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PERSPECTIVE ON $RBa_2Cu_3O_x$ MATERIALS FROM OXYGEN DEFICIENCY STUDIES

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We have measured the electrical resistivity, thermoelectric power, magnetic susceptibility, Hall coefficient and upper critical field near T_c in $EuBa_2Cu_3O_x$, where $6.09 < x < 7.0$. These data suggest a Mott–Hubbard-like transition near a critical oxygen concentration $x_c \sim 6.4$–6.5. Our results, combined with those reported elsewhere, show a striking similarity between the addition of oxygen to $EuBa_2Cu_3O_6$ and the substitution of divalent atoms M for La in $La_{2-y}M_yCuO_4$. We suggest that superconductivity in both systems is associated with the Cu–O planes and is driven electronically.

1. Introduction

The origin of superconductivity at temperatures exceeding 90 K in $RBa_2Cu_3O_x$ ($x \simeq 7$) compounds has been the subject of some speculation. However, without substantial knowledge of the basic interactions present in the normal state of these materials, it is difficult to decide which of the several theoretical models [1] holds most promise. Soon after the discovery [2] of superconductivity in $YBa_2Cu_3O_x$, additional compounds were found [3], with R one of the rare-earth elements, which had transition temperatures T_c nearly identical to that of non-magnetic Y. Those observations suggested immediately that superconductivity was due primarily to the Cu–O planes/chains associated with the oxygen-defected structure of these layered perovskites [4]. Subsequent work showed that transition metal substitutions [5] for Cu or oxygen removal [6] substantially depressed T_c, in some cases completely suppressing superconductivity.

To date there have been several studies of both structural and physical properties of high-T_c superconductors in which oxygen was removed intentionally. Neutron scattering measurements [7] as a function of oxygen content showed that oxygen is removed preferentially from the linear Cu–O chain sites that run along the orthorhombic b-axis. For an oxygen content $x = 6.5$, the structure became tetragonal with a concommitant depression of T_c to zero [8]. More recent work [9], however, suggests that these observations depend sensitively on the way oxygen is removed. Depleting oxygen by a low-temperature gettering anneal presumably provides spatial ordering of the oxygen defects such that the structure remains orthorhombic to an oxygen content $x \gtrsim 6.0$ with a corresponding weaker dependence of T_c on x [9]. Measurements of the electrical resistivity ρ and T_c on these samples showed a minimum and a plateau respectively for $6.6 \lesssim x \lesssim 6.8$ which has been interpreted as evidence for a new ordered oxygen deficient structure having a transition temperature of 55–60 K.Magnetic susceptibility χ measurements [10] on similarly prepared samples supported this interpretation. Considerable controversy persists, however, concerning what these observations imply for an understanding of high temperature superconductivity as well as the importance of Cu–O planes relative to Cu–O chains.

Although it is clear from these earlier studies that oxygen content plays a central role in determining the superconducting and structural properties, no investigation has been made that employs a variety of techniques to understand the normal state properties as the oxygen content is varied. Such experiments should provide additional insight into the underlying physical mechanisms that are important in these materials. To this end, we have studied the effect of

varying oxygen content in $EuBa_2Cu_3O_x$ through electrical resistivity, thermoelectric power S, dc magnetic susceptibility, Hall coefficient R_H, and upper critical field H_{c2} measurements. To ensure consistency in these measurements, all experiments were performed on the same oxygen deficient samples which themselves were cut from a single large button having a density $\sim 80\%$ of theoretical.

2. Experimental

For these experiments a large (~ 1 g) button of $EuBa_2Cu_3O_x$ was prepared by conventional ceramic techniques. Wet chemical analysis of pieces from this button gave an oxygen content $x = 7.0 \pm 0.1$. Direct current magnetization measurements on the starting material in 100 G showed a sharp onset of superconductivity at 95 ± 1 K and shielding of magnetic flux at 7 K corresponding to 120% of perfect diamagnetism, not corrected for demagnetizing effects. To remove oxygen, sections of the button were subjected to vacuum and heated to between 300–600 °C for 2 to 24 hours, depending on how much oxygen was to be removed. After the heat treatment, the sample was allowed to cool slowly to room temperature. Weight loss resulting from this treatment was assumed to arise solely from the removal of oxygen from the samples. The maximum relative weight loss produced a calculated oxygen content of $x = 6.09$, assuming $x = 7.0$ in the starting material.

