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Superconductivity in an anomalously tetragonal $YBa_2Cu_3O_{6.62}$ single crystal: A possible singularity in the structural phase diagram

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During systematic studies of the structural phase diagram of $YBa_2Cu_3O_{6+x}$ (YBCO), a YBCO single crystal of oxygen concentration $x=0.62$ turned out to have a tetragonal crystal structure. By magneto-optical imaging of the expulsion of an applied magnetic field, it was shown that the sample was bulk superconducting. This makes the sample highly anomalous in two respects: with a stoichiometry of $YBa_2Cu_3O_{6.62}$ the sample should have an orthorhombic symmetry, and a tetragonal undoped sample should not be superconducting at all. Our results corroborate previous findings of Topnikov *et al.* [JETP Lett. **46**, 577 (1987)] of a tetragonal superconducting YBCO crystal with $x=0.62$.

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I. INTRODUCTION

The superconducting and structural behavior of $YBa_2Cu_3O_{6+x}$ (YBCO) depend strongly on the oxygen concentration x. The oxygen content can be varied in a well-controlled manner by in- and out-diffusion of the oxygen atoms in the basal CuO_x plane at temperatures higher than 600 K. For $x<0.35$ YBCO is an antiferromagnetic insulator, the oxygen atoms in the basal plane are more or less randomly distributed, and the crystal structure is tetragonal. For $x>0.35$ YBCO becomes a metallic superconductor, and the crystal structure undergoes a transition from the tetragonal to an orthorhombic state. The critical transition temperature T_c increases with the oxygen content and reaches a maximum around 93 K when $x\approx 0.93$. It has been well established for more than a decade[1] that when the oxygen content x exceeds ≈ 0.35 the oxygen atoms in the basal plane of the unit cell tend to align in chains along one of the crystal axes (by convention taken as the b axis). This chain formation is accompanied by the structural transition from the tetragonal state to a weakly distorted orthorhombic state, and the one-dimensional chains order along the a axis, with a characteristic spacing that varies with x.[2] The connection between the spatial arrangement of the oxygen chains and T_c can be explained by looking at the charge transfer of holes from the basal plane to the superconducting CuO_2 planes.[3,4] Most noticeably, there is the 60-K plateau in T_c around $x=0.5$ coinciding with the formation of the so-called ortho-II structure.[4–6] Here the oxygen occupancy is one oxygen atom in every second unit cell, and the oxygen chains arrange spontaneously in such a way that every other oxygen site along the a axis is unoccupied. A sequence of oxygen ordering superstructures has been found experimentally by electron,[5] neutron,[7] and x-ray diffraction,[2,8] and a structural phase diagram has been established.[2,8] Theoretically, most of the orthorhombic superstructure ordering properties have been accounted for by a simple extension of the asymmetric next nearest neighbor interaction (ASYNNNI) model,[9] originally introduced by de Fontaine *et al.*[10]

During the systematic studies of the orthorhombic phase diagram,[2,8] a surprising feature appeared: a crystal prepared to an oxygen composition of $x=0.62$ turned out to be both tetragonal and superconducting. This was completely unexpected, and it was decided to investigate this peculiar sample in greater detail, as described below.

II. EXPERIMENT

A. Sample preparation

A high-quality single crystal of YBCO, prepared from high-purity powders of Y_2CO_3 (99.999%), CuO (99.999%), and $BaCO_3$ (99.997%) was grown by the flux growth method in an yttria-stabilized zirconia (YSZ) crucible as described in Ref. 11. From a chemical analysis by inductively coupled plasma mass spectroscopy, the impurity levels were found to be less than 10 ppm for Zr, and the total content of Al, Fe, and Zn amounts to be less than 0.002. Further investigations of sample purity was made by energy dispersive x-ray (EDX) analysis using a JSM-840 electron microscope equipped with an EDX detector. Silicon was found on the crystal surface, probably originating from the YSZ crucible (SiO_2 is sometimes used as sintering aid during crucible manufacture). The silicon was mainly concentrated near the growth steps. These impurities could be easily removed using adhesive paper. The Y:Ba:Cu ratio was the same in the regions where Si was present than in the clean places, showing that Si hardly enters the YBCO lattice. Si being only loosely bound to the crystal surface, it can safely be assumed that its presence will not affect bulk properties as those studied in the present work. The weight of the crystal was 8 mg. In addition to this crystal that turned out to have the anomalous tetragonal symmetry, another YBCO crystal grown from chemicals of purity 99%–99.9% in a SnO_2 crucible was studied for reference purposes.[12] The weight of the crystal was 11 mg, and no chemical analysis was performed on this sample. Both samples were prepared simultaneously to the desired oxygen stoichiometry by a gas-volumetric method[13] using ceramic YBCO powder as buffer material. The oxygen concentration can be controlled to an accuracy better than $\Delta x = \pm 0.01$ by this method. The two crystals were positioned less than 1 cm apart in the furnace during the gas-volumetric annealing procedure. After the oxygen preparation was finished both crystals were annealed at 80 °C for 1 week to develop the oxygen superstructures. The value of 80 °C is taken from dynamical studies of the ortho-II phase formation.[2,14]

