Incommensurate One-Dimensional Fluctuations in $YBa_2Cu_3O_{6.93}$

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A novel neutron scattering technique has been utilized to discover one-dimensional fluctuations with a very sharply defined modulation period of 16.65 Å along the **b**(**a**) direction in $YBa_2Cu_3O_{6.93}$. The fluctuations are found to be absent in the reduced oxygen compound $YBa_2Cu_3O_{6.15}$. The wave vector of the fluctuations is consistent with accepted values of $2k_F$ for the Cu-O chains. [S0031-9007(96)00623-0]

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$YBa_2Cu_3O_{7-\delta}$ (YBCO) is probably the most widely studied of the high temperature superconductors. However, in this Letter, we present measurements which show the existence of one-dimensional fluctuations that have not been observed previously by scattering measurements performed on YBCO. The observed periodicity is essentially identical with the value given for $2k_F$ derived from band calculations [1,2] for the Cu-O chains so it is likely that the fluctuations are connected with the Fermi surface for the one-dimensional chains. The geometry of the scattering is also that expected from the chains.

Most of the studies on YBCO have concentrated on the CuO_2 planes which are thought to be the source of the superconductivity. However, the one-dimensional Cu-O chains have interesting physical properties. The chains in YBCO are especially important as they may play a fundamental role in the superconductivity. Indeed, far-infared spectrometry has recently detected a superfluid component in the Cu-O chains [3]. An understanding of the electronic properties of YBCO may therefore be complicated by the fact that many measurements cannot distinguish between the planes or the chains.

The one-dimensional fluctuations were observed in an experiment that was designed to study the scattering from the one-dimensional chains. The distinguishing feature of the scattering from a one-dimensional object is that it occurs in planes in reciprocal space, and we have used this feature to isolate the one-dimensional scattering. The chains in YBCO are located along the **b** direction in the crystal so that the scattering planes are perpendicular to the **b** direction which in this crystal is parallel to $\mathbf{b}^*$ in the reciprocal lattice. Large YBCO crystals are now available, but these crystals are highly twinned and contain impurity phases. Since the crystals are twinned, $\mathbf{a}^*$ cannot be distinguished from $\mathbf{b}^*$ in the scattering measurements, making the measurements even more difficult as only half the total chain scattering intensity is generally available. The experiment to investigate the one-dimensional scattering is set up as shown in Fig. 1 so that the outgoing neutron wave vector $\mathbf{k}_f$ is contained in the scattering plane of interest. The incoming neutron wave vector $\mathbf{k}_i$ is fixed in length by the neutron monochromating crystal, but $\mathbf{k}_f$ can take any length, thus integrating over the excitations in the plane. The momentum transfer $\mathbf{Q}$ is given by $\mathbf{k}_i - \mathbf{k}_f$. A scan is performed so that $\mathbf{k}_f$ is always perpendicular to the $\mathbf{b}^*$ direction and thus contained within the scattering plane from the one-dimensional structure. The drawing shows $\mathbf{k}_f$ placed along $\mathbf{c}^*$, but any direction in the plane would be satisfactory. Of course, because of the twinning,