3. Results

The effect of oxygen stoichiometry on the resistivity is summarized in fig. 1 where, for clarity, we show only representative curves for $x > 6.48$. Although the absolute magnitude of ρ is larger than found in well-sintered [11] or single crystalline [12] samples, relative changes in $\rho(T)$ are expected to reflect intrinsic changes in the conduction process. In the interval $6.48 < x < 6.53$, a temperature range above T_c exists in which $\partial\rho/\partial T < 0$. For lesser amounts of oxygen, the resistivity increases substantially at room temperature and increases monotonically at temperatures below 300 K. Analysis of the temperature dependent resistivity for $x = 6.33$, 6.18 and 6.09 samples shows that all follow a form $\ln \rho \propto T^{-\alpha}$, where $\frac{1}{4} \leqslant \alpha \leqslant \frac{1}{2}$, i.e. none show simple activated behavior but are typical of conduction due to localized states and mediated by variable range hopping [13]. Results for the $x = 6.33$ sample are given in fig. 2 where this behavior is observed for 14 K $< T <$ 125 K during which the resistance changes by more than two orders-of-magnitude.

The thermoelectric power of $EuBa_2Cu_3O_7$ is positive, suggesting that conduction is dominated by hole-like carriers, and essentially independent of temperature above T_c, which is not characteristic of simple, metallic-like entropy transport. With decreasing oxygen, the thermopower grows in magnitude until for $x = 6.09$ it changes sign (electron-like) at room temperature [14]. (See fig. 3.) For $x \gtrsim 6.5$

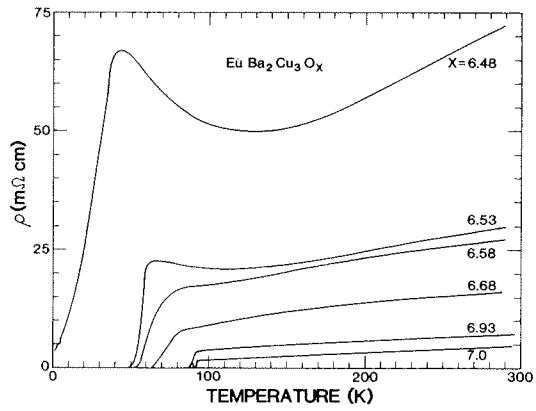

Fig. 1. Eletrical resistivity of sintered $EuBa_2Cu_3O_x$ as a functior of temperature for various values of x. For clarity only represent ative curves are shown for $x > 6.48$.

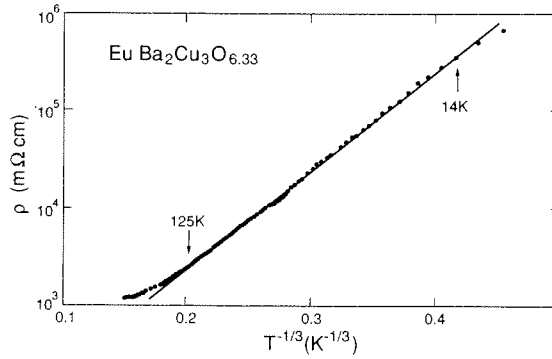

Fig. 2. Logarithm of the resistivity of $EuBa_2Cu_3O_{6.33}$ versus temperature to the negative 1/3 power. Note the linear relationship for $14 < T < 125$ K.

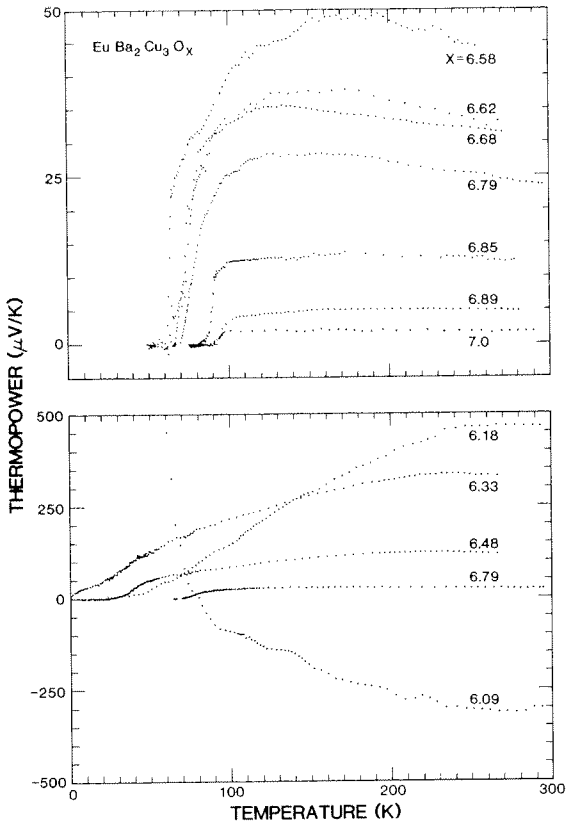

Fig. 3. Thermoelectric power S as a function of temperature for $EuBa_2Cu_3O_x$ with $6.09 < x < 7.0$.

the thermopower remains nearly temperature independent but begins to acquire a significant temperature dependence for smaller x. For $x = 6.33$ and 6.18, $S \propto T^{\beta}$, with $\frac{1}{4} < \beta < \frac{1}{2}$, over an appreciable temperature interval below 300 K, again suggestive of localized-like transport [13,15]. Results for $x = 6.33$ are shown in fig. 4. We note that the precise temperature dependence may be distorted somewhat by unknown anisotropy effects [16], which is also true for the electrical resistivity [12,16].