B. Superconducting properties

Critical transition temperatures were determined by ac susceptibility, using a commercial Lake-Shore DCS-7000 magnetometer/susceptometer. Further investigations were made by the magneto-optical (MO) technique, based on Faraday rotation in Bi-doped yttrium iron garnet (Bi:YIG) indicator films.[15] By this technique the expulsion or trapping of an applied magnetic field by superconducting currents can be imaged with high spatial resolution. The particular MO setup used in this study is described in Ref. 16. The samples were glued onto a copper plate with General Electric varnish. The plate was mounted on the cold finger of the MO cryostat, and the indicator film was placed on top of the sample.

C. Structural properties

The crystal structure was studied by high-energy synchrotron x-ray diffraction, using photon energies of 100 keV. For the hard x rays, the penetration depth is ~1 mm for our samples. In this way it is possible to use the Laue (transmission) geometry, thus probing the bulk of the sample. The diffraction experiments were performed at the dedicated high-energy Wiggler beam line BW5 at HASYLAB, DESY. A detailed description of the triple-axis spectrometer is found in Ref. 17. For the studies of oxygen superstructures where the reflections are weak and diffuse, a low-resolution setup was used with mosaic Si/$TaSi_2$ crystals for both monochromator and analyzer.[18] When the basic symmetry of the crystal structure was studied, we used a high-resolution setup with perfect Si crystals.

III. RESULTS

The anomalous tetragonal symmetry was first detected with the low-resolution setup for superstructure studies. Since the crystal was grown from high-purity chemicals, we conclude that the unexpected tetragonal symmetry was not due to bad sample quality. In order to see if the tetragonal symmetry was due to mistakes in the gas-volumetric preparation, which could have lead to an oxygen concentration $x < 0.35$, the reference crystal that had been prepared in exactly the same way was briefly characterized by recording the diffraction pattern on a two-dimensional charge-coupled device detector. It was clearly orthorhombic with twinning of the basal axes and an orthorhombic superstructure. Thus, we can rule out with certainty that the unexpected tetragonality was simply due to a too low oxygen concentration from a faulty gas-volumetric preparation.

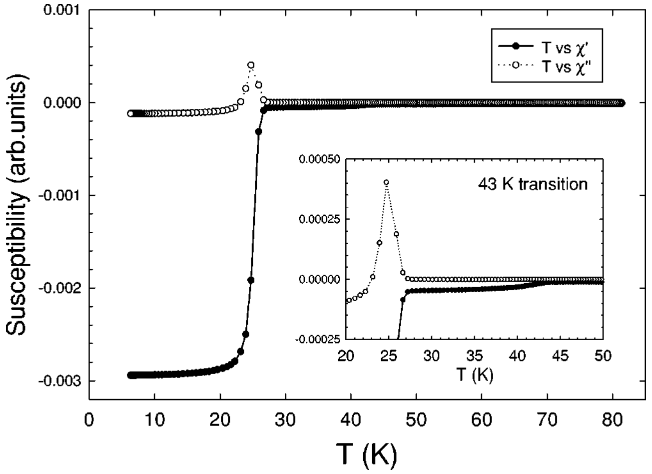

FIG. 1. Ac susceptibility of the tetragonal $YBa_2Cu_3O_{6.62}$ single crystal. Inset shows the susceptibility curve around 43 K in greater detail. The applied field was 3 G rms, frequency 125 Hz.

The anomalous tetragonal crystal was checked for superconductivity by ac susceptibility, and it turned out that it was superconducting with two transition temperatures: a small volume fraction with T_c of 43 K and a larger one with T_c of 27 K; see Fig. 1. The reference sample showed a T_c of 57 K, which is fairly good agreement with the expected T_c of a less pure YBCO sample with an oxygen concentration $x = 0.62$.

