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High-temperature order-disorder phase transition in the superconductor $Y_1Ba_2Cu_3O_{6+\delta}$ observed by electrical resistivity measurements

P. P. Freitas and T. S. Plaskett
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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The order-disorder transition involving oxygen atoms and vacancies in the Cu-O basal planes of the superconductor $Y_1Ba_2Cu_3O_{6+\delta}$ was studied under several oxygen partial pressures. The transition is second order in nature, shows small hysteresis probably due to twin boundary kinetics, and always occurs at the same oxygen concentration. The average site energy for an oxygen atom in the lattice is -3.41 eV. No superconductivity is found for a fully disordered sample.

The recent discovery of high-T_c superconductivity in Cu oxides has led to an enormous effort in the study of the low-temperature properties of these materials.[1,2] Furthermore, great importance was given to the structural characteristics of these compounds, and especially to the character and coordination of the oxygen atoms and vacancies in the structure.[3] X-ray studies at room temperature indicate an orthorhombic structure for the superconducting compound $Y_1Ba_2Cu_3O_{6+\delta}$. However, samples quenched from higher temperatures, typically above 750° C, show a tetragonal structure, therefore implying an orthorhombic-to-tetragonal phase transition below this temperature. X-ray measurements by Schuller *et al.*[4] in pure oxygen first showed that this transition occurs around 750° C and suggested that it was first order in character. Later, neutron data taken at room temperature[5] showed an ordered distribution of oxygen atoms and vacancies in the basal Cu-O planes, with linear Cu-O chains forming along the *a* or *b* axis of the orthorhombic structure. Twin boundary formation was also found as a consequence of the tetragonal-to-orthorhommbic distortion. More recently, high-temperature neutron data[6] have positively shown that above the orthorhombic-to-tetragonal transition, the oxygen-vacancy ordering disappears, giving rise to a two-dimensional (2D) order-disorder transition in the Cu-O basal planes. Our aim in this work was to do a detailed study of the transition in different oxygen partial pressures, in a open system where the sample is in equilibrium with the oxygen atmosphere. Resistivity measurements were chosen, as they provide a very sensitive technique to investigate further the nature of the ordering transition and its dependence on the oxygen concentration in the solid.

The behavior of the resistivity $\rho=(m^*/n_e e^2\tau)$ near an order-disorder (OD) phase transition reflects the changes in the relaxation time τ and the number of carriers per unit volume n_e through the transition. Simons and Salamon[7] have shown that near T_0, and sufficiently above the Debye temperature, the Fisher-Langer relation[8] (FL) comparing the critical behavior of $d\rho/dT$ with that of the specific heat also holds for OD transitions. In this case, the critical behavior is dominated by short-range concentration fluctuations leading to a $\ln\epsilon$ or $\epsilon^{-\alpha}$ divergence for $d\rho/dT$. Away from T_0, a regime dominated by long-range fluctuations can occur, giving a $\epsilon^{2\beta-1}$ contribution to $d\rho/dT$.[9] Here, ϵ is the reduced temperature and α and β the critical exponents for the specific heat and order parameter, respectively. Although generally second order in nature, first-order transitions are also observed when the ordering process is accompanied by a structural transformation, as is the case in layered dichalcogenides.[10] In the latter case, hysteresis effects are expected in the resistivity curve, due to nucleation phenomena. This will also give rise to a downward shift in T_0 as the sample is cooled, as compared with data taken upon heating.[11]

Resistivity measurements with a resolution of 1 part in 10^4 were made on single-phase ceramic disks 1 mm thick, 6 mm in diameter. The ceramic preparation was described elsewhere.[12] We used a dc four-probe method with Pt pressure contacts.

In our experiments, great care was taken to reach equilibrium with the oxygen partial pressure (P_{O_2}) at each temperature. This was achieved by using very slow heating and cooling rates (0.1–0.5 K/min). The resistivity curves were reversible during several heating and cooling cycles taken over a number of days, except near the critical region where some hysteresis occurs.

In Fig. 1, we show the resistivity curves versus temperature measured from 400 to 800 °C, under different P_{O_2}. The data clearly show a progressive deviation from the low-temperature linear behavior, as we go towards high temperatures and lower P_{O_2}. Each resistivity curve, with the exception of that in pure Ar, shows a slope change at T_0, the OD phase transition for a particular pressure. The transition temperatures marked with circles on the figure were determined at the peak of the $d\rho/dT$ curve, taken at each different P_{O_2}.

