Neutron scattering search for static magnetism in oxygen ordered YBa$_2$Cu$_3$O$_{6.5}$

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We present elastic and inelastic neutron scattering results on highly oxygen ordered YBa$_2$Cu$_3$O$_{6.5}$ ortho-II. We find no evidence for the presence of ordered magnetic moments to a sensitivity of $\sim 0.003 \mu_B$, an order of magnitude smaller than has been suggested in theories of orbital or d-density-wave (DDW) currents. The absence of sharp elastic peaks, shows that the d-density-wave phase is not present, at least for the superconductor with the doping of 6.5 and the ordered ortho-II structure. We cannot exclude the possibility that a broad peak may exist with extremely short-range DDW correlations. For less ordered or more doped crystals it is possible that disorder may lead to static magnetism. We have also searched for the large normal state spin gap that is predicted to exist in an ordered DDW phase. Instead of a gap we find that the Q-correlated spin susceptibility persists to the lowest energies studied, $\sim 6$ meV. Our results are compatible with the coexistence of superconductivity with orbital currents, but only if they are dynamic, and exclude a sharp phase transition to an ordered d-density-wave phase.

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I. INTRODUCTION

The search for the origins of high-temperature superconductivity has led to many new concepts in condensed matter science. One of these is that antiferromagnetism can originate from orbital currents. This idea underlies the staggered flux phase of Marston and Affleck, the proposed dynamic orbital currents of Wen and Lee, and the d-density wave (DDW) order of Chakravarty et al. The orbital currents would flow in the planes of cuprate superconductors around a region of the size of the unit cell. They would be equivalent to a small magnetic moment to which neutrons are sensitive. The theory of Chakravarty et al. predicts that static d-density wave (DDW) order would appear as an elastic Bragg peak well above the superconducting transition temperature. Most models require a breaking of the translational symmetry of the CuO$_2$ planes at $Q = (\pi, \pi)$, but the orbital currents predicted by Varmazyriak do not.

There have been several reports of a static magnetic signal at $(\pi, \pi)$ in the YBa$_2$Cu$_3$O$_{6+x}$ (YBCO) at a surprisingly large ordering temperature of $\sim 300$ K. Siddis et al. have performed both unpolarized and polarized neutron scattering measurements along with zero-field $\mu$SR experiments on YBCO$_{6.5}$. They observed an elastic magnetic peak at $Q = (1/2 1/2 L)$ for $L=2$ but not for $L=0$. This they found to be consistent with Cu$^{2+}$ moments of $\sim 0.05 \mu_B$ pointing in the a-b plane and antiferromagnetically coupled within the plane and between the bilayers. However, the $\mu$SR results conducted on a piece from the same sample did not display oscillations consistent with the magnetic moment observed by neutron scattering.

At a slightly larger oxygen doping Mook et al. observed an elastic peak at $(1/2 1/2 2)$ in YBCO$_{6.6}$ below 300 K. They derived an effective ordered magnetic moment of $\sim 0.02 \mu_B$ and noted that the form factor drops rapidly with $|Q|$ as would be expected from orbital currents. The $\mu$SR results by Sonier et al. on YBCO$_{6.67}$ and YBCO$_{6.95}$ were initially interpreted as showing the existence of static magnetism consistent with the d-density wave or other orbital current theories. However, further work has shown that the complex $\mu$SR results are more likely to arise from the charge inhomogeneities of a stripe structure rather than from d-density wave order. For YBCO$_{6.5}$ in a magnetic field, Miller et al. have described their $\mu$SR results with a model that gives an improved fit when a static antiferromagnetic moment is included in the vortex cores. At doping $x > 0.5$ we note that filled Cu-O chain segments may lie adjacent, while for YBCO$_{6.5}$, ortho-II ordered, the chains lie two cells apart and an empty Cu chain separates them.

Chakravarty et al. state that the results of Ref. $^3$ are consistent with the DDW theory. This claim is based on three observations. An elastic magnetic peak was observed at $(\pi, \pi)$, its intensity decreases much faster with $|Q|$ than does the Cu$^{2+}$ spin form factor $^3$ and finally, since the DDW is Ising-like and breaks a discrete symmetry, there should be a gap, which they point out is consistent with the $\sim 20$ meV gap reported by Dai et al. in YBCO$_{6.6}$ $^4$.

It is clearly important to know whether static magnetism, regardless of its microscopic origin, plays a universal role in the superconductivity of YBCO, and whether it depends on oxygen concentration, oxygen order, and orthorhombic twinning. To answer this we have carried out elastic and inelastic neutron scattering on de-twinned orthorhombic YBCO$_{6.5}$ in which the oxygen is well ordered in the ortho-II phase. In this phase copper chains along $b^*$ filled with oxygen occur every second...
cell along the \( a^* \) direction. We establish the absence of elastic magnetic signal with a high sensitivity that would have easily detected the peaks seen in Ref. 8 and Ref. 9. We also observe low-energy spin fluctuations in the normal state well below 20 meV where a spin-gap has been claimed.