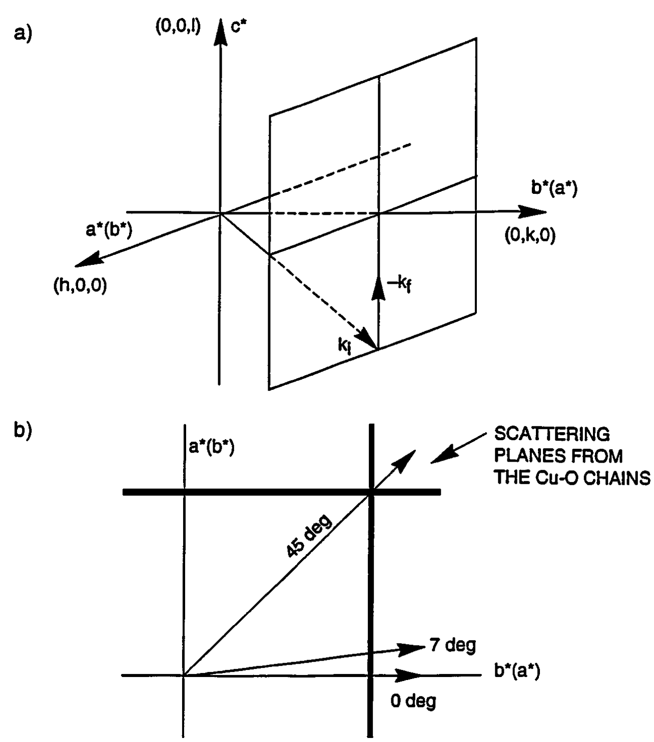

FIG. 1. (a) The scattering diagram used to achieve integration in planes perpendicular to $\mathbf{b}^*$. (b) The scan directions used in the measurements. Two sets of planes result from the twinned crystal. These planes cross on the 45° scan which is in the [1, 1, 0] direction.

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$\mathbf{a}^*$ for essentially half the crystal lies along the scan direction as well, but the plane of scattering distinguishes the one-dimensional structure.

The one-dimensional scattering is too weak to be easily observed in a standard triple-axis configuration, but the preferential integration in the plane greatly increases its visibility. This type of experimental setup has been used previously to study lower dimensional effects [4]. However, in the case of YBCO a vital addition to the technique is needed. This addition involves the use of pyrolitic graphite (PG) filters to essentially eliminate the elastic scattering that occurs when $\mathbf{k}_f$ and $\mathbf{k}_i$ become equal in length. If this is not eliminated the scattering pattern is dominated by intense elastic scattering from impurity phases in the sample. It is known that the transmission of the standard PG filters normally used to suppress higher order scattering is small for energies near 60 and 18 meV. Detailed measurements of the transmission of the filters used showed the transmission to be a minimum at 59.93 and 18.78 meV so the incident energy E_0 was chosen to be one of these energies and two PG filters were placed in the scattered beam for a total thickness of about 10 cm. The only scattering recorded passes through the PG filters which reduces the elastic scattering by about 5 orders of magnitude for the E_0 of 59.93 meV and about 4 orders of magnitude for 18.17 meV. The scattering that passes the filters depends on the PG transmission which has peaks and valleys at a number of energies, but is high over most of the whole band below about 15 meV. The experiment thus is arranged to do a partial energy integration of $S(Q,\omega)$. The energy distribution measured depends on the filter transmission, the spectrometer resolution function, the thermal factor, and the cross section. If an energy independent cross section is assumed, most of the scattering would occur over a wide energy band between about 10 and 55 meV with the weight centered around 35 meV for the measurement with an E_0 of 59.93 meV. Most of the scattering would result from excitations between 3 and 15 meV for the E_0 of 18.17 meV.

A particularly careful study of the lattice constants of YBCO as a function of oxygen content has recently been completed [5] so that an accurate value of the oxygen content of the samples used could be determined from the lattice parameters. The data shown were obtained with crystals with room temperature lattice parameters of 3.8188, 3.8856, and 11.6920 Å for a, b, and c. The oxygen content for these lattice parameters corresponds to the nearly ideally doped concentration of 6.93. We will first discuss the measurements made with an E_0 of 59.93 meV. The measurements were performed on the triple-axis spectrometers at the High-Flux Isotope Reactor at Oak Ridge National Laboratory. Figure 2(a) shows the result of an integrating measurement at 293 K in which the scan direction is along $\mathbf{b}^*(\mathbf{a}^*)$. The momentum scale for the scan is in $\mathbf{b}^*$ reciprocal lattice units. The scan shows a generally increasing count rate with increasing angle or momentum transfer Q as expected given that the measurement samples an integral over the phonon scattering which has a cross section that increases with Q. Superposed on the general scattering are peaks which occur at the position of the Bragg peaks and small additional peaks or satellites found around the Bragg peaks. The satellites are largest around the strong peak at (2) that comes from Bragg scattering not rejected by the filter. Figure 2(b) shows an enlarged region of the scan. The satellites are found near 1.75 and 2.25 in reciprocal lattice units. Higher resolution measurements discussed below give a more accurate position for the satellites. A number of crystals were studied and the same pattern was found. The data shown were obtained with a 45 g crystal with a mosaic spread of 1.4° (FWHM) for the (2, 2, 0) reflection. The crystals used in the experiments need to have a reasonably good mosaic spread since a considerable momentum space integration is performed.