Neutron data[6] show that the oxygen content $\langle N(T)\rangle$, (defined in atoms per formula unit) progressively decreases from 7 at room temperature ($\delta=1$) to 6.5 at the transition ($\delta=0.5$), the decrease being more accentuated above 400 °C. This explains the sharp increase in resistivity observed above this temperature. From the Hubbard model we expect that for $\langle N(T)\rangle=6.5$ the compound will behave as an insulator (filled band), while for $\langle N(T)\rangle=7$, it will have metallic character (half-filled band). However, an insulating behavior is only observed for the sample measured in Ar [$\langle N(T)\rangle\simeq 6$]. All other

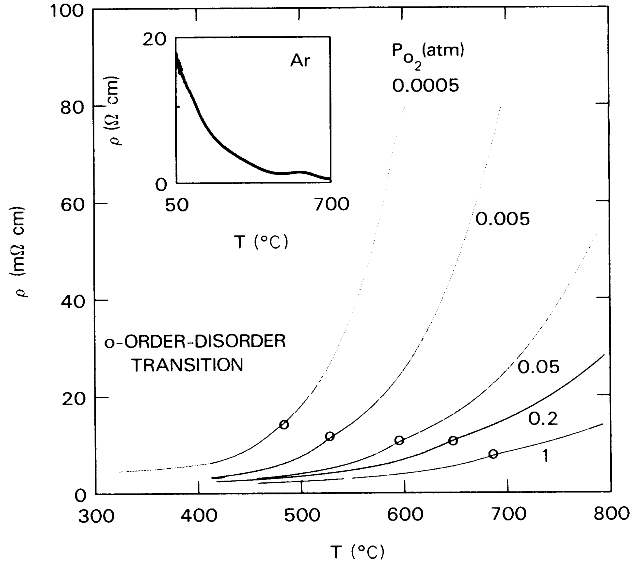

FIG. 1. Temperature dependence of the resistivity under several P_{O_2}. In the inset we show the resistivity of the same sample in equilibrium with an Ar atmosphere.

curves measured in finite P_{O_2} pressures show metallic behavior, even above T_0, despite the fact that $\langle N(T)\rangle$ is less than 6.5.

We will now discuss in detail the behavior of $d\rho/dT$ near the transition, Fig. 2, for a sample heated and cooled successively at a rate of 0.1 K/min in a oxygen atmosphere ($P_{O_2}=1$). The derivative is obtained by a linear fitting of the resistivity data at every three points, corresponding to a temperature interval of 1°.

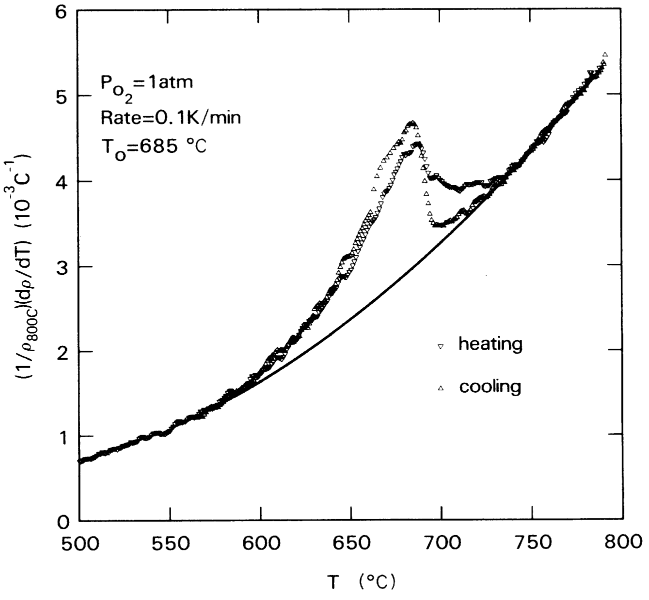

FIG. 2. Critical behavior of the resistivity derivative near the OD transition, for a sample heated and cooled in pure oxygen. The solid line corresponds to the noncritical resistivity background.