II. EXPERIMENT

The sample consisted of six orthorhombic YBa\(_2\)Cu\(_3\)O\(_{6.5}\) crystals of YBa\(_2\)Cu\(_3\)O\(_{6.5}\) grown at the University of British Columbia using a top-seeded melt growth technique which in common practice requires the addition of small amounts of platinum and Y\(_2\)BaCuO\(_5\) (green phase) to modify growth dynamics. In our case 0.5 wt% of platinum and 2 wt% of Y\(_2\)BaCuO\(_5\) were added, which are at the low range of values used in this technique. It was found by EDX composition mapping that platinum exists in the Ba\(_3\)Y\(_2\)PtCu\(_2\)O\(_{10}\) phase and the YBCO matrix is essentially free of platinum. By scaling the diffraction intensities of impurity phases to the weak extinction free YBCO (1 1 2) Bragg peak, we found that the dominant impurity was the green phase of \( \sim 5\% \) by volume; all other impurities were less than 1% by volume. We note that green phase fractions as large as 14\% have been reported in other studies.

The oxygen content of the crystals was set to 6.5 by annealing at 760°C in oxygen flow followed by quenching to room temperature in nitrogen gas flow. Partially detwinned crystals were obtained by mechanically applying a pressure of 100 MPa along the \( a \)-direction at 400°C in nitrogen gas flow. The ortho-II ordering, which has alternating full and empty chains, was developed by annealing the crystals at 60°C for 2 weeks in a sealed bottle. The crystals show a sharp superconducting transition at 59 K with a width of 2.5 K, as observed by field cooling magnetization shown in Fig. 1. Each crystal, about 1 cm\(^3\) in size, was sealed in an aluminum can under a dry helium atmosphere (kept at dewpoint \( < -40°C \) to eliminate water). The Stycast sealant was masked with gadolinium paint. The six crystals were mutually aligned on a multi-crystal mount at the E3 spectrometer at NRU reactor, Chalk River. The rocking curve width was about 1° for each crystal and approximately 2.2° for the composite.

From the (2 0 0) radial scan of Figure 1 we find from a gaussian fit that the majority domain occupies 70% of the sample volume. The peak at higher \( |\mathbf{Q}| (H=2) \) is the (2 0 0) Bragg peak from the majority domain, and the peak \( H=1.98 \) is the (0 2 0) of the minority domain. An independent check is obtained from the satellites produced by oxygen chain order peaks, (3/2 0 0) and (0 3/2 0) (Fig. 2). Their widths along \( H \) and \( K \) were nearly resolution limited. Fits to resolution-convolved lorentzians showed that the oxygen correlation lengths exceeded \( \sim 100 \text{ Å} \) in both the \( a \) and \( b \) directions, while it was approximately 50 Å along the \( c \) direction. These correlation lengths compare favorably to the x-ray characterization of highly ordered ortho-II indicating the high quality of our crystals. We find that the degree of oxygen order derived from the ratio of (3/2 0 0) and (0 3/2 0) oxygen satellite peak intensities equals the twinning ratio of 70%. This shows that the chains are fully oxygen ordered within each orthorhombic domain.

Elastic scattering measurements were carried out at the C5 and E3 neutron spectrometers at the NRU reactor at Chalk River Laboratories using filtered beams of both 2.37 Å and 4 Å neutrons. A focusing graphite (002) monochromator and a graphite (002) analyzer were used. Pyrolytic graphite filters (with a total thickness 10 cm) were placed in the incident and scattered beams to eliminate higher order reflections. Before the monochromator, filters of cold sapphire and beryllium were installed for 2.37 Å and 4 Å neutron beams respectively. For elastic scattering, the collimation was [24’ 29’ 51’ 120’] horizontally and [80’ 240’ 214’ 429’] vertically. The sample was mounted in a closed-cycle refrigerator on a C-crade so that the (H H L) plane was horizontal when the refriger-ator was vertical. The cradle’s [001] rotation axis allowed access not only to (1/2 1/2 L), L=0, 1, 2, where DDW order was sought, but also to (H 0 0) and (0 K 0) where the detwining and oxygen order could be measured.