The pending question was of course whether the crystal was bulk superconducting or if the superconductivity originated from a minor, orthorhombic part of the crystal where, e.g., the oxygen concentration for some reason was higher. To settle this issue the sample was investigated by magneto-optical imaging. The sample was accidentally cleaved into two pieces along the ab plane when it was mounted for the MO investigations. Both pieces were investigated, and they gave identical MO results.

The sample was first cooled to 10 K, i.e., below T_c, in zero field. Then the external field was increased in small steps, and for each step an image was recorded. The MO images show beyond doubt that the crystal is bulk superconducting as seen in Fig. 2. At fields lower than 3 mT, the external field is completely shielded by the crystal (not shown in the figure). Between 3 and 5 mT, the flux penetrates into the crystal and divides it into a major domain and an elongated edge domain [Fig 2(b)]. Above 5 mT the crystal is divided into three domains [Figs. 2(c,d)]. The T_c could be determined individually for the three domains by changing the temperature in small steps and observing at which temperature the domains no longer were shielding off the applied field. We found that the two larger sections have a T_c of 27 K and the elongated edge domain has a T_c of 43 K [Fig. 2(e)], consistent with the ac susceptibility results. External fields greater than 75 mT could fully penetrate the sample at 16 K. These results were reproduced when the sample was investigated by MO imaging again after a period of more

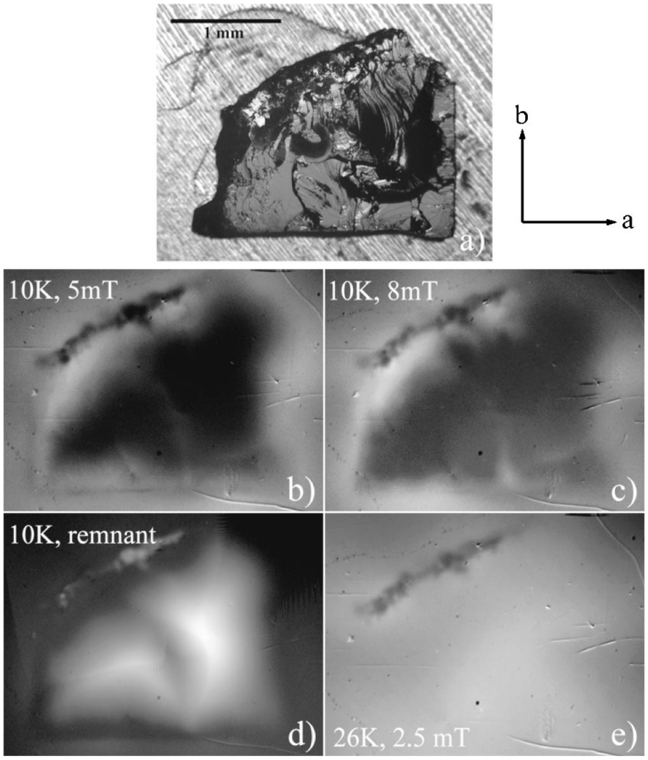

FIG. 2. MO images of the tetragonal $YBa_2Cu_3O_{6.62}$ single crystal. The magnetic flux density increases with brightness. (a) The crystal mounted on the Cu plate before covering it with the Bi:YIG indicator film. The scale bar is 1 mm long and the crystallographic axes are indicated to the right. (b) Field shielding at 10 K, $B_a = 5$ mT. (c) B_a increased to 8 mT. (d) Remnant state at 10 K after full field penetration. (e) Only the edge domain is shielding at 26 K, $B_a = 2.5$ mT.

than 3 yr. Flux penetration into the reference sample was also studied by MO imaging, and it showed no unexpected behavior.

With the knowledge of the superconductive domains, the sample was investigated with hard x rays again, this time in greater detail. We performed grid scans of the (0 2 0) reflection, since this reflection is quadruply split in the orthorhombic state due to twinning of the *a* and *b* axes.[19] The setup using perfect Si crystals for optimum resolution was chosen. The Si (2 2 0) reflection was chosen to investigate the (0 2 0) reflection of the tetragonal crystal, as there is a close lattice match for these reflections. In this way we were close to the nondispersive setting that offers maximum resolution.[20,21] The lattice parameters of the YBCO crystal were determined to be $a = b = 3.8652$ Å and $c = 11.7289$ Å. The *d* spacings of the monochromator/analyzer crystals and sample crystal were 1.920 05 Å for Si_{220} and 1.9326 Å for $YBCO_{020}$.

