Model for the low-temperature magnetic phases observed in doped YBa$_2$Cu$_3$O$_{6+x}$

Niels Hessel Andersen

Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark

Gennadi Uimin

Institut für Theoretische Physik, Universität zu Köln, Zülpicher Str.77, D-50937 Köln, Germany

and

Landau Institute for Theoretical Physics, Chernogolovka, 142432 Moscow District, Russia

Abstract

A classical statistical model for the antiferromagnetic (AFM) ordering of the Cu-spins in the CuO$_2$ planes of reduced YBa$_2$Cu$_3$O$_{6+x}$ type materials is presented. The magnetic phases considered are the experimentally observed high-temperature AFI phase with ordering vector $Q_i = (\frac{1}{2} \frac{1}{2} 0)$, and the low-temperature phases: AFII with $Q_{II} = (\frac{1}{2} \frac{1}{2} 1)$ and intermediate TA (Turn Angle) phases TAI, TAI and TAI with components of both ordering vectors. It is shown that the AFII and TA phases result from an effective ferromagnetic (FM) type coupling mediated by free spins in the CuO$_x$ basal plane. Good agreement with experimental data is obtained for realistic model parameters.
It is well-established that the CuO\textsubscript{2} layers in the high-temperature superconductor materials, like La\textsubscript{2}CuO\textsubscript{4} and YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6+x} (YBCO), form an \textit{antiferromagnetic} (AFM) state when they are insufficiently hole doped for superconductivity \cite{1}. The nearly 2\textit{d} quantum state of these magnetic phases makes them intrinsically interesting, but a major motive for studying their properties is clearly the unsettled question, whether the magnetic fluctuations contribute to establish the superconducting state or compete with and eventually destroy it.

Despite the many detailed studies of the static and dynamic properties of the magnetic phases in YBCO type materials, the origin of the low-temperature AFII magnetic phase has not been satisfactorily understood. The AFII phase has been found in the same range of oxygen stoichiometries (\textit{x} < 0.35) as the high temperature AFI phase in apparently pure YBCO \cite{2,3} and the homologous rare earth (RE) substituted REBCO \cite{4,5}. However, recent experimental studies have shown that it is \textit{not} present in high-purity single crystals of YBCO \cite{6,7} and NdBCO \cite{8}, whereas it is found in Al \cite{6,7}, Co \cite{9} and Fe \cite{10} doped YBCO, and in YBCO with La doped onto the Ba site \cite{11}. The early observations of the AFII phase in nominally pure YBCO single crystals \cite{2,3} may therefore result from corrosion of the alumina crucibles used for the crystal growth.

Experimentally it has been shown that the Cu magnetic structures in YBCO materials are characterized by a simple AFM ordering of the Cu spins within the CuO\textsubscript{2} double layers as shown in Fig. 1a. The Cu spins are lying in the plane but the in-plane easy direction has not been established yet. Well below the Néel temperature, (\textit{T}_{N} = 410 K for \textit{x} \approx 0), the Cu\textsuperscript{2+} spins in the CuO\textsubscript{2} double layers form a rigid collinear 2\textit{d} structure. In the AFI phase adjacent double layers (\textit{i.e.} next nearest CuO\textsubscript{2} planes) are AFM coupled via the CuO\textsubscript{x} basal plane. Thus compared to the chemical unit cell, the magnetic unit cell of the AFI structure is doubled along the \textit{a} and \textit{b} axes, but not along the \textit{c} axis giving an ordering vector \textbf{Q}_{I} = (1\textsubscript{1}1\textsubscript{0}). In the AFII structure the spins on next nearest CuO\textsubscript{2} planes are aligned by an effective \textit{ferromagnetic} (FM) coupling via the CuO\textsubscript{2} basal plane with a magnetic unit cell.
doubled along the $c$ axis, and hence $Q_{II} = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$. In an intermediate phase, which we shall denote the TA (Turn Angle) phase, components of both vectors, $Q_I$ and $Q_{II}$, are observed experimentally. It has been debated whether the TA phase is a mixed AFI–AFII phase or results from a continuous transformation between the two spin configurations. In this letter we establish a classical statistical model that explains the origin of the interaction leading to the AFII phase at low temperatures, and the transition to the AFI phase via the TA phase. For pure YBCO there is essentially no free magnetic moment on the Cu sites in the CuO$_x$ basal plane even for the oxygen content close to the transition into the superconducting state, ($x \approx 0.3$), where significant amount of magnetic Cu$^{2+}$ ions should be present. This may be explained by the formation of randomly distributed singlet spin-pairs of Cu$^{2+}$–O$^{2−}$–Cu$^{2+}$ fragments, which like isolated Cu$^{+}$ ions are non-magnetic, and onwards shall be referred to as such. Not only shortest, but also longer chain fragments, like Cu$_3$O$_2$, should be considered as non-magnetic because the holes may redistribute inside the chains and leave the spin state of such a "molecule" as a singlet. It is argued that free Cu spins may be formed by direct substitution of magnetic ions like Co [9] and Fe [10] for non-magnetic Cu, or indirectly when Al$^{3+}$ substitutes for Cu [6,7] or RE$^{3+}$ for Ba$^{2+}$ [8,11]. In the latter case, which may occur for light RE, it is likely that additional oxygen is introduced into the basal plane to assure charge neutrality and gives rise to additional oxidation of Cu$^{+}$ to Cu$^{2+}$. With RE$^{3+}$ substitution for Ba$^{2+}$ one free Cu$^{2+}$ spin is expected to result, whereas Al$^{3+}$ may give rise to two Cu$^{2+}$ spins, e.g. as shown in Fig. 1a. These two Cu$^{2+}$ spins are essentially free because they are linked via non-magnetic Al or the O-O orbital overlap.