For the inelastic neutron scattering measurements at \( E_f = 14.6 \text{ meV} \) and for energy transfers below 10 meV, where the scattering is weaker, the horizontal collimation was changed to [31’ 48’ 51’ 120’], but was kept the same as the elastic measurements for higher energy transfers. A pyrolytic graphite filter (5 cm thick) was placed in the scattered beam. Inelastic scans were made along the [100], [010], and [001] directions independently with
III. RESULTS

To search for static magnetic order at \((\pi, \pi)\) we made radial and transverse elastic scans at \((1/2 1/2 L)\) positions with \(L = 0, 1,\) and \(2\). In Fig. 3 we show the scans with 2.37 Å neutrons through \((1/2 1/2 2)\) at 13 K, and the intensity change with temperature in the normal phase at 290 K, where the peak seen by others has almost vanished. The configuration is similar to that of Ref. \(5\) and covers the same range of wave vector. We find, in searches at \(L=0, 1,\) and \(2,\) that no static ordering peak exists in YBa2Cu3O6.5 ortho-II that exceeds about 5% of the 13 K background. In contrast, the signal for YBCO6.6 (results for \(L=2\) are inset in Fig. 3), which lies on a background of 1850 counts, represents a modulation of 13% above background, and would have been easily detected. From the statistical accuracy of each point alone we would have been sensitive to a moment at least three times smaller than that reported for YBCO6.5. We do not understand the substantial increase of the Q-independent scattering with decreasing temperature amounting to 300 counts at 70 K and 1300 counts at 290 K. In the context of the \(\sim 300 K\) transition seen in other samples, this might signify the growth below room temperature of a broad peak that extends over much of the Brillouin zone and cannot be resolved from the background. It would correspond to highly localized correlations.

To establish an improved limit on the maximum magnetic moment to which our experiment is sensitive we put our measurements on an absolute scale. We calculated our sensitivity in terms of what moment would produce an intensity corresponding to the average of the error bars in the Fig. 3 scan through \((1/2 1/2 2)\). To do this we assumed an antiferromagnetically ordered array of Cu\(^{2+}\) moments pointing along the \(a^*\) direction (different directions in the \(a\)-plane give a qualitatively similar estimate). We compared the average error bar with the integrated intensity of the H-scan through \((3/2 0 0)\) and the rock scan through \((1 1 2)\). These two peaks are ideal for normalization since they have weak structure factors for normalization since they have weak structure factors and should not be subject to extinction. These independent methods test the reliability of our estimate, since the H-scan through \((3/2 0 0)\) requires knowledge of the instrumental resolution, while the rocking scan through \((1 1 2)\) does not, as shown by Cowley and Bates.\(^{3,4}\) We can conclude that our sensitivity is such that we could have detected any static moment greater than \(\sim 0.003 \, \mu_B\). This is approximately an order of magnitude less than the moments reported in other experiments.\(^{6,7}\) We
have also forced a weak gaussian, with the calculated resolution width, to go through the 13 K data (Fig. 3) and reached a similar conclusion - moments of the size observed in these experiments do not occur in well-ordered ortho-II YBa$_2$Cu$_3$O$_{6.5}$.

Although we find no static peak we have searched for other signatures of orbital magnetism. For example, the DDW theory requires an opening of a gap in the spin spectrum well above $T_c$. For this reason it is claimed that the reported spin gaps $\sim 20$ meV for YBCO$_{6.6}$ and $\sim 16$ meV for YBCO$_{6.5}$, are a confirmation of the DDW theory. However, these are superconducting, not normal-phase gaps, since they were derived by subtracting the spin correlation data above $T_c$ from that below $T_c$. In contrast there is no evidence for a spin gap in disordered YBCO$_{6.5}$ in its normal phase obtained by Fong et al.\textsuperscript{5} or Bourges et al.\textsuperscript{6,7}

Since the presence of a gap would be a key piece of evidence that the orbital currents of the DDW had broken a discrete symmetry below a sharp phase transition temperature, we made careful Q-scans in the low-energy regime to establish whether a spin gap had occurred in the presence of oxygen order. Previous polarized neutron experiments have shown that the Q-correlated peak near $(\pi, \pi)$ is magnetic\textsuperscript{8,9} and we have confirmed this from its form factor and temperature dependence.\textsuperscript{2} As shown in Fig. 4, our experiments provide compelling evidence that a Q-correlated signal near $(\pi, \pi)$ persists to the lowest energies.\textsuperscript{2} In particular, it exists in the normal phase for energies well below 20 meV and is still seen at energies as low as $\sim 6$ meV in the normal phase. Its spectral weight declines roughly with $E$ at low energies. We conclude that there is no normal state spin gap for YBCO$_{6.5}$ ortho-II.

