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NEUTRON SCATTERING STUDY OF THE $YBa_2Cu_3O_{6+x}$ SYSTEM

J. ROSSAT-MIGNOD[1,2], L.P. REGNAULT[1], C. VETTIER[3,4], P. BOURGES[2], P. BURLET[1], J. BOSSY[4], J Y. HENRY(1) AND G. LAPERTOT(1)

[1]Centre d'Etudes Nucléaires de Grenoble, DRFMC/SPSMS/MDN, 85X, 38041 Grenoble Cedex, France
[2]Laboratoire Léon Brillouin, CEN-Saclay, 91191 Gif-sur-Yvette Cedex, France
[3]European Synchrotron Research Facility, BP 220, 38043 Grenoble Cedex, France
[4]Institut Laue Langevin, 156X, 38042 Grenoble Cedex, France

Inelastic neutron scattering experiments have been carried out on $YBa_2Cu_3O_{6+x}$ single crystals in order to perform a systematic investigation of the spin dynamics in the various typical regimes : the pure and doped AF-states (x = 0.15, 0.37), the weakly doped metallic and superconducting state (x = 0.45, 0.51) and the heavily doped metallic state with the T_c = 60 K (x = 0.69) and T_c = 90 K (x = 0.92) phases. The major results are the strong effect of hole doping on the AF-order, the persistence of dynamical AF-correlations in the metallic state and the observation of an energy gap in the spin excitation spectrum at low temperatures in superconducting samples.

1. INTRODUCTION

Five years after the discovery of superconductivity in copper oxide materials by J.G. Bednorz and K.A. Muller[1], the origin of the physical mechanism involved in the Cooper pair formation is still controversial. Accurate experimental results are needed to make further progress. In particular, the knowledge of the wave-vector and energy dependences of the spin excitation spectrum is a crucial test for the numerous theories. In that context, the inelastic neutron scattering technique together with NMR measurements are expected to provide key informations. We have focused on the $YBa_2Cu_3O_{6+x}$ system because the availability of large crystals (~ 0.3 cm^3) in which the oxygen content can be changed from O_6 to O_7 has allowed us to investigate continuously the phase diagram (see Fig.1 in ref.9). Since the determination in 1988 [2,3] of this phase diagram by means of neutron diffraction, we have successively investigated the spin dynamics in the five typical characteristic regimes, i.e. the pure (x = 0.15) and doped (x = 0.37) AF states[4-10], the weakly doped metallic state (x = 0.45 and 0.51)[5-10], the strongly doped metallic state which develop superconductivity below T_c = 60 K (x = 0.69)[9-10] or T_c = 90 K (x = 0.92). The obtained results will be summarized with a special emphasis on the superconducting samples, especially those for the oxygen content x = 0.92 which are quite recent and are reported here for the first time. The main results are the observation of AF spin correlations and the opening of an energy gap in the spin excitation spectrum at low temperatures in the superconducting materials.

2. EXPERIMENTAL

Neutron scattering experiments were performed on good quality single crystals (mosaic spread ~ 1°) grown with a special technique which allows to change easily the oxygen content from x = 0 to x ≃ 1 with good accuracy and homogeneity. Recently we have discovered that the crystal actually contains 3% of Sr substituted to Ba because the raw material BaO did not have the required purity. The only effect of a such small amount of Sr is to reduce T_c by a few Kelvin, for x = 0.92 T_c is reduced from 93 K to 91 K.

The experiments were carried out on the three axis spectrometer IN8 at the Institut Laue Langevin. For the most recent experiment (x = 0.92) we used the spectrometer 2T at the Laboratoire Léon Brillouin which provides a quite high neutron flux at the expense of resolution by using both vertical and horizontal focusing monochromators and analysers. In all experiments the single crystal sample (~ 0.4 cm^3) was mounted in a standard ILL cryostat with the [110] and [001] axes within the horizontal scattering plane.

