RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 4 1 FEBRUARY 1989

Extraordinary effect of aluminum substitution on the upper critical field of $Ba_2YCu_3O_7$

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(Received 27 July 1988; revised manuscript received 3 October 1988)

A 10% substitution of Al on the Cu(1) (chain) site of single crystals of $Ba_2YCu_3O_7$ drives the material to the edge of the orthorhombic-tetragonal transition and strongly decreases the resistivity and upper critical field, compared to the unsubstituted parent compound, but has little effect on T_c. The coherence length in the $\hat{a}$-$\hat{b}$ plane increases twofold, while the coherence length along the $\hat{c}$ axis is unchanged. These results can be reconciled with the conventional relationships between superconducting and normal-state properties only if a twofold change in the Fermi-surface area is postulated.

Controlled incorporation of impurities in the high-T_c superconductor $Ba_2YCu_3O_7$ can yield significant insight into the physics and chemistry of this material. The study of single crystals[1] offers many advantages compared to polycrystalline samples: the structure can unequivocally be determined by refinement of x-ray data, the extraneous influence of grain boundaries on electrical characteristics (such as the normal-state resistivity) is eliminated, and anisotropic properties can be measured directly. In this paper we examine the effect of Al substitution in single crystals of $Ba_2YCu_{3-x}Al_xO_7$. The structural consequences of Al incorporation have been determined by x-ray and neutron diffraction studies;[1] because of the large difference in scattering factors between Cu and Al it was possible to show unequivocally that Al exclusively occupies the Cu chain site. The T_c of these crystals was found to depend weakly on x for $x < 0.1$, in contrast to the results for similar levels of metals substituted on the Cu plane site.[2] The effect of Al substitution on T_c is stronger for $x > 0.1$, so we have chosen samples with $x \sim 0.1$, with $T_c \sim 84$ K, for detailed study. The dependence of T_c on x correlates with the change in crystal symmetry from orthorhombic below $x < 0.1$ to tetragonal for larger x, and both results are consistent with ceramic studies. Based on analogy with $Sr_2YCu_{3-x}Al_xO_7$, the incorporation of Al^{3+} in $Ba_2YCu_3O_7$ produces local tetrahedral sites[1] about the Al^{3+} ions, disordering the regular O(4) (i.e., chain) lattice and driving the orthorhombic-tetragonal (O-T) transition. X-ray refinement and thermogravimetric analysis on polycrystalline samples[1] indicate that the net oxygen content does not increase in fully oxygenated $Ba_2YCu_{3-x}Al_xO_y$ from its nominal value of $y = 6.96 \pm 0.02$. There is no sign of short-range ordering of the Al, though this cannot be definitively ruled out by the x-ray studies. The microscopic effect of aluminum substitution is, then, to introduce disorder on the Cu(1) site and randomize the O(4) lattice, disrupting the Cu-O chains. The substitution of Al for Cu maintains the formal electron count while altering the Cu-O chains to a degree governed by the doping level. Thus, Al substitution probes the influence of the Cu-O chains on the properties of $Ba_2YCu_{3-x}Al_xO_7$ with minimal chain-plane charge transfer compared to the system when perturbed by enforcing substoichiometric oxygen content.[3] The effect on band structure of complete substitution of Al on the Cu(1) site has been calculated[4] using a tight-binding model, showing a dramatic change, although the effect of partial substitution appears not to have been explored theoretically.

Single crystals of $Ba_2YCu_{3-x}Al_xO_7$ were grown from CuO-rich melts as described previously[5] and were postannealed for ~450 h in flowing oxygen at 500 °C and ~200 h at 400 °C to maximize the oxygen content. Crystals grown in alumina crucibles are inadvertantly doped at small levels by aluminum from the crucible, or, alternatively, Al can be introduced as a constituent of the melt [as e.g., $Al(NO_3)_3$] contained in a less reactive zirconia crucible. Crystals with dimensions $\sim 1 \times 1 \times 0.1$ mm^3 were mechanically separated from the melt and Al doping levels were determined by energy dispersive x-ray analysis (with a relative error of ~2 at.%). Good-quality contacts, nonrectifying with a low resistance and moderate mechanical stability, were reproducibly made by attaching fine Ag wires with Ag cement to Ag pads sputtered onto the crystals. Critical-field measurements were made using standard techniques at the Francis Bitter National Magnet Laboratory. The resistive transitions were measured as a function of temperature and applied field strength and orientation. Measuring currents were less than 10 A/cm^2. The large anisotropy of H_{c2} found in these materials makes accurate alignment of the field with respect to the crystal axes critical if the full value of the anisotropy is to be measured.