The size of the incoming beam was reduced to 0.4×0.4 mm^2 by a slit and the crystal was mounted with the ab plane horizontally in the scattering plane. Because the 43-K region was at the sample edge, it was possible to illuminate essentially either the 27-K domain or the 43-K domain and determine the structure of the domains separately. Grid scans were performed for the (0 2 0) reflection, and the results are shown in Fig. 3. The peak shape was Lorentzian squared and the full width at half maximum (FWHM) width of the 27-K domain was $\Delta k = 4 \times 10^{-4}$ in the longitudinal direction and $\Delta h = 4 \times 10^{-4}$ in the transverse direction. A rocking scan in the ab plane yielded a mosaic spread of 57 arc sec. For the 43-K domain $\Delta k = 7 \times 10^{-4}$ longitudinally, $\Delta h = 8 \times 10^{-4}$ transversely. By orienting the sample with the ac plane horizontally and translating the sample position through the monochromatic beam while monitoring the (2 0 0) reflection, it became clear that near the center of the sample there was a small-angle *c*-axis tilt of 20 arc sec. Thus, the superconducting weak link boundary separating the two 27-K domains seen in Figs. 2(c,d) is due to a *c*-axis tilt boundary.

The transverse resolution Δh is not affected by departures from the nondispersive setting.[20] The longitudinal resolution Δk is reduced in the dispersive setting, but with the close lattice match we have, we shall merely assume that the longitudinal resolution is a little larger than for the perfect nondispersive geometry. The longitudinal resolution for 100-keV photons using Si(2 2 0) perfect crystals in the nondispersive setting has been both calculated and determined experimentally by Bouchard *et al.*,[17] and they find a longitudinal 2θ width with FWHM 0.56 arc sec corresponding to $\Delta k \approx 1.4 \times 10^{-4}$. With the transverse resolution being of the order of 10^{-5}, we should be able to detect an orthorhombic splitting of $\Delta h \approx 10^{-5}$ (≈ 0.05 arc sec)

Since we are slightly off from the nondispersive setting we see that for the 27-K domain Δk is resolution limited,

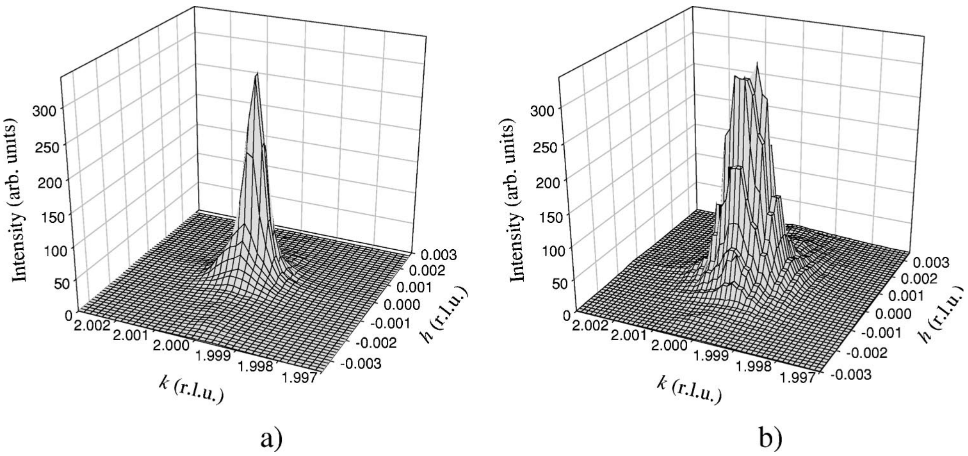

FIG. 3. Grid scan of the (0 2 0) reflection for (a) the 27-K domain and (b) the 43-K edge domain.

TABLE I. Lattice parameters for the anomalous tetragonal $x=0.62$ YBCO samples compared to ''normal'' sample values. First and second columns are for this study and Topnikov *et al.* (Ref. 24), respectively. Third and fourth columns are generally accepted values from Andersen *et al.* (Ref. 13) for orthorhombic YBCO with $x=0.62$ and for tetragonal YBCO with $x=0.30$.

	This study	Topnikov *et al.*	$x=0.62$ (normal)	$x=0.30$ (normal)
a (Å)	3.8652	3.869	3.825	3.855
b (Å)	3.8652	3.869	3.880	3.855
c (Å)	11.7289	11.723	11.70	11.79

while Δh is governed by the mosaicity. It should be mentioned that the typical mosaicity (FWHM) for the present type of YBCO samples is of the order of 130 arc sec or more,[8] meaning that this sample has an unusually low mosaicity. Compared to the 27-K domain, the 43 K domain is broadened considerably, both transversely and longitudinally, and it may be a sign of a very weak orthorhombic splitting.