3. SPIN DYNAMICS IN THE PURE AND DOPED AF STATES :

Up to x = 0.20 the AF ordering is not affected by the oxygen doping because no hole are transferred from Cu(1) to Cu(2) planes. So the excitation spectrum, which can be described by the spin wave theory, yields a large in-plane spin wave velocity c_0 = 1 eV.Å (see Fig.1) ($J_{Cu.Cu}$ = 0.15 eV) and a large AF coupling between the two Cu(2) layers ($J_b \simeq 10^{-2}$-10^{-1} J). Actually this AF coupling persists in the metallic and superconducting state. However the coupling between bilayers is weak ($J' \simeq 10^{-5}$ J) as well as the planar anisotropy ($\Delta J/J \simeq 10^{-4}$).

For x > 0.20 transferred oxygen p-holes strongly affect the AF ordering which indeed disappears for a critical concentration $n_h^c \simeq 2\%$ (x_c = 0.4). These holes give rise to some spin disorder in the moment direction within the basal plane yielding a strong damping of in-plane spin excitations and a renormalization of the spin wave velocity (c = 0.45 eV.Å for x = 0.37, see Fig.1). Actually, this renormalization is q-dependent and decreases as q becomes larger than Γq (1/ξ), a behaviour which is explained by a recent numerical study of the ground state and spin-wave dynamics of a disordered XY model in two dimensions[11].

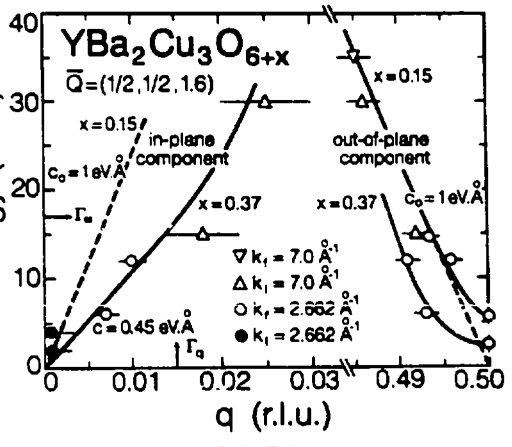

FIGURE 1
Excitation energies of in-plane and out-of-plane spin components in the pure AF- ($YBa_2Cu_3O_{6.15}$) and the doped AF- ($YBa_2Cu_3O_{6.37}$) states. The dotted line corresponds to the spin-wave velocity c_0 = 1 eV in the undoped AF-state.