The free spins may be polarized and establish an effective FM coupling between the rigid spin configurations of two adjacent CuO$_2$ double layers at low temperatures. For sufficiently high concentrations of free spins the FM coupling will dominate and form the AFII phase, but at higher temperatures it gradually becomes ineffective and the ordering will be controlled by the AFM couplings mediated by the non-magnetic Cu ions (cf. Fig. 1a). Thereby the AFII structure is transformed into the TA phase and further into the AFI structure via two continuous phase transitions. For low concentrations of free spins the AFII phase does not
form and the TA phase is the stable ground state. Including a fourfold easy-axis anisotropy in addition to a well-established in-plane anisotropy for Cu spins in the bilayers first order phase transitions to various TA phases, TAI, TAIi and TAIi may result.

The total Hamiltonian for the spin system can be represented via the sum $H_{\text{tot}} = \sum_{k=0}^{5} H_k$, and the relevant interaction parameters are defined in Fig. 1. $H_0$ is the intra-plane Heisenberg spin-exchange and $H_1$ is the Heisenberg exchange between the Cu spins in the nearest CuO$_2$ planes. $H_2$ is the easy-plane anisotropy and $H_3$ reflects the anisotropy for spin rotation in the easy-plane. The indirect Heisenberg exchange interactions between Cu spins in the next nearest CuO$_2$ planes via non-magnetic Cu ions, and via free spins in the basal CuO$_x$ plane, are given by Hamiltonians $H_4$ and $H_5$, respectively. We do not include the interactions between spins in the CuO$_2$ basal plane, which may be estimated to have little influence for low concentrations of free spins.

In principle the model is applicable for the above mentioned dilute doping mechanisms and their combinations. However, in the following we shall focus on the properties of Al-doped YBCO. We shall consider any basal plane as consisting of free Cu$^{2+}$ spins, of non-magnetic Cu ions, and of Al-occupied sites with relative concentration, $x$, $y$ and $\delta$, that satisfy the equality $x + y + \delta = 1$. Non-magnetic Cu and Al ions are supposed to be randomly distributed, while free Cu$^{2+}$ spins correlate spatially with Al, *e.g.* as shown in Fig. 1a. The Cu spins in the $j$-th bilayer which form a rigid 2$d$ collinear AFM structure are characterized by a classical spin $S_j$, that is the $j$-th layer order parameter. The justification for this assumption is that the values of the intra-plane and inter-plane coupling constants, $J_0 \approx 170$ meV in $H_0$ and $J_1 \approx 10^{-1} J_0$ in $H_1$, significantly exceed all other contributions to $H_{\text{tot}}$ [12][13] (cf. the experimentally observed temperatures of the AFII and TA ordering: $T_{\text{AFII}} \leq T_{\text{TA}} \leq 20$ K in YBCO). To be specific we ascribe $S_j$ to the lattice site $\rho = (0, 0)$ of the bottom plane $(b)$ of the $j$-th double layer. Then, evidently, the spin-field in the bottom plane is $S_j^{(b)}(\rho) = S_j \exp(iQ\rho)$ and in the top $(t)$ plane $S_j^{(t)}(\rho) = -S_j^{(b)}(\rho)$. Each spin of the set $\{S_j\}$ governed by the main contribution $H_{\text{tot}}^{(0)} = H_0 + H_1$ is still freely oriented, but this degeneracy is removed by smaller interactions, that regulate the relative orientations of
adjacent double layer spins and their orientations with respect to the easy axes. Because the energy scale of $H_2$, $H_3$ and $H_4$ is much below that of the temperature it is allowed to replace them by their "mean"-field expressions in the free energy. Thus $H_2$ restricts the spins to lie in the basal plane, and $H_3$ leads to the fourfold easy-axis anisotropy given by:

