RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 18 1 MAY 1993-II

Effect of gold impurities on the superconducting fluctuations and the upper critical field of $YBa_2Cu_3O_{7-\delta}$ single crystals

U. Welp, S. Fleshler, W. K. Kwok, J. Downey, and G. W. Crabtree
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

H. Claus
Department of Physics, University of Illinois at Chicago, Chicago, Illinois 60680

A. Erb and G. Müller-Vogt
Universität Karlsruhe, Fakultät für Physik, W-7500 Karlsruhe, Germany
(Received 28 August 1992)

High-resolution measurements of the reversible magnetization of $YBa_2Cu_3O_{7-\delta}$ single crystals which were grown in gold crucibles and zirconia crucibles reveal that, within the experimental accuracy, gold impurities do not influence the normal-state susceptibility, the upper critical field, nor the superconducting fluctuation phenomena.

The high-T_c compounds, especially those based on double or triple CuO_2 layers, are characterized by large unit cells containing many atoms giving rise to the possibility of various structural and chemical defects. The question to what extent the "intrinsic" properties of these materials are governed by defects has become increasingly important.[1] The very short superconducting coherence lengths might allow the superconducting properties as well as the normal-state properties to be influenced significantly by these imperfections. It has been suggested[2] that the characteristic dependence of T_c in the 2:1:4 compounds[3] on the doping level is caused by short-scale phase-segregation phenomena and chemical instabilities at high doping levels. Recently, also for $YBa_2Cu_3O_{7-\delta}$ a maximum in the T_c vs δ curve (i.e., in the doping level dependence) around $\delta=0.1$ (Ref. 4) and indications for phase separation at lower δ have been reported.[5]

Apart from intrinsic phenomena related to the oxygen content there are additional extrinsic defects characteristic for $YBa_2Cu_3O_{7-\delta}$ crystals. It has been observed[6,7] that crystals grown in gold crucibles may contain a substantial amount of gold impurities, predominantly on the chain copper sites. Neutron activation analysis on crystals grown at Argonne revealed gold concentrations of about 9 at. % (of the chain copper). Similar numbers have been reported for crystals grown in other laboratories. This rather high impurity level has prompted questions about the extent that Au impurities change the properties of $YBa_2Cu_3O_{7-\delta}$. The incorporation of Au is known to increase T_c.[6] As a naturally trivalent ion, Au is expected to alter (locally) the oxygen arrangement in the chain layer and apparently optimizing the electronic structure for high values of T_c. Much larger (five times) diffusion constants for in-plane oxygen motion[8] in gold-containing crystals underline the importance of Au for the oxygen sublattice. As an additional scattering center for electron transport along the chains, the Au impurities are expected to have a pronounced effect on the *ab* anisotropy ρ_a/ρ_b of the normal-state resistivity in untwinned crystals. The smaller value of ρ_a/ρ_b in gold-grown crystals ($\rho_a/\rho_b\approx1.8$) (Ref. 9) as compared to zirconia-grown crystals ($\rho_a/\rho_b\approx2.2$) (Ref. 10) is consistent with this interpretation. The effect of Au on some Raman modes and the implications for the superconducting gap have been discussed frequently.[11] However, a clear correlation was not obtained, partly because neither the Cu(1) nor the O(1) sites are involved in the investigated Raman-active phonons, and therefore the effects are indirect and difficult to distinguish from crystal-to-crystal variations in oxygen concentration. In order to explain magnetization data on polycrystalline samples it has recently been suggested[12] that the upper critical field and the Ginzburg-Landau parameter κ are considerably enhanced in the Au-free material.