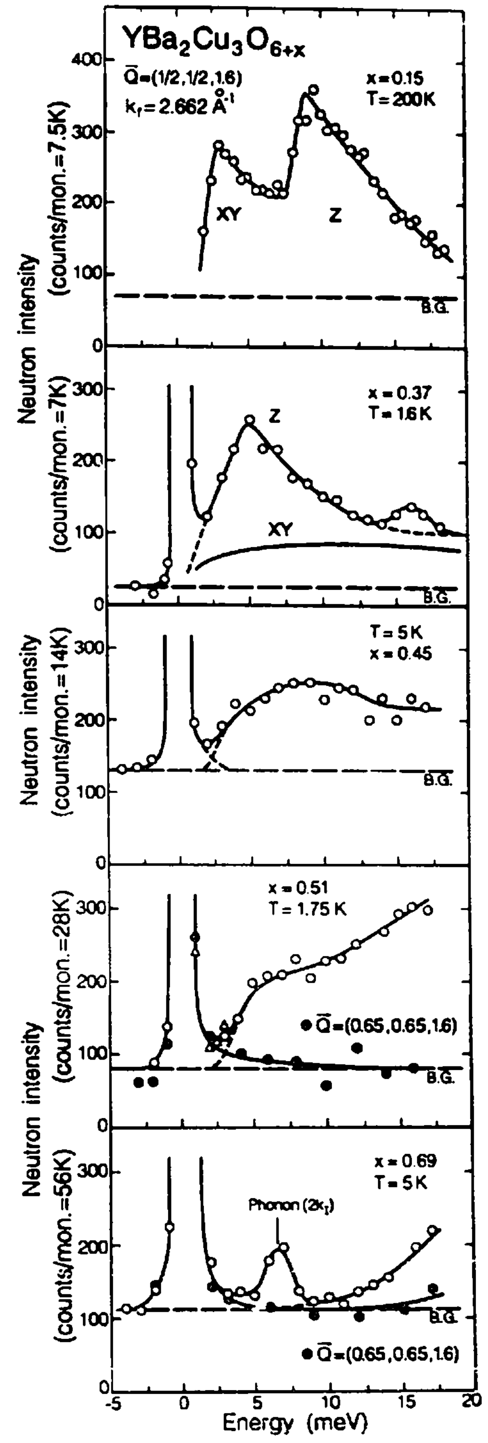

FIGURE 2
Energy scans performed at $\vec{Q}$ = (1/2, 1/2, 1.6) for $YBa_2Cu_3O_{6+x}$ with different oxygen contents x = 0.15, 0.37, 0.45, 0.51 and 0.69. Contributions of excitations from the in-plane (XY) and out-of-plane (Z) spin components are shown.

4. SPIN DYNAMICS IN THE WEAKLY DOPED METALLIC STATE

For $x > x_c = 0.41$, an insulating-metal (I-M.) transition occurs due to a sudden transfer of a large amount of p-holes (10-15%) in CuO_2 planes which suppresses the 3d AF ordering and leads to a superconducting state at low temperatures. Experiments on samples with oxygen content x = 0.45 (T_c = 37 K) and 0.51 (T_c = 47 K)[12] have proved that dynamical AF correlations persist ($\Delta q = 0.10 \pm 0.01$ r.l.u., $\xi_{AF}/a = 2.2$ for both samples). Energy scans (see Fig.2 and 3) show that propagative spin excitations do not exist any more, but a broad excitation spectrum extends up to about 40 meV. The maximum of the spectrum defines an energy scale Γ_ω which varies strongly from 8 meV (x = 0.45) to 20 meV (x = 0.51). Moreover, the spectrum lineshape is not lorentzian and falls off very rapidly at high energies (see Fig.3). Q-scans performed at different energies (Fig.4) and different temperatures clearly show q-widths which are independent of the energy transfer and temperature up to 250 K. A behaviour which would indicate that the Cu spin dynamics is governed by the quasi-particle motion. Therefore, the energy scale Γ_ω, i.e. the hole mobility, increases rapidly at the I-M transition, but the AF correlation length, i.e. the hole density, does not change. So, for x = 0.51, with an energy scale Γ_ω = 20 meV it is quite normal to have no temperature variation of the magnetic correlation length up to room temperature.

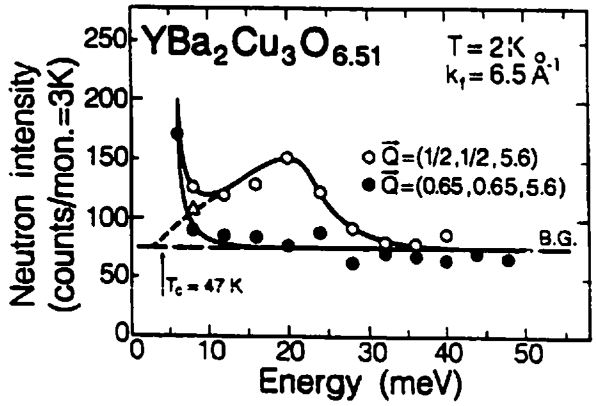

FIGURE 3

Energy scans performed at $\vec{Q}$ = (1/2, 1/2, 1.6) and out of $\vec{Q}$ = (0.65, 0.65, 1.6), the magnetic peak for $YBa_2Cu_3O_{6.51}$.

