

Time-dependent Meissner fraction as a function of aging in an oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal

K. G. Vandervoort

*Department of Physics, University of Illinois at Chicago, Chicago, Illinois 60680
and Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

G. W. Crabtree and Y. Fang

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

S. Yang

Department of Physics, University of Illinois at Chicago, Chicago, Illinois 60680

H. Claus

*Department of Physics, University of Illinois at Chicago, Chicago, Illinois 60680
and Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

J. W. Downey

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

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Meissner- and shielding-effect measurements were made on an oxygen-deficient single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as a function of aging time at room temperature following a quench from 225°C. It is seen that the Meissner fraction systematically increases from 11.1% to 13.2% as T_c changes from 11.2 to 25.0 K. All aging was done within the helium exchange gas environment of the sample chamber. The results point to oxygen vacancy ordering rather than oxygen absorption as the mechanism for both the T_c and Meissner-fraction increase.

Since the discovery of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ it has been found that varying the oxygen stoichiometry between $\delta=0$ and 1 changes the transition temperature from 0 to 93 K.¹ In addition to this, it has recently been discovered² that, after initial quenching, the transition temperature in oxygen-deficient crystals increases with aging time at room temperature, as much as 25 K. The fact that T_c is a reversible function of the annealing temperature was used as an argument to rule out oxygen compositional changes as the mechanism behind the aging process. It was, instead, suggested that the aging was due to ordering of the oxygen vacancies in the chains.

In this paper we report measurements of T_c , the Meissner effect, and the shielding effect on a crystal aged at room temperature in a helium environment. We confirm the aging effect in T_c seen earlier for crystals aged in an air environment, and show that the Meissner fraction (defined as the ratio of field-cooled to zero-field-cooled magnetization) systematically increases with time. This implies that pinning decreases with aging, as would be expected if the oxygen vacancy ordering is the mechanism behind the aging effect. Oxygen compositional changes could not have occurred in our experiment and are ruled out as the aging mechanism.

The sample used was a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal, grown by a self-flux method,³ of dimensions $1.1 \times 1.1 \times 0.4 \text{ mm}^3$ with the c axis along the short di-

mension. The original T_c was 91.2 K with a magnetic transition width of $<0.5 \text{ K}$ in a field of 1 G. Preparation of the low- T_c oxygen-deficient phase consisted of a 2-h vacuum anneal ($<20 \text{ mTorr}$) in a quartz tube at 650°C to remove any surface impurities followed by a 7-day anneal at 530°C in a 1.5-Torr oxygen environment. The sample was then quenched to room temperature by pouring water over the evacuated tube containing the sample. After aging at room temperature for several weeks, the crystal had a T_c of 27.0 K and a transition width of $<2 \text{ K}$.

Magnetization versus temperature data were taken on a low-field noncommercial SQUID magnetometer equipped with a μ -metal shield and a ^4He cryostat. Flux exclusion (shielding) was measured by cooling in zero field to well below T_c , applying a field at low temperatures, and recording the magnetic moment as the sample warmed. Flux expulsion (Meissner) was measured by cooling and warming in a field, to below and above T_c , recording data in both directions. All measurements were in a field of 1 G with the field aligned along the c crystallographic axis.

To introduce the oxygen vacancy disorder, the sample was heated in flowing oxygen to 225°C for 3 h in a quartz tube furnace. The crystal was then quenched in acetone and transferred within 2 min to the sample chamber of the helium cryostat where it was subsequently cooled in zero field to 4 K. Shielding and Meissner curves were recorded, after which the sample was warmed to 300 K

and held there for 0.5 h followed by another measurement at low temperature. This procedure, room-temperature annealing followed by Meissner and shielding measurements, was repeated five times. During the entire experiment the sample remained in the same position and orientation (which was necessary since Meissner fraction depends on sample orientation⁴) in the helium-gas atmosphere of the cryostat.