Figure 1 shows the temperature dependence of the resistivity in the $\hat{a}$-$\hat{b}$ plane, $\rho_{ab}(T)$, of a crystal with the composition $Ba_2YCu_{2.9}Al_{0.1}O_7$, as well as that of an undoped sample for comparison. The absolute accuracy of the resistivity is $\sim \pm 20\%$ due to the small crystal size.

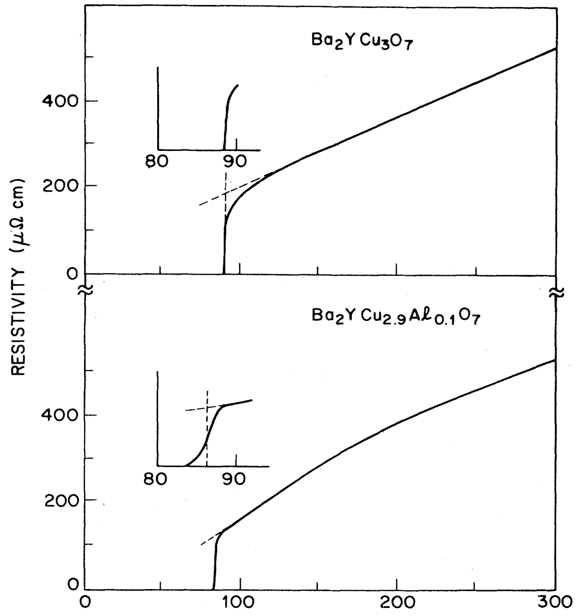

FIG. 1. Temperature dependence of the resistivity $\rho_{ab}(T)$ of $Ba_2YCu_3O_7$ and $Ba_2YCu_{2.9}Al_{0.1}O_7$ samples. The dashed lines indicate the construction used to infer $\rho_{ab}(T_c)$. Insets: $\rho_{ab}(T)$ near T_c.

While the resistivity at 300 K is quite similar in the two crystals, the temperature dependence is anomalous in the $Ba_2YCu_{2.9}Al_{0.1}O_7$ crystal, leading to a lower resistivity near T_c in the doped sample. A similar but not identical temperature dependence is seen in other crystals with similar Al content. The decrease in the low-temperature resistivity with increased disorder in the chains is unexpected, and possible origins will be discussed below. Studies of oxygen-deficient material have shown that the Cu-O chains can influence the resistivity and T_c of $Ba_2YCu_3O_7$, and the effects are attributed[3] primarily to charge transfer to the Cu-O planes. The system under study here, which shows a large change in resistivity despite the low Al doping level (and no change in formal oxidation state), implies that the Cu-O chains contribute directly to the conductivity of $Ba_2YCu_3O_7$. The insets to Fig. 1 expand the region near 90 K to illustrate the decreased T_c and broadening of the superconducting transition in the doped crystal, which is attributed to a slight inhomogeneity in the Al distribution.

The resistive transitions in an applied field **H** parallel to the **c** axis of the crystal (i.e., $H_{c2\parallel}$) are shown for both a doped and an undoped sample in Fig. 2. Clearly the transition is sharper for the doped sample, despite the broader $\rho_{ab}(T)$ transition in zero field. We interpret this as indirect evidence for $\hat{a}$-$\hat{b}$ anisotropy in the upper critical field of $Ba_2YCu_3O_7$, which has not been directly observed due to ubiquitous $\hat{a}$-$\hat{b}$ twinning in undoped samples.[6] The disordering of the chains in the essentially tetragonal Al-doped sample removes the asymmetry, resulting in sharper transitions. The effect is less noticeable for $\mathbf{H}\perp\hat{c}$ since the transition is dominated by the short coherence length in the $\hat{c}$ direction, which is unchanged by the disorder (*vide infra*). In any case the sharp field transitions attest to the quality of the doped crystals and lend confidence to further interpretation of the data.

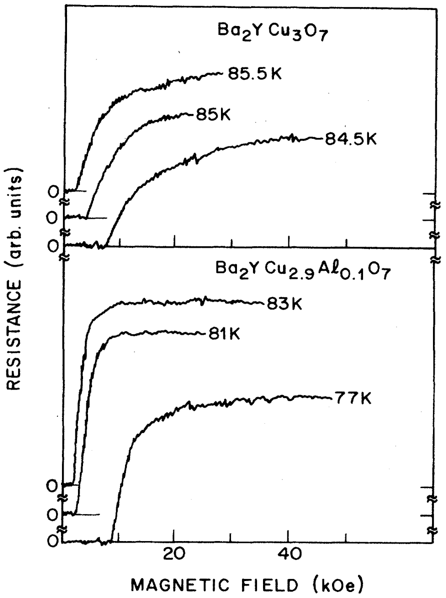

FIG. 2. Resistance as a function of field at temperatures as indicated. Notice the relative sharpness of the transitions for the Al-doped sample for comparable values of H_{c2}. The field was applied parallel to the **c** axis of the samples.