The general shape of the $d\rho/dT$ curve is characteristic of a second-order phase transition, showing a specific-heat-like anomaly at T_0. We do not observe any shift of the $d\rho/dT$ peak upon heating or cooling as we would expect were we dealing with a first-order transition. Scanning calorimetric analysis also failed to detect any latent heat at the transition confirming the lack of first-order character. The observed hysteresis is probably related to the formation of twin boundaries occurring after the onset of the orthorhombic ordered phase, as twinning is observed by transmission electron microscopy in this material. Since long-range order is necessary before twin boundaries can be formed, a sharp second-order transition will occur on cooling. However, on heating disorder occurs within each domain at a well-defined temperature (see sharp decrease in $d\rho/dT$ curve on heating, at T_0), but twin boundaries still persist as scattering centers at higher temperatures due to pinning forces. This will limit the divergence of the coherence length at T_0, leading to a broader transition upon heating. From Fig. 2 it can be seen that the ordering process is essentially complete around 580 °C, where the peak in $d\rho/dT$ due to ordering merges with the main background due to change in the oxygen content.

Let us now fit the $d\rho/dT$ data to theoretical models. We will use data taken on cooling, where the transition is sharper. We will assume, as a first approximation, that the oxygen concentration $\langle N(T)\rangle$ does not have a critical behavior, varying smoothly through T_0. In this case, the ordering process can be described by an Ising model, and using the FL relation (valid for $T>\theta_D\simeq 400$ K) we expect in the critical region

$$(1/\rho_0)(d\rho/dT)\propto C_v \propto \epsilon^{-\alpha} \text{ 3D} , \tag{1}$$

where C_v is the volume specific heat, and ρ_0 is the resistivity in the disordered state at 800 °C. As $\alpha=0.013$ for Ising 3D, it will be difficult to differentiate a $\epsilon^{-\alpha}$ regime from a $\ln\epsilon$ dependence expected in the Ising 2D case. Indeed, the $\ln\epsilon$ behavior has been obtained also for 3D systems, like TbZn and Ni, near their Curie points. It seems, therefore, difficult to determine the dimensionality of the ordering system just from this fitting. To fit our data to the previous equations, we first remove the noncritical resistivity background by fitting the resistivity data, away from the transition, to a polynomial curve. This noncritical contribution to $d\rho/dT$ is shown as the solid line in Fig. 2, and corresponds in our interpretation to the oxygen content variation. Our data, above and below T_0, are best fitted with a weak $\ln\epsilon$ divergence, characteristic of short-range fluctuations and an energy-like regime. We obtain

$$(1/\rho_0)(d\rho/dT)=-1.047\times10^{-3}\ln\epsilon-3.99\times10^{-3} , \tag{2a}$$

$$5\times10^{-3}<\epsilon<2\times10^{-2} ,$$

$$(1/\rho_0)(d\rho/dT)=-9.0\times10^{-4}\ln|\epsilon|-1.89\times10^{-3} , \tag{2b}$$

$$-2\times10^{-2}<\epsilon<-8\times10^{-2} .$$

The observed logarithmic singularity can be interpreted as a $\epsilon^{-\alpha}$ dependence, with $\alpha=\alpha'=0$ as predicted by the

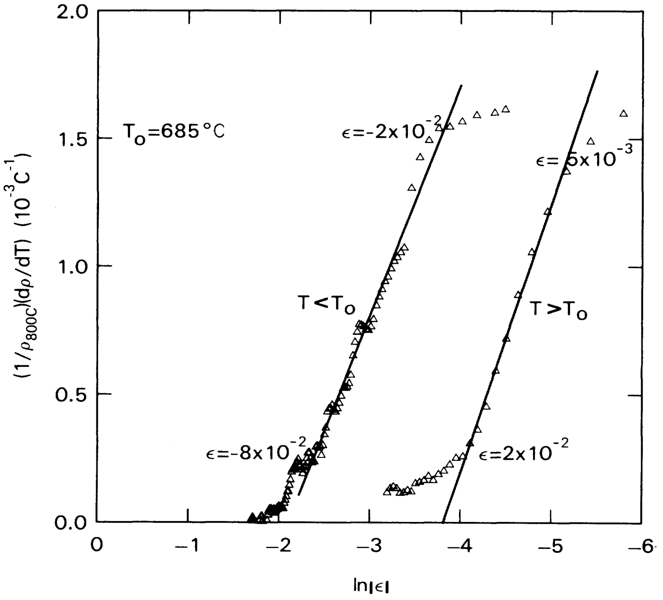

FIG. 3. Plot of the resistivity derivative data on cooling vs lnϵ, as predicted when the critical behavior is dominated by short-range fluctuations.