Here we present a comparison of magnetization measurements on gold- and zirconia-grown crystals. We find that the normal-state susceptibility for both samples is temperature independent and that within the experimental uncertainty the susceptibilities are the same: $\chi_c=(5.9\pm0.1)\times10^{-7}$ cm^3/g, $\chi_{ab}=(3.6\pm0.1)\times10^{-7}$ cm^3/g. The superconducting fluctuation diamagnetism on both samples can be scaled according to the high-field scaling relation[13] yielding upper critical-field slopes of -1.7 and -1.8 T/K, respectively. The field dependence of the magnetization has been analyzed according to the model of Hao and Clem[14] yielding an upper critical field slope of -1.8 T/K for both crystals, in good agreement with earlier determinations on gold-grown crystals.[13–15]

Recently large zirconia-grown crystals have become available.[16] The crystal studied here had a mass of 22.57 mg and a T_c of 89.8 K, and was grown at the University of Karlsruhe.[4] Absorption spectroscopy on these crystals yields a zirconium content below the detection limit of 0.1 wt. % (or 0.007 Zr atoms per unit cell).[17] The gold-grown crystal had a mass of 2.57 mg and $T_c=91.6$ K. Neutron activation analysis yields a gold concentration of 8 at. % (of the chain copper) for this crystal. Both crystals are twinned. The low-field magnetic transition curves in a field of 1 G applied parallel to the **ab** plane for both crystals are shown in Fig. 1. The magnetization in

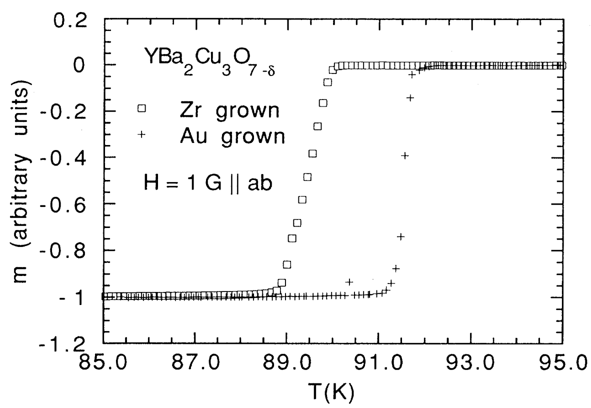

FIG. 1. Zero-field cooled superconducting transition in 1 Oe applied parallel to **ab** for the zirconia-grown crystal and the gold-grown crystal.

fields up to 7 T was measured in a commercial superconducting quantum interference device (SQUID) magnetometer. For these measurements the crystals were mounted on long quartz fibers in order to minimize the background signal and to avoid problems arising from thermal expansion of the sample holder.

The temperature dependence of the susceptibility in the normal state in a field of 1 T applied perpendicular and parallel to the CuO_2 planes is shown for both crystals in Fig. 2. Both crystals show the same behavior: χ_c and χ_{ab} are essentially temperature independent at temperatures above about 120–130 K. It has been suggested[18] that the presence of specific, isolated oxygen arrangements (T-like centers) induces an additional paramagnetic susceptibility. However, the absence of a Curie-Weiss contribution to the susceptibility of both crystals indicates that effects due to Au-induced oxygen disorder have a negligible contribution to the total magnetization. The absolute values for χ_c, χ_{ab}, and the anisotropy are in good agreement with other reports on twinned and untwinned crystals[19] as well as with grain aligned powders.[20] Upon decreasing the temperature towards T_c a strong temperature dependence develops in χ_c whereas χ_{ab} stays almost temperature independent. This behavior is a signature of strong superconducting fluctuation effects which for the **ab** directions are suppressed by the anisotropy ratio ξ_{ab}/ξ_c as compared to the **c** direction of the applied field.

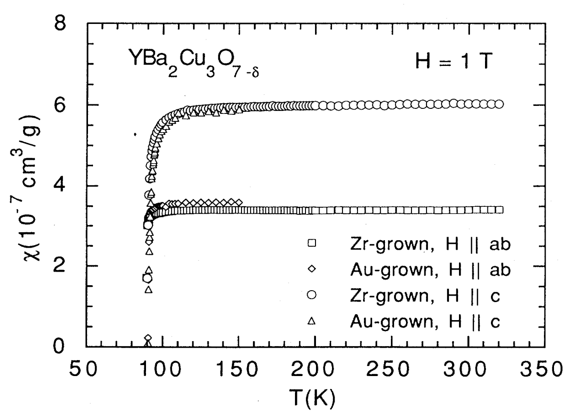

FIG. 2. Comparison of the temperature dependence of the normal state susceptibilities of the zirconia- and gold-grown crystals.