We define H_{c2} as the field required to return the resistance to half its extrapolated normal-state value. In Fig. 3

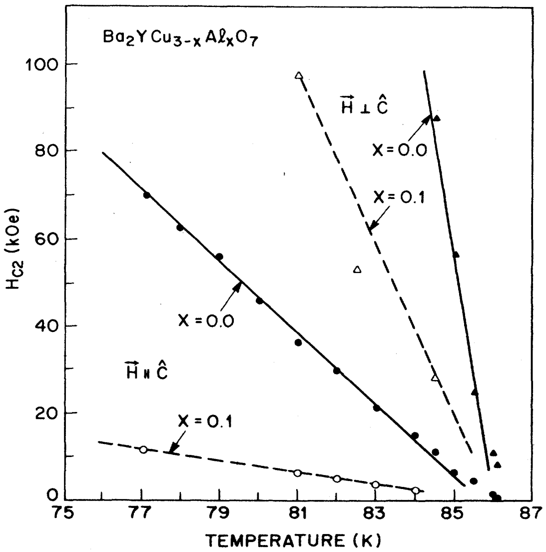

FIG. 3. Temperature dependence of the upper critical field of $Ba_2YCu_3O_7$ and $Ba_2YCu_{2.9}Al_{0.1}O_7$ samples. The solid line represents linear fits for the undoped sample, while dashed lines are fits for the Al-doped sample. Data for $\mathbf{H}\perp\hat{c}$ were taken for the doped sample at fields up to 200 kOe and were used to determine the indicated linear fit.

we plot the resulting values as a function of temperature for the doped and undoped crystals for fields applied parallel and perpendicular to the **c** axis. Clearly, H_{c2} of the Al-doped sample is significantly reduced, especially for $H \| \hat{c}$. The dependence of H_{c2} on the angle between the applied field and the **c** axis is accurately described for both samples by the conventional 3D anisotropic effective-mass model.[7] Data taken as a function of angle were also used to determine precisely the $\mathbf{H} \| \hat{c}$ and $\mathbf{H} \perp \hat{c}$ orientations.

The lines through the data of Fig. 3 indicate linear fits, and the slopes of the lines are tabulated, along with representative data from the literature, in Table I. We infer the zero-temperature coherence length from the critical field slopes by first calculating (as a representative zero-temperature critical field) the orbital $H_{c2}(0)$ for each field direction:

$$H_{c2\perp,\|}(0) \equiv 0.693 T_c [dH_{c2\perp,\|}(T)/dT] \,|_{T_c} .$$

We then find the coherence lengths from: $\xi_{ab}^2(0) = \Phi_0 \times [2\pi H_{c2\|}(0)]^{-1}$ and $\xi_c^2(0) = \Phi_0 H_{c2\|}(0) [2\pi H_{c2\perp}^2(0)]^{-1}$. These values are included in Table I as well. A rough consensus is seen in the data for undoped samples. In the Al-doped sample, the coherence length ξ_c is seen to be essentially unchanged, but there is a dramatic and unequivocal increase in the basal-plane coherence length, ξ_{ab}.

To explore the possible origins of this unexpected change in ξ_{ab}, we will make the working hypothesis that the conventional Ginzberg-Landau-Abrikosov-Gor'kov (GLAG) relationship for the Ginzburg-Landau coherence length in terms of microscopic parameters[8] is valid, and examine the conclusions to which we are led:

$$\xi_{ab}^{\mathrm{GL}}(0) = [(2.90 \times 10^{32}) T_c^2 \gamma^2 (n^{2/3} S/S_F)^{-2} + (1.60 \times 10^{12}) \rho_{ab} \gamma T_c]^{-1/2} [R(\lambda_{\mathrm{tr}})]^{1/2} \, \mathrm{cm}, \quad (1)$$

$$\rho_{ab} = (1.27 \times 10^4) [l_{\mathrm{tr}} (n^{2/3} S/S_F)]^{-1} \, \Omega \, \mathrm{cm}, \quad (2)$$