Figure 1 shows shielding and Meissner warming curves as a function of the room-temperature annealing time. The Meissner cooling data (not shown) had more noise due to thermal *emf*'s caused by temperature gradients in the sample chamber. The Meissner signal for each transition is on the order of 10% of the shielding signal. It should also be noticed that each transition remains sharp, ~ 2 K in width, showing that the T_c enhancement with aging is a bulk effect as seen previously.² On closer inspection (Fig. 2), the data show a definite trend of an increasing Meissner signal with T_c and annealing time. The Meissner cooling curves also exhibited this same behavior. In contrast, the shielding curves remained constant to within 1%. The Meissner fraction (ratio of Meissner to shielding signals) steadily increased from 0.111 to 0.132, corresponding to a 20% change.

Figure 3 shows both Meissner fraction and T_c as a function of room-temperature aging. Both curves follow a similar trend of large changes for short annealing times followed by a saturation as the equilibrium T_c of 27.0 K is approached. The Meissner fraction saturates more quickly than T_c .

As a check on the above results, the same Meissner fraction versus aging experiment was performed on a second $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ oxygen-deficient crystal grown by a different sample grower. The Meissner fraction was measured immediately after the initial quench from 225°C and later after 45 h of room-temperature aging. The transition temperature and Meissner fraction increased from 8.0 K and 6.5% to 26.1 K and 12.7%, respectively.

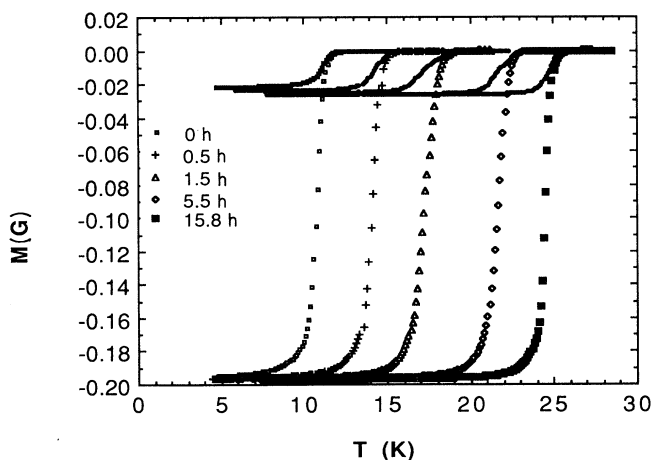


FIG. 1. Diamagnetic shielding (zero-field-cooled) data with corresponding Meissner (field-cooled) warming curves for various room-temperature annealing times. The Meissner expulsion is approximately 10% of the shielding exclusion for each curve.

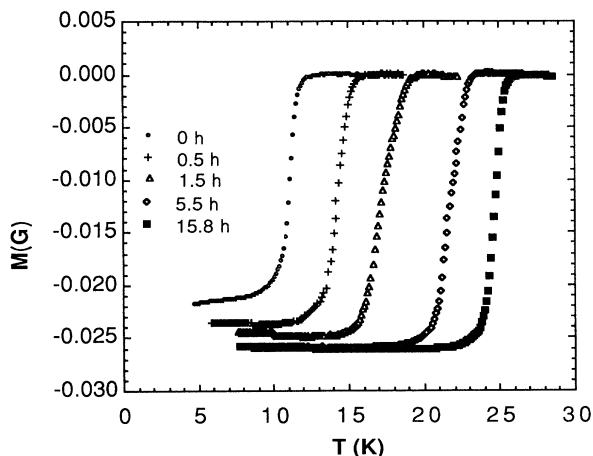


FIG. 2. A magnified view of Fig. 1 showing only the Meissner effect and its systematic increase with aging.