Figure 3 shows the temperature dependence of the magnetization near the diamagnetic transition in various fields parallel to **c** after subtracting the normal-state contribution. Both crystals show similar behavior: at a temperature around 1.5 K below T_{c0} the magnetization curves in each crystal seem to cross at a single point. This behavior has been observed in twinned and untwinned $YBa_2Cu_3O_{7-\delta}$ crystals,[13] in oxygen deficient $YBa_2Cu_3O_{7-\delta}$ crystals,[21] in $(La_{1-x}Sr_x)_2CuO_4$ (Ref. 22) as well as in Bi 2:2:1:2 (Ref. 23) and Bi 2:2:2:3.[24] It is a signature of superconducting fluctuation effects. The diamagnetic transition of a superconductor in the presence of high magnetic fields has been analyzed theoretically in two different ways. In the first approach the system is described in the model of a three-dimensional (3D) XY critical point,[25] whereas in the second the Ginzburg-Landau free energy is evaluated using the lowest Landau-level approximation.[26] In the studied field range both methods describe the data in the transition region equally well. Here we apply the second method which allows the determination of the mean-field transition temperature $T_c(H)$ and a comparison to the mean-field treatment by Hao and Clem.[14] The temperature and field dependence of the magnetization for a 3D superconductor near the H_{c2} line can be expressed in the form of a scaling relation: $M/(TH)^{2/3}=F\{[T-T_c(H)]/(TH)^{2/3}\}$. Here F is the scaling function. In the presence of strong fluctuation effects $T_c(H)$ marks the crossover to a sizable diamagne-

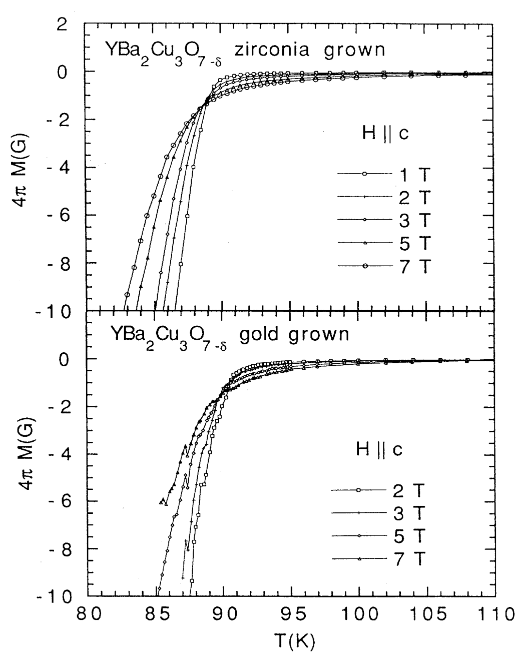

FIG. 3. Temperature dependence of the superconducting magnetization in various fields applied parallel to **c** for both crystals.

RAPID COMMUNICATIONS

tism, i.e., a sizable magnitude of the superconducting order parameter. This scaling behavior has been found for twinned and untwinned $YBa_2Cu_3O_{7-\delta}$ crystals.[13] For oxygen deficient $YBa_2Cu_3O_{7-\delta}$ crystals,[20] $(La_{1-x}Sr_x)_2CuO_4$ (Ref. 22) and Bi 2:2:2:3 (Ref. 24) a similar scaling relation with exponents appropriate for a 2D superconductor has been observed. The theoretical descriptions discussed above consider the effect of fluctuations in the amplitude of the superconducting order parameter. Recently, for the 2D-like superconductors the effects of phase fluctuations, i.e., fluctuations in the vortex positions, at temperatures sufficiently below the transition have been evaluated.[27]