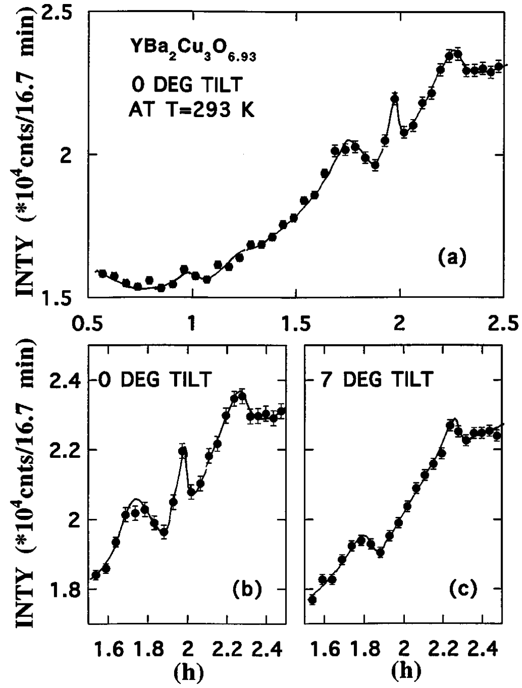

FIG. 2. (a) The result of a scan along $\mathbf{b}^*$ or along the 0° line. (b) An expanded version of the scan while (c) is the result obtained along the 7° direction [see Fig. 1(b)]. Superlattice or satellite peaks are found around the Bragg peak positions for the larger Q reflections. Solid lines are guides to the eye.

The next series of experiments was performed to confirm that the scattering really was found in planes. Various integration directions were tried, and the scattering was found to remain if $\mathbf{k}_f$ was in the scattering plane perpendicular to $\mathbf{b}^*(\mathbf{a}^*)$ and vanished as the direction of $\mathbf{k}_f$ deviated from the plane. In addition, a number of scans were done at angles to the $\mathbf{b}^*(\mathbf{a}^*)$ or [1, 0, 0] direction, sampling directions between the [1, 0, 0] and [1, 1, 0] directions. It is observed from Fig. 1(b) that such scans pass through the scattering planes at different positions, providing confirmation of the planar nature of the scattering. In this case,

$\mathbf{k}_f$ is aligned along $\mathbf{c}^*$ so that the integration always takes place in the plane.

Figure 2(c) shows a scan taken at 7° from the b* direction as shown in Fig. 1(b). The scale (h) is the component of the scan along $\mathbf{b}^*$ since that is the only direction of importance for the one-dimensional scattering. We see here only the satellite peaks near 1.75 and 2.25 as the scan does not cross a Bragg reflection. Scans were taken at a number of other angles with similar results. Figure 3(a) shows a scan along a direction 45° from $\mathbf{b}^*$ or along the [110] direction. This scan was taken with a 95 g crystal that had a mosaic spread of 1.7° (FWHM) for the (2, 2, 0) reflection. Again we see the Bragg reflections, and a satellite now becomes visible near 1.25 on the projected scale since the actual Q is larger than for the 0° scan. The satellite near 1.75 is also observable as it is in the scans at other angles. Note now that planes from the two twin directions cross in the 45° scan so that the full plane intensity is available.

To further confirm that we are observing scattering from the chains, measurements were made with the 95 g sample with oxygen removed so that the O content is 6.15. Figure 3(b) shows the 45° scan for this sample. We now see the scattering clearly from the magnetic fluctuations at 0.5 and 1.5 on the projected scale which represents the square lattice (π, π) point where the magnetic fluctuations are expected. The Bragg peaks are also observable in the scan, but no scattering is observed at the satellite positions found for the 6.93 sample. Figure 3(c) shows an expanded version of the 45° scan for the 6.93 sample in which we see the Bragg scattering and the satellite near 1.25. Figure 3(d) shows the same scan for the 6.15 sample showing the Bragg scattering and the magnetic scattering at 1.5. No extra intensity is observed at the satellite position near 1.25.