$$F_3 = -D_4 \sum_r \cos 4\phi_r \to -2N_\rho D_4 \sum_j \cos 4\phi_j$$

where $\phi_j$ is the angle between $S_j$ and one of the fourfold easy axes, which, in lack of information we take to be the $x$ (or equivalently the $y$) axis. $N_\rho$ is the total number of Cu sites in a CuO$_2$ plane. Further,

$$F_4 = J_2 \sum_{j,\rho'} S_j^{(t)}(\rho')S_{j+1}^{(b)}(\rho') \to -yN_\rho J_2 \sum_j S_jS_{j+1}$$

where the sum runs over the double layers, $j$, and over the $N_\rho y$ in-plane sites $\rho'$ which are bridged by non-magnetic Cu ions in the basal plane.

The Hamiltonian $H_5$ realizes coupling via free Cu spins:

$$H_5 = J_3 \sum_{j,\rho''} \sigma_{j+\frac{1}{2}}(\rho'')(S_j^{(t)}(\rho'') + S_{j+1}^{(b)}(\rho''))$$

where now the summation is over $j$ and the $xN_\rho$ sites $\rho''$ which are bridged by free Cu spins, $\sigma_{j+\frac{1}{2}}$. The corresponding free energy obtained from a classical statistical average over the angular degrees of freedom of $\sigma_{j+\frac{1}{2}}$ is:

$$F_5 = -xN_\rho k_BT \ln \left( \frac{\sinh(\sqrt{|J_3|}\sigma |S_j - S_{j+1}|/(k_BT))}{|J_3|\sigma |S_j - S_{j+1}|/(k_BT)} \right)$$

which behaves as $-xN_\rho |J_3| \sigma |S_j - S_{j+1}|$ when $T \to 0$ and goes to zero for $T \to \infty$. Thus we arrive at the effective free energy, $F_{\text{eff}} = \sum_{i=3}^5 F_i$, which takes the form of an effective 1d spin-system $\{S_j\}$. Then our goal is to minimize $F_{\text{eff}}$. The polarization type of coupling leading to $F_5$ tends to align the order parameters $S_j$ and $S_{j+1}$ in antiparallel at low temperatures, whereas it becomes ineffective at high temperatures, where the parallel alignment of $S_j$ and $S_{j+1}$ will prevail, due to $F_4$ if $J_2 > 0$. At intermediate temperatures the competition between AFI (parallel) and AFII (antiparallel) alignments of the spins in adjacent bilayers will lead to the TA phases. To show this we note, that the in-plane angles may be presented by
\[ \phi_j = \psi_0 + (-1)^j \psi \]  

where \( \psi \) is the turn angle and \( \psi_0 = n \frac{\pi}{4} \). In \( \psi_0 \) odd \( n \) (TAII phase) as well as even \( n \) (TAI and TAIII phases) are necessary to establish all the minima of \( F \). Fig. 1b illustrates the various possibilities, including the pure states, AFI and AFII, corresponding to \( \psi \) equal to 0 and \( \frac{\pi}{2} \), respectively. Note, that Eq. (5) defines the spin rotation angles as strictly alternating: \( \Delta \phi_j = \phi_{j+1} - \phi_j = (-1)^{j-1} \cdot 2\psi \). For \( D_4 = 0 \), this is not justified because \( \Delta \phi_j \) may take the form of degenerate configurations \( R_j \cdot 2\psi \) with \( R_j \) being a random set of \( \pm 1 \). As a result the spin configuration becomes disordered along \( z \). A similar disordering occurs in the TAII phase for \( \psi = \frac{\pi}{4} \), which means \( \Delta \phi_j = R_j \cdot \frac{\pi}{2} \) and is just the case shown in Fig. 1a. In principle, longer range interactions prevent the above mentioned disordering to happen. \( \psi = \frac{\pi}{8} \) or \( \frac{3\pi}{8} \) would also be candidates for disordering but because they appear at first order transitions between TAI and TAII or TAIII phases, this kind of a disordering is inaccessible.