In Fig. 4 the data of Fig. 3 scaled according to the relation $M/(TH)^{2/3}=F\{[T-T_c(H)]/(TH)^{2/3}\}$ are shown. In the temperature range around $T_c(H)$ the data for both crystals display the expected scaling behavior yielding upper critical-field slopes of -1.7 ± 0.1 and -1.8 ± 0.1 T/K. These values are in good agreement with earlier reports on gold-grown crystals.[13,14,28] However, our data on the zirconia-grown crystal are not compatible with upper critical-field slopes ranging from -4 to -10 T/K as reported from magnetization measurements on gold-free polycrystalline samples.[12] The dashed line in the bottom panel of Fig. 4 represents the 5 T data of the zirconia-grown crystal showing that the scaling function for both crystals is the same, i.e., the Au impurities do not affect the superconducting fluctuations. Deviations from scaling which occur below -0.2×10^{-3} K/(OeK)$^{2/3}$ can be caused by vortex-vortex interactions, the onset of irreversibility, or the breakdown of the lowest Landau-level approximation.

Figure 5 shows the magnetization of the two crystals at several temperatures in increasing and decreasing field on a logarithmic scale. The data are characterized by an almost logarithmic field dependence (dotted lines) which at high temperatures and fields crosses over into the fluctuational regime marked by the downward curvature. For the Au-grown crystal a rather sharp change in the slope of M vs $\ln(H)$ and the gradual onset of irreversibility occur at the low-field side of the logarithmic regime. Similar behavior has been observed previously.[15] For the zirconia-grown crystal a large hysteresis (outside the scale of the figure) occurs at fields below the lowest field point shown. However, in the 83 K data a slope change of M vs $\ln(H)$ is discernible. The nature of this kink, onset of a critical current or a different transition in the flux line system, is subject of further studies.

The data in the logarithmic regime are analyzed according to the mean-field relation $-4\pi M=\alpha H_{c1}/2\ln\kappa \ln(\beta H_{c2}/H)$ using a fit with $H_c=H_{c2}/\sqrt{2}\kappa$ and κ as parameters as outlined in Ref. 14. The values $\alpha=0.77$ and $\beta=1.44$ are used.[14] Then, with the requirement of H_c being field independent, κ values of 50 and 52 for the zirconia- and gold-grown crystal, respectively, are obtained. The results for the upper critical field are shown in Fig. 6. For both crystals H_{c2} as determined from the logarithmic behavior is well described by a linear temperature dependence giving a slope of -1.8 T/K. The values of κ and H_{c2} agree very well with values reported earlier for gold-grown crystals.[14,21] We note that the field range of applicability of the Hao and Clem model is limited by fluctuations and irreversibility as indicated in Fig.

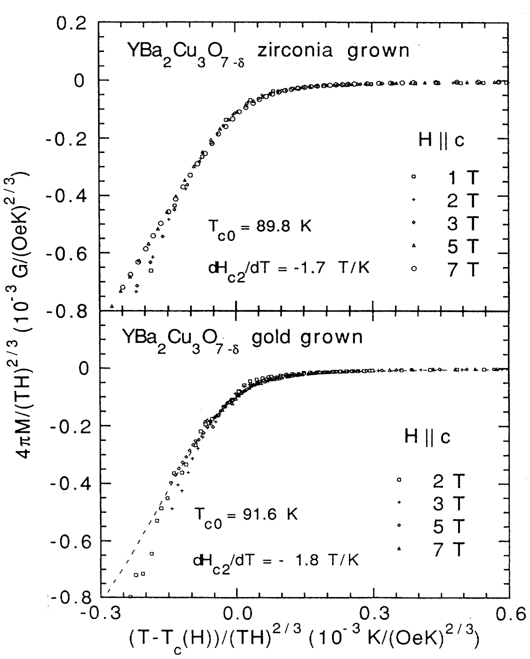

FIG. 4. Scaling of the superconducting magnetization according to the 3D scaling relation. The dashed line in the bottom panel represents the scaling function measured for the zirconia-grown crystal at 5 T.