Several other crystals from this same batch have shown similar dramatic increases in the Meissner fraction with aging.⁵

The fact that room-temperature aging is observed on a crystal kept in a helium-gas atmosphere rules out oxygen stoichiometry changes as the cause of the aging effect. This conclusion is consistent with recent neutron-diffraction results on polycrystalline samples which showed no change in oxygen site occupancy during the aging process.⁶

The fact that the Meissner fraction and T_c follow approximately the same time dependence suggests that they have a common origin. The reduction of the oxygen vacancy disorder with aging proposed to explain the change in T_c can also explain the increase in the Meissner effect, assuming that the increased Meissner effect reflects a decrease in pinning. For the unaged crystal, the quenched-in disorder has a tendency to trap many flux lines which leads to a relatively small Meissner fraction. As the oxygen vacancy order increases during aging, the ability to

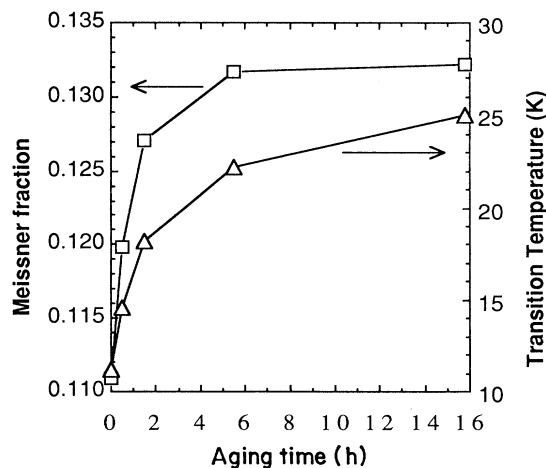


FIG. 3. The Meissner fraction (squares) and T_c (triangles) plotted as a function of room-temperature aging.

pin flux is reduced and the Meissner fraction increases. As monitored through the Meissner fraction data, the majority of the ordering occurs quickly after initial quenching followed by a progressively slower ordering as the final equilibrium T_c is reached. The pattern in the time dependence of the pinning and T_c can be naturally explained by an increasing oxygen vacancy order.

In summary, the Meissner and shielding effects have been measured on an oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal as a function of room-temperature aging. The measurements reveal a noticeable increase in both T_c and the Meissner fraction during aging. We rule out oxygen compositional changes and instead attribute these increases to an increased oxygen vacancy order. This con-

clusion is consistent with the similarity of time dependence of the Meissner fraction and T_c in the aging process.

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¹R. J. Cava, B. Batlogg, K. M. Rabe, E. A. Rietman, P. K. Gallagher, and L. W. Rupp, Jr., *Physica C* **156**, 523 (1988); S. I. Park, C. C. Tsuei, and K. N. Tu, *Phys. Rev. B* **37**, 2305 (1988); W. K. Kwok, G. W. Crabtree, A. Umezawa, B. W. Veal, J. D. Jorgensen, S. K. Malik, L. J. Nowicki, A. P. Paulikas, and L. Nunez, *ibid.* **37**, 106 (1988); A. J. Jacobson, J. M. Newsam, D. C. Johnston, D. P. Goshorn, J. T. Lewandowski, and M. S. Alvarez, *ibid.* **39**, 254 (1989); P. Monod, M. Rebault, F. D'Yvoire, J. Jegoudez, G. Collin, and A. Revcolevschi, *J. Phys. Paris* **48**, 1369 (1987).

²B. W. Veal, A. P. Paulikas, Hoydoo You, Hao Shi, Y. Fang, and J. W. Downey, *Phys. Rev. B* **42**, 6305 (1990); H. Claus, S. Yang, A. P. Paulikas, J. D. Downey, and B. W. Veal, *Physica C* **171**, 205 (1990).

³D. L. Kaiser, F. Holtzberg, M. F. Chisholm, and T. K. Worthington, *J. Cryst. Growth* **85**, 593 (1987).

⁴K. G. Vandervoort (unpublished).

⁵H. Claus and S. Yang (unpublished).

⁶J. D. Jorgensen, Shiyu Pei, P. Lightfoot, Hao Shi, A. P. Paulikas, and B. W. Veal, *Physica C* **167**, 571 (1990).