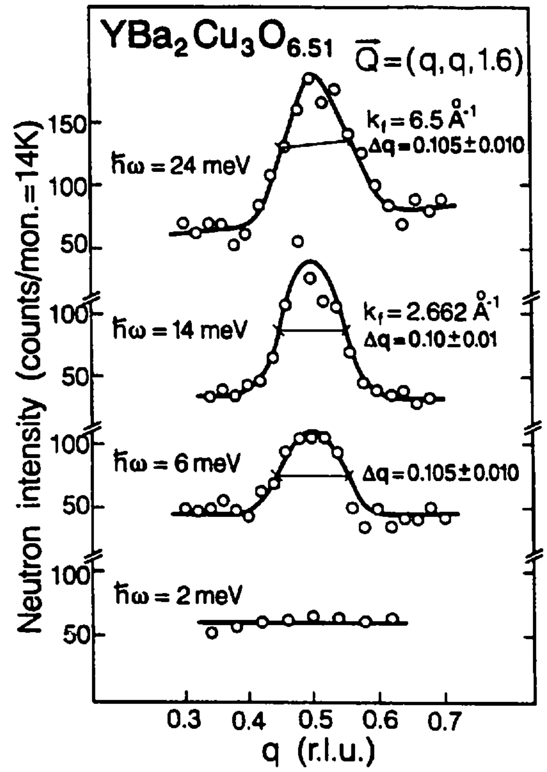

FIGURE 4

Q-scans performed at increasing energy transfers at T = 1.7 K for $YBa_2Cu_3O_{6.51}$.

Another quite important result is the observation of an energy gap in the spin excitation spectrum, at low energy transfers (Fig.5) corresponding to $\hbar\omega_G$ = 3 meV and 4 meV for x = 0.45 and 0.51, respectively. The T-dependence of the low energy part of the spectrum, reported in Fig.5, is better characterized by plotting the imaginary part of the dynamical susceptibility $\chi(\vec{q},\hbar\omega)$ which is related to the dynamical structure factor $S(\vec{Q},\hbar\omega)$ by the relation :

$$S(\vec{Q},\hbar\,\omega) = \frac{1}{\pi}\,\frac{1}{1-\exp(-\hbar\omega/kT)}\;\mathrm{Im}\{\chi(\vec{q},\hbar\omega)\}.$$

We observe that superconductivity induces a transfer of the low energy part of the spin excitation spectrum to higher energies. The slope of $\mathrm{Im}(\chi)/\hbar\omega$, which is nothing but $1/T_1T$ as measured by NMR, exhibits a large temperature dependence : an increase up to T_c and then a strong

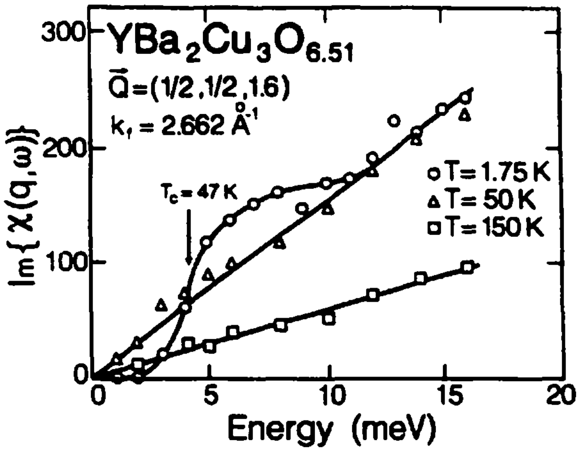

FIGURE 5

Im $\{\chi(q,\omega)\}$ (in arbitrary units) as a function of the energy for $YBa_2Cu_3O_{6.51}$ below (T = 1.75 K) and above (T = 50, 150 K) the superconducting transition (T_c = 47 K). An energy gap ($E_G \simeq 4$ meV) is observed in the spin excitation spectrum.

decrease. It must also be emphasized that the energy gap E_G is quite small in comparison with a BCS prediction (~ 3.5 T_c) which may indicate a gap less superconductivity on approaching the I-M transition.

5. SPIN DYNAMICS IN THE HEAVILY DOPED METALLIC STATES

In order to understand the difference between the 60 K and 90 K superconducting phases we have investigated successively samples with an oxygen content x = 0.69 (T_c = 59 K, ref.12) and x = 0.92 (T_c = 91 K, ref.12).

For x = 0.69, the results were reported for the first time a year ago at the LT 19 conference[10]. As shown in Fig.6 a magnetic scattering has been clearly identified. q-scans show an increase of the q-width by 40% ($\Delta q = 0.14 \pm 0.02$ r.l.u.) yielding a magnetic correlation length $\xi/a = 1.5$ and indicating an increase of the density of p-holes in CuO_2 layers. The energy spectrum is broad and is maximum around $\Gamma_\omega \simeq$ 25-27 meV. Below T_c a measurable magnetic scattering is found only above 12 meV (see Fig.2) indicating a larger energy gap in the spin excitation spectrum. This gap is clearly seen in Fig.7 which shows the T-dependence of $Im\{\chi(\vec{q},\hbar\omega)\}$. The value of the energy gap, defined as the inflexion point, E_G = 16 meV is much larger than for x = 0.51 and is close to the BCS value (3.2 T_c).