Thus we arrive at the normalized free energy functionals (\( f^\pm = \frac{F_{\text{eff}}}{2N\rho|J_3|S\sigma} \)):

\[ f^\pm(z) = y_jz^2 \pm q(z^2 - z^4) \mp \frac{q}{8} - xt \ln \frac{\sinh(z/t)}{z/t} \]  

where the normalized parameters are:

\[
j = \frac{J_2S}{|J_3|\sigma}, \quad q = \frac{8D_4}{|J_3|S\sigma}, \quad t = \frac{k_BT}{2|J_3|S\sigma}, \quad z = \sin \psi \]  

and \( f^+ \) and \( f^- \) refer to the turn angles centered around the easy (TAI and TAIII phases) and hard (TAII phase) directions, respectively.

For the concentration of free spin, \( x \), we shall assume that each \( \text{Al}^{3+} \) ion generates two free Cu spins, i.e. \( x = 2\delta \) (cf. Fig. 1a) and thereby: \( y = 1 - \frac{3}{2}x \).

\( f^\pm(z) \) have been minimized with respect to \( z \) as function of parameters, \( t \) (reduced temperature) and \( x \), for a few values of the normalized interaction parameters \( j \) and \( q \). A realistic estimate for \( J_2 \) is \( \sim 0.1 \) K. Much less is known about \( J_3 \) and \( D_4 \). We shall leave \( D_4 \) as a free parameter. \( J_3 \) cannot be too small, because like in the planes this spin interaction is mediated via oxygen ions. However, hybridization via apical oxygens is not as effective as hybridizations within the planes or chains because the involved orbitals are orthogonal. Since
the AFI - AFII transition temperature is of order a few Kelvin we estimate $J_3$ as 10 K and thereby: $j = 0.01$ and $T = 5t$ K.

Fig. 2 shows the corresponding phase diagram for three values of the anisotropy parameter $q$. Full lines represent continuous transitions, dotted lines are first order transitions, and dots are tricritical points. The dashed lines are the disorder line at $z = \frac{\pi}{4}$. Although the anisotropy $q$ does not change the phase diagram boundaries significantly, it influences the nature of the phase transitions even when $q \ll j$. The AFI–TAI transition is always continuous, and if $q = 0$, the AFI–AFII transition always takes place via two continuous transitions through the intermediate TA phase. For low concentrations of free spins ($x < 2jy$), the pure AFII state is inaccessible even at $t \to 0$ (see Fig. 2). Increasing $j$ to 0.1 does not change the morphology of the phase diagram but for obvious reasons higher concentrations of free spins are required for the characteristic features to occur. One can subdivide the order parameter in the TA phases into AFI and AFII parts as $m_{AFI} = \frac{1}{2}|S_j + S_{j+1}| = S\sqrt{1-z_g^2}$ and $m_{AFII} = \frac{1}{2}|S_j - S_{j+1}| = S\sqrt{z_g}$. $z_g$ is the $z$ value at which the global minimum of the free energy is achieved from $f^\pm$ in Eqs.(8). The inserts in Fig. 2 show examples of the temperature variation of the global order parameter, $z_g$, as composed from the optimal $z^\pm$. Without anisotropy ($q = 0$) continuous transitions are observed, but for $q = 0.001$ and $x = 0.02$ a continuous transition from AFI ($z_g = 0$) to TAI ($z_g = z^+$) is followed by the first order transition to TAI ($z_g = z^+$) and then to AFII ($z_g = 1$).