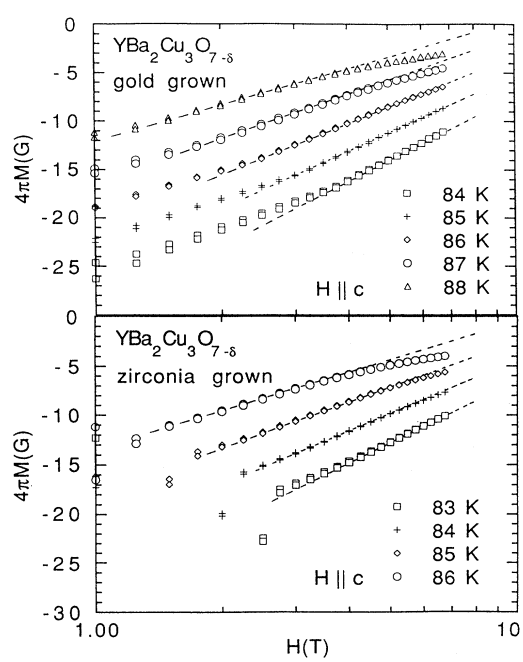

FIG. 5. Field dependence of the magnetization of both crystals at several temperatures. The dashed lines indicate the logarithmic field dependence. Departures from these lines at high fields are due to superconducting fluctuations and those at low fields are due to irreversibility.

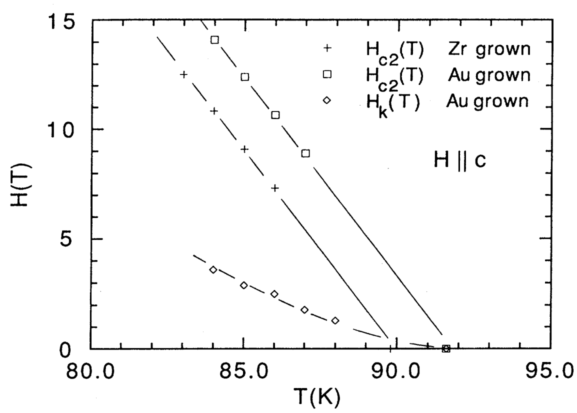

FIG. 6. Temperature dependence of the upper critical field of the zirconia- and gold-grown crystals for $H \| c$ as determined from the data in Fig. 5. H_k marks the kink in M vs $\log(H)$ for the gold-grown crystal.

5, giving rise to a larger uncertainty in H_{c2} at high temperatures than at low temperatures. However, since the mean-field treatment presented here and the fluctuation analysis discussed above give very similar results we obtained a consistent description for both crystals. We do not observe any significant enhancement[12] of the critical fields in the gold-free crystal.

Our study relies on the comparison of two crystals which, besides a difference in the gold content, could also have different oxygen contents. Earlier measurements[13-15] on various "fully oxygenated" gold-grown crystals with slightly varying T_c values yielded results identical with those reported here. Thus, it appears unlikely that the critical fields depend significantly on δ in this range of oxygen content and that therefore the findings of this study are unaffected by possible small differences in oxygen concentration between the two crystals.

In conclusion, we have shown that the normal state magnetization and the superconducting properties near T_c are not affected by Au impurities on the chain copper sites in $YBa_2Cu_3O_{7-\delta}$ single crystals.

This work was supported by the U.S. Department of Energy, Basic Energy Sciences-Materials under Contract No. W31-109-ENG-38 (S.F., W.K.K., J.D., G.W.C.) and by the NSF Office of Science and Technology Centers under Contract No. DMR 91-20000 (U.W. and H.C.).

[1]R. S. Markiewicz, J. Phys. Chem. Solids **52**, 1363 (1991); J. C. Phillips, Phys. Rev. Lett. **64**, 1605 (1990); Phys. Rev. B **43**, 6257 (1991).

[2]B. Dabrowski *et al.*, Physica C **162-164**, 99 (1989); H. Takagi *et al.*, Phys. Rev. Lett. **68**, 3777 (1992); M. Lang *et al.*, *ibid.* **69**, 482 (1992).

[3]J. B. Torrance *et al.*, Phys. Rev. Lett. **61**, 1127 (1988); Y. Tokura *et al.*, Phys. Rev. B **38**, 7156 (1988); J. B. Torrance *et al.*, *ibid.* **40**, 8872 (1989).