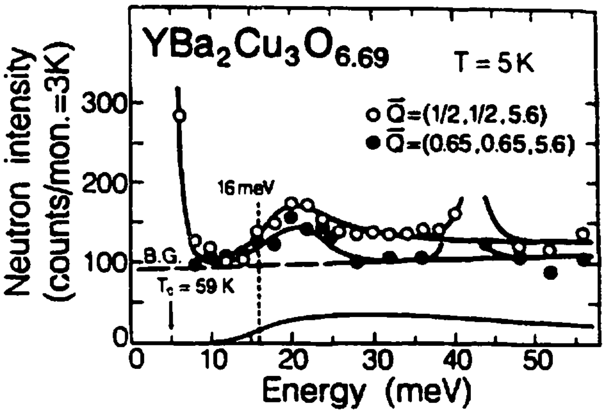

FIGURE 6

Energy scans performed on $\vec{Q}$ = (1/2, 1/2, 1.6) and out of $\vec{Q}$ = (0.65, 0.65, 1.6), the magnetic peak for $YBa_2Cu_3O_{6.69}$.

Another quite important result concerns measurements performed above T_c which show a persistence of a pseudo gap well above T_c (see Fig.7). Imχ recovers a linear energy dependence only above 150-200 K. To illustrate this unusual behaviour we have reported in Fig.7, the T-dependence of Imχ at $\hbar\omega$ = 8 meV and $\vec{Q}$ = (1/2 1/2 1.6) which represents actually the slope of Imχ. This slope

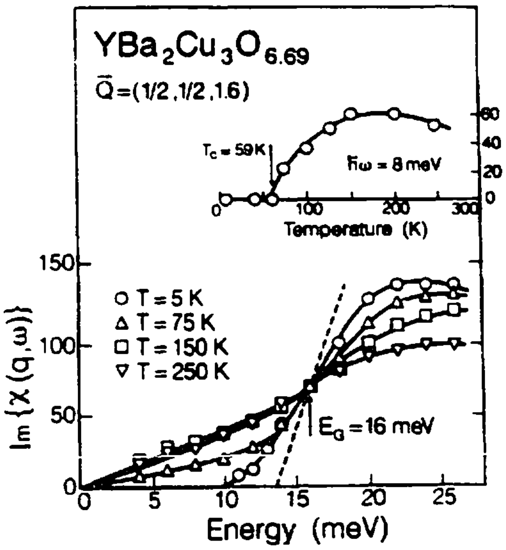

FIGURE 7

Im $\{\chi(q,\hbar\omega)\}$ (in arbitrary unit) as a function of the energy for $YBa_2Cu_3O_{6.69}$ below (T = 5 K) and above (T = 75, 150, 250 K)the surperconducting transition (T_c = 59 K). An energy gap ($E_G \simeq 16$ meV) in the spin excitation spectrum clearly persists above T_c.

starts to increase above T_c and goes through a maximum around 150 K and then decreases. The similarity with the T-dependence of $1/T_1T$, [13,14], is quite remarkable and demonstrates that this behaviour is not due to a T-dependence of the magnetic correlation length, as was suggested[15], but rather to the opening of an energy gap in the spin excitation spectrum.

Recently we have performed inelastic neutron scattering experiments on a superconducting sample with an oxygen x = 0.92 (T_c = 91 K, ref.12). For the first time, a magnetic response has been identified above an energy transfer of about 25 meV. Energy scans (Fig.8) at various temperatures have a rather complex lineshape. It should be noted that the peak at 24 meV is a contamination from the (006) Bragg peak. Q-scans (Fig.9), across the AF ridge and performed for different energy transfers, clearly show evidence for a magnetic scattering signal and allow us to define the nuclear contribution. The T-dependence of this contribution (see Fig.8) can be explained by assuming two contributions on top of a flat background : a contribution peaked around 20 meV and a broad response extending over the whole energy range. The first contribution is not yet understood because it has a quite unusual T-behaviour : the intensity actually decreases slightly as T increases. The second contribution exhibits a normal T-behaviour : after correction from the Bose factor $(1-e^{-\hbar\omega/kT})^{-1}$, scans at all temperatures give the same contribution (called Imϵ in Fig.10). This contribution can well be explained by a damped harmonic oscillator ($\hbar\omega_0$ = 21.5 meV, Γ_ω = 26 meV) and could correspond to large fluctuations of oxygen atoms in Cu(1) planes (apical oxygen or oxygen in Cu chains) because no energy gap is found in the superconducting state.