where n is the conduction electron density (cm^{-3}), S is the Fermi surface area, S_F is the Fermi surface area of a free-electron gas of density n, γ is the normal-state electronic specific-heat coefficient, $\lambda_{\mathrm{tr}} \equiv h v_F / 2\pi k_B T_c l_{\mathrm{tr}}$ (where l_{tr} is the mean free path), $R(\lambda_{\mathrm{tr}})$ is related to the Gor'kov χ function and is bounded by 1.00 and 1.17 in the dirty and clean limits, respectively, and the other symbols are defined above. In Eq. (1), the first term reflects the BCS coherence length (i.e., the clean limit) while the second term introduces the effect of transport scattering and dominates in the dirty limit ($\lambda_{\mathrm{tr}} \gg 1$). The extraordinary increase in the coherence length ξ_{ab} is consistent with the decrease in the normal-state resistivity in the basal plane, $\rho_{ab}(T_c)$, which is ~ 100 $\mu\Omega$ cm in the doped sample and ~ 160 $\mu\Omega$ cm in the unsubstituted crystal. Leaving aside the issue of how increasing disorder could decrease rather than increase ρ_{ab}, we note ρ_{ab} decreases only by a factor of 1.6, which would increase ξ_{ab}^{GL} by a factor of at most $(1.6)^{1/2} = 1.3$ (i.e., even in the extreme dirty limit). Since this is far less than the observed twofold increase, we infer that the other parameters—γ, T_c, and/or $n^{2/3}(S/S_F)$—would have to be significantly altered.

Since T_c is only slightly affected by the substitution, we further infer that γ, which is related to the density of states at the Fermi level and to which T_c is exponentially sensitive in most theories of superconductivity, must change little, if at all. We conclude that the factor $n^{2/3}(S/S_F)$ must be responsible within this analysis, i.e., that the Fermi surface area would have to be substantially modified by the incorporation of Al. The twofold increase in ξ_{ab} could imply as much as a twofold increase in $n^{2/3}(S/S_F)$ (in the clean limit). From Eq. (2) we see that an increase in $n^{2/3} S/S_F$ results in a corresponding decrease in ρ_{ab}. If we make the physically plausible assumption that the mean free path, l_{tr}, does not increase in the disordered Al-doped sample, then $n^{2/3} S/S_F$ would have to increase by at least 1.6 to account for the observed change in ρ_{ab}. A more quantitative analysis would require independent knowledge of either l_{tr} or γ. Presumably the change in $n^{2/3}(S/S_F)$ is driven by disorder in the Cu-O chain sublattice and the change in symmetry of the crystal, although it is not clear exactly how this would affect the area of the Fermi surface. It is surprising that the hypothetical change in $n^{2/3}(S/S_F)$ has such a dramatic effect on the superconducting coherence length ξ_{ab} and yet barely affects T_c, and also that the disorder on the chain Cu and O sublattices have almost no direct effect on T_c at this doping level.

Aluminum substitution alters the properties of $Ba_2YCu_3O_7$ in a profound yet subtle manner, reducing the in-plane resistivity and upper critical field without substantially modifying T_c. Within the conventional GLAG

TABLE I. Measured transition temperatures, resistivities, critical field slopes, and anisotropies, and coherence lengths inferred as described in the text, for undoped $Ba_2YCu_3O_7$ (including representative data from the literature) and for $Ba_2YCu_{2.9}Al_{0.1}O_7$.

	T_c (K)	$\rho_{ab}(T_c)$ ($\mu\Omega$ cm)	$H'_{c2\|}$ (kOe/K)	$H'_{c2\perp}$ (kOe/K)	$\xi_{ab}(0)$ (nm)	$\xi_c(0)$ (nm)	Anisotropy
		$Ba_2YCu_3O_7$					
Iye *et al.* (Ref. 9)	~90	~900	5.0	30	3.3	0.55	6.0
Worthington *et al.* (Ref. 10)	92.5	· · ·	6.0	40	3.0	0.45	6.7
Oh *et al.* (Ref. 11)	~87	~400	· · ·	· · ·	1.6	0.38	4.2
This work	88.5	160	7.0	54	2.8	0.36	7.8
		$Ba_2YCu_{2.9}Al_{0.1}O_7$					
This work	84	100	1.3	20	6.5	0.42	15.5

interpretation of phenomenological properties, and making physically plausible arguments, we conclude that this substitution would have to increase the Fermi surface area $n^{2/3}S/S_F$ by a factor in the range 1.6–2.0. So large a change is surprising; this may indicate that the microscopic picture assumed in GLAG theory is fundamentally flawed.

We would like to thank T. Siegrist, L. Mattheiss, and T. P. Orlando for useful discussions. We gratefully acknowledge the help of the National Magnet Lab in performing the experiments. The MIT portion of this work is supported by the Center for Materials Science and Engineering National Science Foundation Grant No. DMR 87-19217.

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