[4]H. Claus *et al.*, Physica C **198**, 42 (1992).

[5]H. Claus *et al.*, Physica C **200**, 271 (1992).

[6]M. Z. Cieplak *et al.*, Appl. Phys. Lett. **57**, 934 (1990); Phys. Rev. B **42**, 6200 (1990).

[7]W. Wong-Ng *et al.*, Phys. Rev. B **41**, 4220 (1990).

[8]S. Yang, H. Claus (unpublished); S. Yang, Ph.D. thesis, University of Illinois at Chicago, 1992.

[9]U. Welp *et al.*, Phys. Rev. B **42**, 10 189 (1990).

[10]T. A. Friedmann *et al.*, Phys. Rev. B **42**, 6217 (1990).

[11]For a review see K. F. McCarty *et al.*, Physica C **192**, 331 (1992).

[12]M. Däumling, Physica C **183**, 293 (1991).

[13]U. Welp *et al.*, Phys. Rev. Lett. **67**, 3180 (1991).

[14]Z. Hao *et al.*, Phys. Rev. B **43**, 2844 (1991); Z. Hao and J. R. Clem, Phys. Rev. Lett. **67**, 2371 (1991).

[15]U. Welp *et al.*, in *Physical Phenomena at High Magnetic Fields,* edited by E. Manousakis, P. Schlottmann, P. Kumar, K. Bedell, and F. M. Mueller (Addison Wesley, Reading, MA, 1992), p. 403.

[16]P. Fischer, Physica C **196**, 105 (1992); R. Liang *et al.*, *ibid.* **195**, 51 (1992); T. A. Vanderah *et al.*, J. Cryst. Growth **118**, 385 (1992); J. P. Rice and D. M. Ginsberg, *ibid.* **109**, 432 (1991); A. Erb *et al.* (unpublished).

[17]V. G. Hadjiev *et al.*, Solid State Commun. **80**, 643 (1991).

[18]M. A. Ivanov *et al.*, Physica C **198**, 171 (1992).

[19]U. Welp *et al.*, in *Superconductivity and its Applications,* edited by Y. H. Kao, P. Coppens, and H. S. Kwok, AIP Conf. Proc. No. 219 (AIP, New York, 1991), p. 139; G. W. Crabtree *et al.*, in *Electronic Properties and Mechanisms of High-T_c Superconductors,* edited by T. Oguchi, K. Kadowaki, and T. Sasaki (North-Holland, Amsterdam, 1992), p. 193.

[20]W. C. Lee and D. C. Johnston, Phys. Rev. B **41**, 1904 (1990).

[21]U. Welp *et al.*, in *High Temperature Superconductivity,* edited by S. K. Malik and S. S. Shah (Nova Science, Singapore, 1992).

[22]B. Janossy *et al.*, Physica C **196**, 73 (1992).

[23]W. Kritscha *et al.*, Physica C **179**, 59 (1991); P. H. Kes *et al.*, Phys. Rev. Lett. **67**, 2383 (1991); K. Kadowaki, Physica C **185-189**, 2249 (1991); in *Advances in Superconductivity IV,* edited by H. Hayakawa and N. Koshizuku (Springer, Verlag, 1992), p. 395.

[24]Q. Li and M. Suenaga (unpublished); Q. Li *et al.*, Phys. Rev. B **46**, 3195 (1992); **46**, 5857 (1992); Z. Tešanovic *et al.*, Phys. Rev. Lett. **69**, 3563 (1992).

[25]M. B. Salamon *et al.*, Phys. Rev. B **47**, 5520 (1993).

[26]G. J. Ruggeri and D. J. Thouless, J. Phys. F **6**, 2063 (1976); R. Ikeda *et al.*, J. Phys. Soc. Jpn. **59**, 1397 (1990); S. Ullah and A. T. Dorsey, Phys. Rev. B **44**,, 262 (1991).

[27]L. N. Bulaewskii *et al.*, Phys. Rev. Lett. **68**, 3773 (1992).

[28]U. Welp *et al.*, Phys. Rev. Lett. **62**, 1908 (1989).