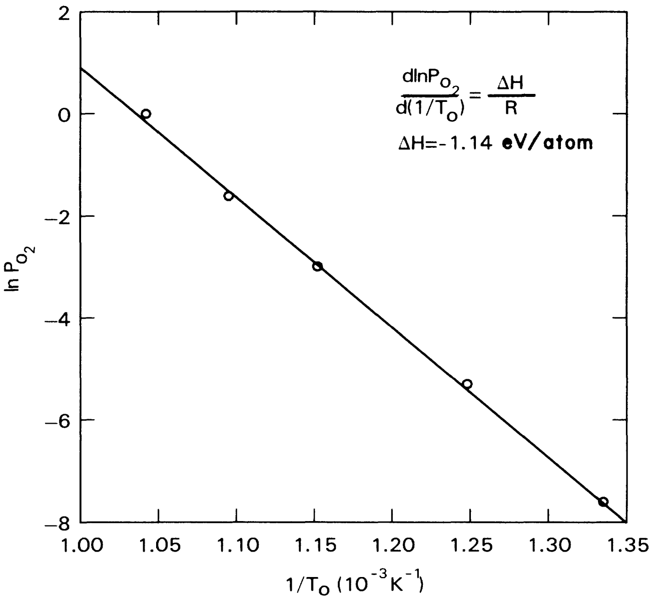

FIG. 4. Plot of lnP_{O_2} vs the reciprocal of the ordering temperature.

scaling hypothesis, and where α and α' have their usual meanings. We cannot get any reasonable fitting to a power law $\epsilon^{2\beta-1}$ as expected when long-range fluctuations are dominant. We took T_0 as a fixed parameter, determined at the point of highest derivative, 685 °C. Figure 3 shows the results of this fitting, both below and above T_0. Notice that the rounding at the transition, seen in Fig. 2, is responsible for the deviations from the lnϵ behavior very close to T_0. The observed rounding is most probably due to the polycrystalline and anisotropic nature of the sample.

Up to now we did not consider any possible critical contribution from $\langle N(T)\rangle$. We could, based on experimental data,[6] assume that $\langle N(T)\rangle \propto S(T) \propto \epsilon^{\beta}$, below T_0, where S is the long-range order parameter. In this case, we will have an extra critical contribution to $(1/\rho_0)(d\rho/dT)$. Assuming $n_e \propto \langle N(T)\rangle$, we obtain $(1/\rho_0)(d\rho/dT) \propto A\epsilon^{(-\beta-1)}+B$. Again this contribution predicts a much stronger divergence than the one observed.

Finally, we would like to comment on the ordering temperature dependence on P_{O_2}. As seen in Fig. 1, the ordering temperature is strongly dependent on P_{O_2}. For a system where the oxygen in the ambient is in equilibrium with the solid, we can write the thermodynamic relationship (Clausius-Clapeyron equation)

$$[d\ln P_{O_2}/d(1/T)] = \Delta H/R \ , \tag{3}$$

where ΔH is the heat of solution per mole of O_2 and R the ideal gas constant. At the phase transition a plot of lnP_{O_2} vs $1/T$ should give a straight line if $\langle N(T)\rangle$ is fixed. This plot is shown in Fig. 4 as a straight line connecting the five data points, meaning a constant $\langle N(T_0)\rangle$ value at all pressures, within our experimental resolution. From the slope in Fig. 4 we get $\Delta H = -1.14 \pm 0.03$ eV/atom for the heat of solution of an oxygen atom. This agrees with the value used by Bakker *et al.*[11] in their theoretical work, obtained from fits of lattice parameter data, $\Delta H = -1.08$ eV/atom, for samples having the transition at 678 °C. Assuming a dissociation energy E_d of 5.08 eV for an oxygen molecule, we then obtain a site energy $\epsilon = \Delta H - (E_d/2) = -3.41$ eV.

In summary, our data indicate that the OD transition is second order in nature, the ordering process being essentially complete 100° below T_0. The observed hysteresis near T_0 is probably accounted for by twin boundary formation, as no evidence of any latent heat characteristic of a first-order transition was found. The critical behavior of $d\rho/dT$ above and below T_0 is dominated by short-range concentration fluctuations, but we cannot rule out some contribution due to changes in $\langle N(T)\rangle$ near the transition. The transition temperature can be brought down from 685 to 480 °C by reducing P_{O_2} in the atmosphere in contact with the sample, but our results show that the oxygen content of the sample at the transition is always essentially the same. All samples that have achieved perfect degree of ordering at 300–400 °C, where diffusion stops, show the typical sharp superconducting transition at 91 K (P_{O_2}=1, 0.2, 0.05, 0.005). When ordering is imperfect or lacking (respectively, P_{O_2}=0.0005 or Ar) the sample becomes semiconducting or insulating, showing a lower T_c or none at all.

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