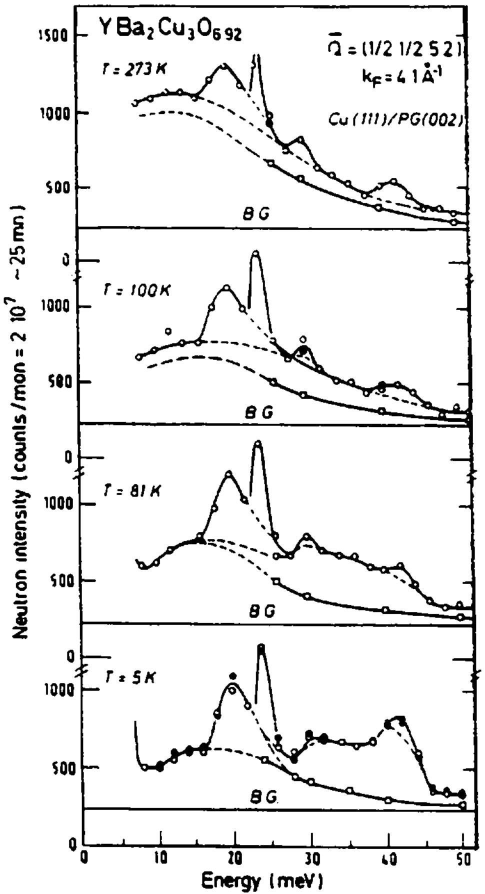

FIGURE 8

Energy scans performed at $\vec{Q}$ = (1/2, 1/2, 5.2) for $YBa_2Cu_3O_{6.92}$ as a function of temperature. Above the background (B.G.) a nuclear contribution is indicated by (□).

Having determined the nuclear contribution, it is now possible to obtain the magnetic contribution at any temperatures (see Fig.8). We have reported in Fig.11 the obtained results for Im{$\chi(\vec{q},\hbar\omega)$}. At T = 5 K, our results show three important features. First, there is no sizeable magnetic scattering below 25 meV (see Fig.9), actually there is a sharp energy gap (resolution limited) $E_G \simeq 28 \pm 1$ meV in the spin excitation spectrum. Second, the magnetic scattering is found to drop rapidly above 45 meV and exhibits a peak around 41 meV. Third, q-scans (see Fig.9) give a q-width $\Delta q = 0.27 \pm 0.02$ r.i.u.,

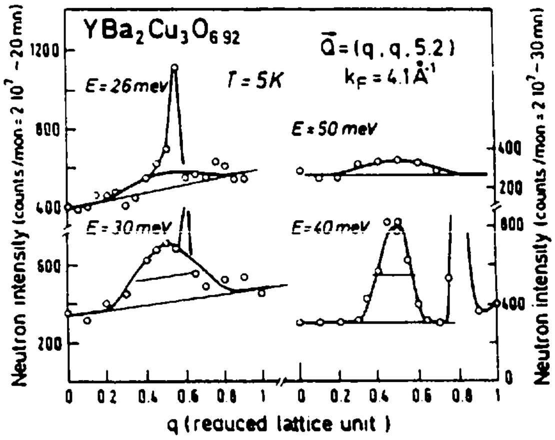

FIGURE 9

Q-scans performed through the (1/2, 1/2, 5.2) rod for $YBa_2Cu_3O_{6.92}$ for different energy transfers at T = 5 K.