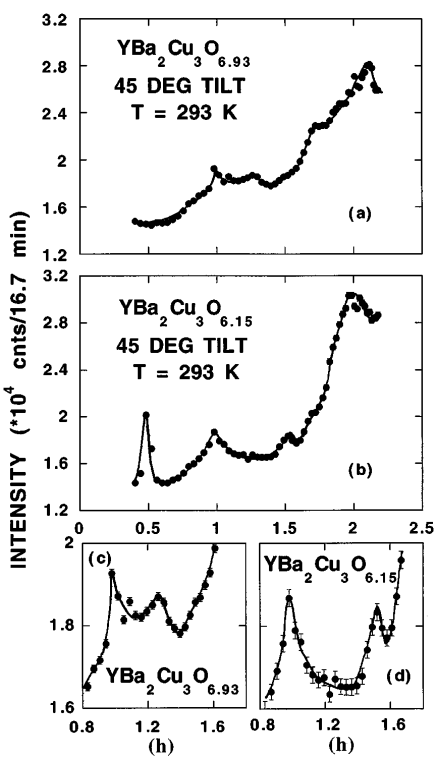

FIG. 3. (a) A scan along the 45° direction for the 6.93 sample while (b) shows the same scan for the 6.15 antiferromagnet. The scale shown is the distance along the 45° direction projected on the $\mathbf{b}^*$ direction. (c), (d) Expanded versions of (a) and (b).

All the measurements shown to this point were made at 293 K. Upon cooling, the satellite intensity diminishes and narrows slightly. This is consistent with the scattering resulting from a sum over the intermediate energy phonons. No obvious change in the satellite intensity was observed at the superconducting transition.

Additional measurements were made using an incident energy of 18.17 meV. For this case, a Si monochromator was used to eliminate second order scattering from the monochromator. The crystal used in the 18.17 E_0 measurements weighed 103 g and had a mosaic spread of 1.3° for the (2, 2, 0) reflection. The rejection of the primary beam by the filters is not as good as for 59.93 meV, and the momentum range is restricted. However, higher resolution is achieved, and the energy transfer is limited to 18.17 meV at a maximum at low temperatures. The top of Fig. 4 shows measurements made in a 7° scan as shown in Fig. 1. We see that the satellite peak narrows and becomes smaller as the temperature is reduced. The higher resolution permits a more accurate value for the satellite position, and least squares fitting results in a value of 1.767 ± 0.003 along $\mathbf{b}^*$ at 15 K and gives a modulation of 16.65 Å. We note the satellite is very well defined in momentum at low temperatures with a width of $(0.01 \pm 0.002)\mathbf{b}^*$ at 15 K, which is consistent with the peak being resolution limited.

Since the experiment involves an energy integration, we do not know the exact energy distribution of the scattering. The two experiments, however, set two energy scales for the scattering. For the 59.93 meV experiment the satellite intensity was found to be only very weakly dependent on temperature (about a 10% reduction between 293 and 100 K) thus setting an energy scale in the 30 to 40 meV region if we assume the standard phonon temperature dependence of the cross section. The data acquired for an E_0 of 18.17 meV are more accurate, and we find the satellite intensity drops about a factor of 2 between 293 and 15 K, thus setting an energy scale on the order of 10 meV. Again the 18.17 data showed no noticeable change at the superconducting transition. We have also made measurements on the satellite peak that occurs near $0.75\mathbf{b}^*$ and find its intensity to be about 5 times weaker than the $1.767\mathbf{b}^*$ satellite. The satellite intensity thus scales approximately the same as Q^2 as is expected for a phonon excitation.

We have simulated the experiment using a shell model to calculate the phonon positions and structure factors. The shell model gives an excellent account of the existing optical and neutron data for the phonons in YBCO. For the E_0 of 59.93 meV we have performed two calculations

