetic correlation above T_N) and a small saturation values for the weak ferromagnetic moments, $M_s(T)$.

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