Our observation that spin fluctuations persist to low energies in ortho-II ordered YBa$_2$Cu$_3$O$_{6.5+x}$ with $x = 0.5$ agrees with the absence of a gap in disordered samples with $x=0.5$ and 0.52. Relative to these disordered crystals with similar doping but lower $T_c$, the low-energy susceptibility in the ortho-II crystal is more highly suppressed relative to the resonance. Our results are also consistent with those of Chou et al.\textsuperscript{3} for disordered, twinned YBCO$_{6.5}$. Our higher resolution and more ordered crystal now reveals the flat topped correlations in Fig 4, indicative of the incommensurate structure of the $(\pi, \pi)$ peak, to be described elsewhere.\textsuperscript{2} Otherwise the measured spin response is similar to that of Chou et al. The overdamped spin-wave model (curves in figure 4) convolved with the instrumental resolution gives a reasonable description of the data. The presence of low-energy spin correlations is not consistent a fully developed spin gap. This makes it unlikely that a new phase has been entered in which the discrete symmetry of the the Ising-like DDW order parameter has been broken.\textsuperscript{8}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Inelastic neutron scattering results in the normal state at energy transfers of 12.4, 8.3, and 6.2 meV. Corrections for higher order contamination have been included. The fits are based on the over-damped spin-wave model of Chou et al. The results show that Q-correlated spin fluctuations persist to the lowest energies.}
\end{figure}

IV. DISCUSSION

In disordered YBCO the spin fluctuations in YBCO with oxygen concentrations between 6.4 and 6.5 weaken with hole doping away from the antiferromagnetic phase and suddenly drop in strength when $x$ reaches 0.5, concomitant with the growth of the orthorhombic and oxygen chain structure.\textsuperscript{2} For ordered ortho-II with $x = 0.5$, we find the spin fluctuations are quite similar being suppressed but not eliminated.

The sample of YBCO$_{6.6}$ used in Ref.\textsuperscript{8} has oxygen ordering correlation lengths comparable to ours by comparison of the peak widths.\textsuperscript{2} However the extra oxygen must find a way into the lattice and interrupt the perfect 2a by 1b cell of the ortho-II structure. The sample of Ref.\textsuperscript{8} has shorter oxygen correlation lengths of 20 Å in the a-b plane and 12 Å along the c direction. These are shorter than in our sample, which exhibits nearly resolution limited superlattice peaks indicating oxygen order over more than $\sim 100$ Å within the CuO$_2$ plane and 50 Å normal to the planes. This might suggest that disorder causing the proximity of adjacent short segments of chains filled with oxygen could lead to magnetic order.

The idea that disorder may induce long-range antiferromagnetic order is not new. Recent examples include Mg doped CuGeO$_3$ which exhibits long-range antiferromagnetic order for finite Mg concentration.\textsuperscript{12} Also Hodges et al.\textsuperscript{13} added only 1.3% of Co to optimally doped YBCO and found long-range antiferromagnetic order below a low temperature, $T = 320$ K, quite similar to the onset of elastic peaks in refs.\textsuperscript{8} and \textsuperscript{3}. They suggest this impurity effect is analogous to the order seen by Sidis et al.\textsuperscript{6} in underdoped YBCO. The latter example is partic-
ularly interesting as Co is known to enter into the copper chains and pull into the structure 0.5 oxygen atoms per Co atom, therefore introducing disorder into the chains.

A number of theories describing the effect of disorder and impurities have been formulated. In the Ginzburg-Landau analysis by Kohno et al., disorder in a region can weaken the superconducting order and allow antiferromagnetic correlations to grow locally. With increasing disorder or impurity concentration the superconducting state will be transformed first into a state with locally nucleated antiferromagnetic moments and later into a state of long-range antiferromagnetic order. We believe our results represent the former state of weak disorder. In our experiments we find that the low-energy response is suppressed but not eliminated. Our results do not exclude the possibility that a broad peak may exist with extremely short-range DDW correlations. The generic phase diagram may allow YBCO at larger doping such as O_{6,6} to lie in the DDW phase while O_{6,5} does not.

One possible way to reconcile the differences between experiments is that structural disorder (of the oxygens, for example) induces a phase transition to a long-ranged ordered state. The absence of sharp static peaks contrasts with theoretical predictions for static orbital currents or d-density-wave states. We cannot exclude an orbital current state that does not break the symmetry of the CuO planes. Spin fluctuations do exist near (π, π) but they are dynamic and are found to extend in the normal phase to low energies (∼6 meV). Instead of the prediction that the spin-fluctuation spectrum “remains fully gapped and has no low-energy structure of any kind” we find that the low-energy response is suppressed but not eliminated. Our results do not exclude the possibility that the superconductivity in underdoped YBCO coexists with dynamic orbital currents, an idea that has received recent theoretical support.

V. CONCLUSION

Static antiferromagnetic long-range correlations that would produce a peak at (π, π) are absent in YBCO6.5 in its ortho-II structure at a level that represents our magnetic moment sensitivity of 0.003 μ_B. This is more than an order of magnitude lower than that of the elastic peaks reported in underdoped cuprate superconductors with somewhat different oxygen doping and/or order. We cannot exclude the possibility that a broad peak may exist with extremely short-range DDW correlations. The generic phase diagram may allow YBCO at larger doping such as O_{6,6} to lie in the DDW phase while O_{6,5} does not.

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