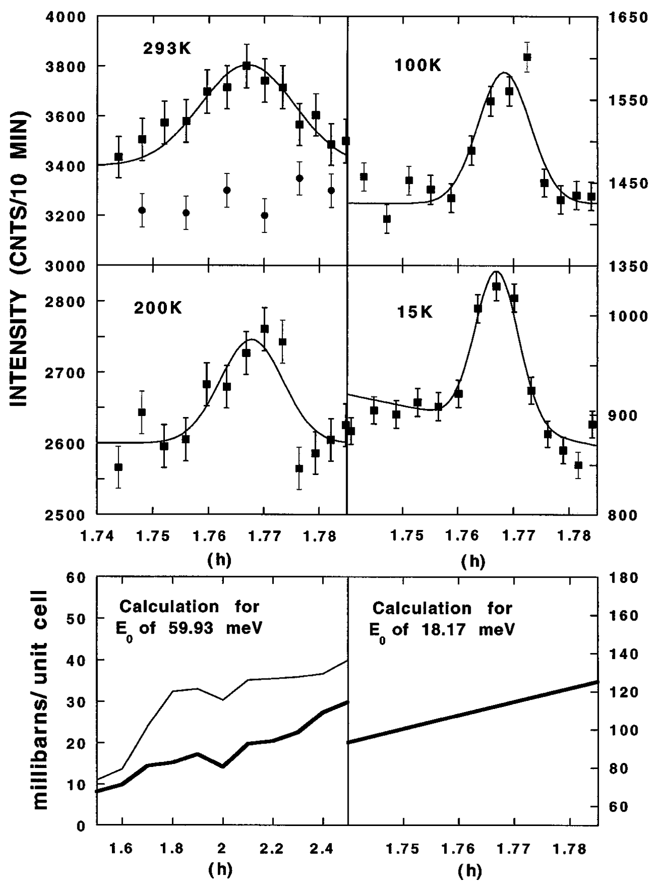

FIG. 4. The top four graphs show measured results obtained with an E_0 of 18.17 meV taken along the 7° direction. The scale shown is the distance along the 7° scan projected on the $\mathbf{b}^*$ axis. Several scans were averaged to obtain the errors shown. The lines are least squares fits to a Gaussian distribution on a sloping background. The round points on the 293 K plot are measurements along an 18° trajectory (see Fig. 1) for which the peak moves out of the scan range and thus serves as a measure of the background scattering. The lower graphs are the model simulations of the scans using a shell model.

to approximate the transmission of the filter. For the first, the filter transmission is set as 100% for energies below 15 meV and zero elsewhere. For the second, the filter transmission was 100% below 15 meV and 10% below 59 meV. The results are shown at the bottom of Fig. 4 for the 7° scan at 293 K to compare with Fig. 1. We note there is structure in the calculations, and indeed a peak occurs at about 1.8 in (h). The structure is broader than the satellite near this position and no peak occurs at 2.25 (h). Nevertheless, it is clear that the normal phonon spectra can give peaks in the energy integrating scans. It is important to perform experiments at a number of positions in reciprocal space, as we have done, to confirm the nature of the scattering. For the 18.17 meV measurements the simulation was done assuming a filter transmission of 100% below 15 meV. The 7° scan was used again, this time for 100 K. There is no structure found that is sharp on the scale of the width of the peaks shown at the top of Fig. 4. The last panel shows the result of the simulation. It is unlikely that the sharp satellites observed stem from the standard lattice phonons. The measurements also show the satellites missing for the lower oxygen content material. No satellite intensity can be observed with standard elastic scattering, although a small intensity could be missed in the large elastic background. The measurements are thus consistent with the existence of a dynamic charge density wave. The experiments show that the frequency range of the fluctuations appears to extend at least over the energy range from 10 to 30 meV. The temperature dependence rules out a large density of low energy excitations.

Scanning tunneling microscopy (STM) measurements [6,7] performed on YBCO find a modulation of 13 ± 1 Å along the length of the Cu-O chains which is noticeably shorter than our periodicity of 16.65 Å. Nevertheless, it seems very likely that the STM and neutron experiments are observing the same effect. Perhaps the samples have slightly different oxygen contents or differ in some other way. Our measurements show that the modulation is dynamic in nature and extremely well localized in momentum space. They also show it to be a bulk effect not limited to the surface.

Since the Cu-O chains are one dimensional, the Fermi surface (k_F) is expected to be a well-defined flat sheet, and thus $2k_F$ effects are likely to be visible in the lattice dynamics and the magnetic excitations from the Cu spins. Fermi surface calculations show that the chain bands hybridize with other bands to some extent, and the chains have been shown to be unstable towards some degree of buckling [1,2]. Even so, the Fermi surface appears to remain flat over much of the zone and is not expected to be strongly affected by chain buckling. Band structure calculations show that $2k_F$ effects are expected to display a periodicity of about 16 Å [1,2], which, within the uncertainty of the calculations, agrees exactly with the periodicity we have observed. It would seem likely that the measured fluctuations are directly related to the chain Fermi surface, although it is not clear that the band calculations would result in Fermi surface so extremely well localized in momentum space. Since the Cu chain atoms have spins, magnetic excitations from the chains should be visible. Experiments are under way to study these excitations.

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