A search was also carried out for superstructure reflections, using the low resolution setting with imperfect Si/$TaSi_2$ (1 1 1). No diffraction reminiscent of the orthorhombic superstructures was observed. Nor were any reflections observed resembling those of the herringbone-type superstructure[22] or the oxygen superstructures observed in tetragonal $NdBa_2Cu_3O_{6.5}$.[23] Weak diffuse scattering with extremely low intensity was found close to some Bragg peaks, but we did not succeed in establishing a symmetry of the reflections, and the results were inconclusive.

IV. DISCUSSION

Superconductivity with $T_c \approx 50$ K has been observed in a tetragonal single crystal of composition $YBa_2Cu_{2.862}O_{6.62}$ in 1987 by Topnikov *et al.*[24] At that time, it was still debated if the orthorhombic state was necessary for having superconductivity in YBCO, and the study has drawn very little attention. In that careful crystallographic study, the tetragonality of the sample was also well established. The sample preparation fundamentally differed from the gas-volumetric method used by us; the sample was annealed in oxygen at high pressures 1–2 bars and cooled very fast to room temperature from 800–850 °C. The pressures involved in the gas-volumetric procedure were typically less than 50 torr and the cooling was always very slow. As shown in Table I the lattice parameters for the anomalous $x=0.62$ samples studied by us and Topnikov *et al.* agree very well, but deviate significantly from the generally accepted values for normal YBCO samples in the orthorhombic state with $x=0.62$, as well as from the underdoped tetragonal state ($x=0.30$). The latter is another strong indication that the unexpected tetragonality in the sample is not due to a mistake in the oxygen preparation.

The tetragonal superconducting phase reported here is also significantly different from the tetragonal phases with high oxygen concentration that have previously been reported. Both the preparation condition and lattice parameters are significantly different from the meta-stable nonsuperconducting tetragonal phase with $x=0.7$ that can be obtained by oxalate coprecipitation using low-temperature synthesis.[25,26] The same is true for the pseudotetragonal superconducting phase with $x=0.8$ that was synthesized by Caignaert *et al.*[27] Furthermore, the impurity level of Fe in our tetragonal crystal is far below the concentration that will induce an orthorhombic-to-tetragonal transition, as reported by Maeno *et al.*[28]

Do we have a singularity in the structural phase diagram at $x=0.62$? There are no indications in the Monte Carlo simulations of this.[9] Studies of another crystal at this particular doping show a mixture of the ortho-II and ortho-V superstructures for $x=0.62$.[2,8] If we have a singularity in the phase diagram, it must be sharp indeed. We can speculate that a reason for the anomalous tetragonality could be the unusually low mosaicity of the tetragonal sample. Studies of the twinning structure[29] show that defects in the crystal structure act as nucleation centers for the tetragonal-orthorhombic transition. An extremely perfect sample could lead to a type of ''undercooled'' situation, where the orthorhombic transition never sets in before the sample is frozen into a nonequilibrium state.

There are also open questions with respect to the existence of superconductivity in the tetragonal sample. There is no long-range superstructure formation as in the orthorhombic state, and the superconductivity is strongly suppressed compared to orthorhombic samples with same oxygen concentration. We cannot expect the same type of orthorhombic superstructures as in ''normal'' samples, as these are intimately connected to the orthorhombic crystal symmetry, but we would expect some sort of chain formation in order to have a charge transfer from the basal plane to the CuO_2 plane. But even if there is no superstructure formation, the density of oxygen atoms in the basal plane at $x=0.62$ is so high that some clustering of oxygen atoms must take place. One would thus expect islands of closely spaced oxygen distributed throughout the sample, where the charge-transfer mechanism described in Refs. 3 and 4 effectively takes place. Clearly, a higher mosaic spread or orthorhombic distortion has a beneficial influence on the superconducting behavior, cf. Fig. 3.

In conclusion, we have demonstrated the existence of a sample of $YBa_2Cu_3O_{6.62}$ with a highly anomalous tetragonal symmetry. Investigations of the reference $YBa_2Cu_3O_{6.62}$ sample prepared under exactly the same conditions and comparisons with an earlier report of tetragonal $YBa_2Cu_{2.862}O_{6.62}$ clearly show that the unexpected tetragonality is not due to faulty sample preparation. The anomalous sample is shown to be bulk superconducting, revealing unambiguously that the orthorhombic crystal symmetry in itself is not a prerequisite for having superconductivity in the $YBa_2Cu_3O_{6+x}$ system.

ACKNOWLEDGMENTS

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