A direct comparison with experimental data requires a detailed knowledge of the number of free spins generated for specific Al doping levels. It is well-established that the sample treatment is very essential for the Al configurations in the basal plane, and quite different concentrations of free spins may develop for the same Al stoichiometry [14]. However, comparing the model results displayed in Fig. 2 with experimental data reported for Al doped YBCO [6,7] we find agreement with the following observations:

1. the sequential transitions AFI–TA–AFII occur below 20 K (*i.e.* below $t \simeq 4$);
2. the AFII and TA phases are not present in nominally pure materials (*i.e.* with $x = 0$);
3. the transition into the AFII phase is not always complete and the TA phase remains...
stable at low temperatures and small $x$;

(4) there is essentially no ordered magnetic moments on the Cu sites in the basal plane;

(5) the intensities of magnetic Bragg peaks at $Q_I$ and $Q_{II}$ are in good agreement with the square of the order parameters $m_{AFI}$ and $m_{AFII}$, (cf. insert to Fig. 2a).

Since apparently no first order transitions or jumps in the $m_{AFI}$ and $m_{AFII}$ order parameters are observed experimentally, the four-fold easy axis anisotropy is very small.

When large amount of free spins are introduced in the basal plane, as may be the case when YBCO is heavily doped with Co [9] or Fe [10], they interact and it is likely that they form a 2d AFM structure. In this case the AFII phase is expected to be stable even at higher temperatures as has been observed experimentally in Fe doped YBCO, where complete suppression of the AFI phase may result [10].

A classical treatment of a spin-$\frac{1}{2}$ system may appear inappropriate. However, it should be recalled, that we are mainly giving a qualitative mechanism for the origin of the AFI, AFII and TA phases. A quantum treatment will be pursued.

In conclusion we have shown by a classical statistical model that the AFII and TA phases, observed experimentally in Al, Co and Fe doped YBCO and in materials with rare earth (RE) ions on the Ba site, result from polarization of free spins created in the basal plane of the structure. Thus, we propose that in nominally pure materials with no RE on the Ba site the AFII phase should not be present. Using realistic values for the interaction parameters a semi-quantitative agreement with the experimental observations is established. Based on the experimental fact that the magnetic transitions appear to be continuous and long range order is established along the $z$ axis we conclude that the in-plane anisotropy parameter, $D_4$ is finite but very small ($< 10^{-5}|J_3|$, cf. Fig. 2b). More model work and experimental studies on carefully prepared materials are needed and in progress for more detailed comparisons.
REFERENCES

[1] J.M. Tranquada, et al. Phys.Rev.Lett. 60, 156 (1988).

[2] H. Kadowaki, et al. Phys. Rev. B 37, 7932 (1988).

[3] S. Shamoto, et al. Phys. Rev. B 48, 13817 (1993).

[4] A.H. Moudden, et al. Phys. Rev. B 38, 8720 (1988).

[5] W.-H. Li, et al. Phys. Rev. B 41, 4098 (1990).

[6] H. Casalta, et al. Phys. Rev. B 50, 9688 (1994).

[7] E. Brecht, et al. Phys. Rev. B 52, 9601 (1995).

[8] E. Brecht, et al. (unpublished).

[9] P.F. Miceli, et al. Phys. Rev. B 39,12375 (1989).

[10] I. Mirebeau, et al. Phys. Rev. B 50, 3230 (1994).

[11] O. Schmidt et al. (unpublished).

[12] J. Rossat-Mignod, et al. Physica B 192, 109 (1993).

[13] S. Hayden, et al. Phys. Rev. B 54, 6905 (1996).

[14] E. Brecht, et al. Physica C 265, 53 (1996).
FIG. 1 Magnetic structures observed in YBCO. (a) Interactions $J_0$ and $J_1$ are responsible for the rigid double layer magnetic structures; $S_j$ is the bilayer order parameter; $J_2$ the coupling via non-magnetic Cu$^+$ that favors AFI structure, while $J_3$ via the free Cu$^{2+}$ spins tends to AFII ordering. The formation of Cu$^{2+}$ spins through Al substitution is also shown. The mutual spin arrangement in the bilayers is related to the TAI phase. (b) displays spin configurations and turn angles (shaded areas) $\psi$ in adjacent layers $j$ and $j+1$; magnetic phases AFI, AFII as well as various TA phases may result from the model studies. $\pm D_4$ are related to hard and easy axis spin anisotropies.
FIG. 2  Magnetic phase diagrams for Al doped YBCO as function of the free spin concentration $x$ and the reduced temperature, $t$, for the normalized interaction constant $j = 0.01$ and different values of the anisotropy $q$. The diagram for $q = 0$ is representative of a finite but infinitely small anisotropy (see the text). The dashed lines are the disorder line as explained in the text. Inserts show the order parameters for the selected $x$ values (vertical dashed lines).