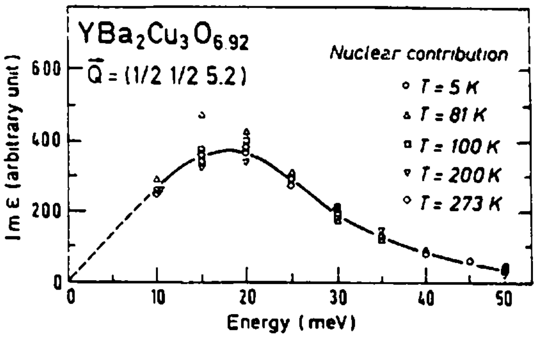

FIGURE 10

Nuclear contribution measured at $\vec{Q}$ = (1/2, 1/2, 5.2) as a function of temperature. For a better comparison the scattering intensity multiplied by $(1-e^{-\hbar\omega/kT})$ is reported and called Im E.

except around 40 meV where it has a much smaller value (0.18 ± 0.02 r.l.u.). This may indicate that the peak around 41 meV, which is actually resolution limited in energy, corresponds to some collective excitation through the superconducting gap. The magnetic origin of this peak is well established by the intensity modulation observed in a q-scan along the (001) direction resulting from the AF coupling between the two Cu(2) layers, and moreover it exhibits a strong temperature dependence. At T = 81 K, (below T_c) the magnetic scattering is similar to that observed at T = 5 K except that the peak at 41 meV shifts to lower energy of ~25 meV, the energy integrated intensity remains constant. This behaviour is quite surprising and is observed for the first time. It is difficult to determine the AF-correlation length, ζ. However, an average q-width Δq = 0.25 r.l.u. is reasonable and yields a quite small value ζ/a = 0.84 ± 0.05.

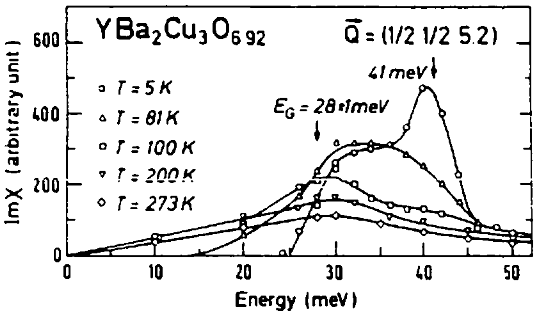

FIGURE 11

Im {χ(q, ħω)} (in arbitrary unit) as a function of the energy for $YBa_2Cu_3O_{6.92}$ for increasing temperatures below and above T_c = 91 K. An energy gap (E_G = 28 meV) is clearly seen in the spin excitation spectrum.

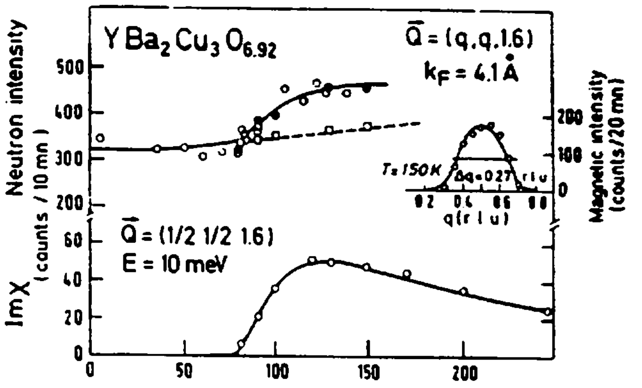

FIGURE 12

Temperature dependence of the magnetic intensity and Im χ at ħω = 10 meV for $YBa_2Cu_3O_{6.92}$

The temperature dependence of the energy spectrum contains also quite important informations. First, for an energy transfer of 10 meV (Fig.12) a measurable magnetic scattering appears around 80 K, i.e. below T_c = 91 K. Second, the T-dependence of Imχ at ħω = 10 meV, actually $1/T_1T$, exhibits a maximum around 120-130 K in excellent agreement with NMR results[13]. Therefore this behaviour, as for the previous sample with x = 0.69, results from the opening of a pseudo gap in the spin excitation spectrum above T_c. Third, high temperature measurements establish that the maximum of the spectrum, i.e. the energy scale $\Gamma_\omega \simeq$ 30 meV, does not change with temperature, nor does the AF-correlation length. The T-dependence is actually due to a decrease of the correlated scattering intensity which may indicate a transfer of the AF-correlated scattering to a q-independent scattering with probably a much larger energy scale which would be related to single site quantum fluctuations as found in heavy fermion systems[16].

In conclusion the spin dynamics found in the superconducting samples is quite unusual in many aspects. There are clearly AF-correlations at any hole concentration. The energy scale of these correlated spin fluctuations is small and the spin excitation spectrum exhibits an energy gap which persists well above T_c. At high temperatures, the weight of the AF-correlated spin fluctuations is progressively reduced. The understanding of these features is not established. There are some theoretical attempts[17-19] to explain the energy gap as resulting from a special feature of single quasi-particle excitations around the AF wave vector within the renormalized band structure. However, these theories do not account for the sharp cut-off of the magnetic response at high energies (45 meV).

Further theoretical progress has to be made, in order to explain the energy scales which has been revealed by our studies of Cu spin dynamics in this high T_C material.

REFERENCES

1. J.G. Bednorz and K.A. Muller, Z. Phys. B 64 (1986) 189.
2. P. Burlet, C. Vettier, M.J. Jurgens, J.Y. Henry, J. Rossat-Mignod, H. Noel, M. Potel, P. Gougeon and J.C. Levet, Physica C 153-155 (1988) 1115.
3. J. Rossat-Mignod, P. Burlet, M.J. Jurgens, C. Vettier, L.P. Regnault, J.Y. Henry, C. Ayache, L. Forro, H. Noel, M. Potel, P. Gougeon and J.C. Levet, J. Physique 49 (1988) C8-2119.
4. J. Rossat-Mignod, J.X. Boucherle, P. Burlet, J.Y. Henry, M.J. Jurgens, G. Lapertot, L.P. Regnault and J. Schweizer, in : Int. Seminar on High-T_C superconductor, Dubna (1989), V.L. Aksenov, N.N. Bogolubov and N.M. Plakida, eds. (World Scientific, Singapore, 1990) p. 74
5. J. Rossat-Mignod, L.P. Regnault, M.J. Jurgens, P. Burlet, J.Y. Henry and G. Lapertot, in : Dynamics of Magnetic Fluctuations in High-T_C Materials, G. Reiter, P. Horsh and G. Psaltakis, eds. (Plenum, New York, 1990).
6. C. Vettier, P. Burlet, J.Y. Henry, M.J. Jurgens, G. Lapertot, L.P. Regnault and J. Rossat-Mignod, Phys.Scr. T 29 (1989) 110.
7. J. Rossat-Mignod, L.P. Regnault, M.J. Jurgens, C. Vettier, P. Burlet, J.Y. Henry and G. Lapertot, Physica C 162-164 (1989) 1269.
8. J. Rossat-Mignod, L.P. Regnault, M.J. Jurgens, C. Vettier, P. Burlet, J.Y. Henry and G. Lapertot, Physica C 163 (1990) 4.
9. J. Rossat-Mignod, P. Burlet, M.J. Jurgens, J.Y. Henry and C. Vettier, Physica C 152 (1988) 19.
10. J. Rossat-Mignod, L.P. Regnault, C. Vettier, P. Burlet, J.Y. Henry and G. Lapertot, Physica B 169 (1991) 58
11. D.R. Grempel and P. Gaviec, Preprint.
12. M. Couach, Private communication.
13. M. Horvatic, P. Butaud, P. Segransan, Y. Berthier and C. Berthier, Physica C 166 (1990) 151
C. Berthier et al., this conference.
14. M. Takigawa, A.P. Reyes, P.C. Hammel, J.D. Thompson, R.H. Heffner, Z. Fisk and K.C. Ott, Phys. Rev. B 43 (1991) 247.
15. A.J. Millis, H. Monien and D. Pines, Phys. Rev. B 42 (1990) 167.
16. J. Rossat-Mignod, L.P. Regnault, J.L. Jacoud, C. Vettier, P. Lejay, J. Flouquet, E. Walker, D. Jaccard and C. Amato, J. Magn. Mag,. Mat. 76&77 (1988) 376.
17. N. Bulut, D.W. Hone, D.J. Scalapino and N.E. Bickers, Phys. Rev. B 41 (1990) 1797.
18. T. Tanamoto, K. Kuboki and H. Fukuyama, Preprint.
19. D. Grempel and M. Lavagna, Preprint.