Defining T_c from the temperature at which $S = 0$ and at which diamagnetism appears in dc susceptibility measurements leads to the T_c versus x phase diagram shown in fig. 5. In agreement with earlier reports [9,17] we find a plateau in T_c for $6.6 \lesssim x \lesssim 6.8$ that is accompanied by a minimum in the resistivity at 250 K which suggests a new ordered oxygen deficient structure having a transition temperature of $\gtrsim 60$ K. Extrapolating T_c to zero gives a critical oxygen concentration for superconductivity of ~ 6.4, which is in the composition range where an orthorhombic-to-tetragonal transition is reported [7] to occur. X-ray analysis of our $x = 6.33$ sample confirmed that it was tetragonal and that there were less than 10% other phases present.

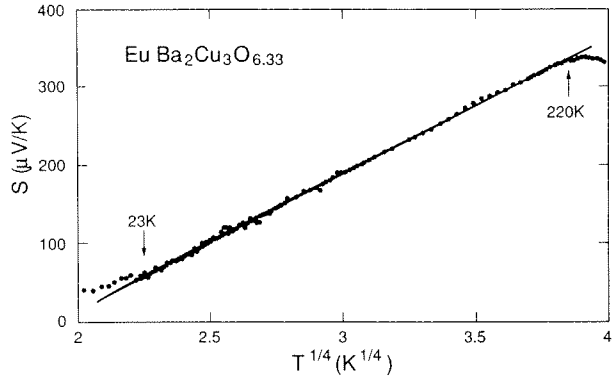

Fig. 4. Thermoeletric power versus temperature to the 1/4 power for $EuBa_2Cu_3O_{6.33}$. The linear relationship observed for $23 < T < 220$ K is consistent with the resistive behavior shown in fig. 2.

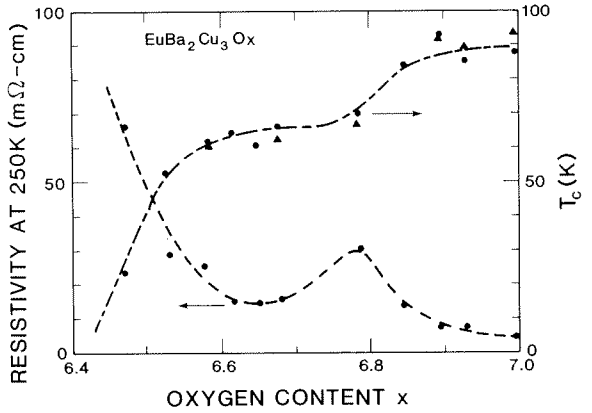

Fig. 5. Resistivity at 250 K (left vertical scale) and on the right vertical scale the superconducting transition temperature T_c defined by the temperature at which the thermopower is zero (solid circles) or at which diamagnetism appears (solid triangles) as functions of oxygen concentration x in $EuBa_2Cu_3O_x$. Dashed lines are guides to the eye only.

From Hall effect measurements on three samples ($x = 7.0$, 6.79 and 6.58) a carrier concentration n was calculated assuming the single band expression $n = 1/R_H ec$, where R_H is the measured Hall coefficient. For $x = 0.7$, n increases linearly with T as ob-

served before [11]. However, for $x=6.8$ and 6.6 a non-monotonic but weakly temperature dependent variation of n is observed, as shown in fig. 6. Similar observations were made by Ong et al. [18] on sintered $YBa_2Cu_3O_x$. From these data we find that n at T_c decreases by about a factor of 3.5 in going from $x=7$ to $x=6.6$. with T_c scaling crudely with $n(T \gtrsim T_c)$.

The upper critical field slope H'_{c2} near T_c was determined resistively in fields to 8 T on the Hall-effect samples. For these measurements the resistive midpoint was used to define $H_{c2}(T)$. In agreement with earlier reports [19] we find $H'_{c2}=-3.1$ T/K for $x=7.0$. However, with decreasing oxygen content, H'_{c2} is suppressed rapidly to values of -1.1 and -0.8 T/K for $x=6.8$ and 6.6 respectively.

The low-field (100 G) magnetic susceptibility at 100 K varies non-monotonically as a function of x. Initial oxygen removal produces a decrease in χ by more than 10% in going from $x=7$ to $x=6.79$ that is interrupted by a sudden increase for $x=6.64$ and 6.68, signalling the appearance of the ordered oxygen defect phase. This variation in χ versus x is qualitatively similar to that reported by Cava et al. [10] for $YBa_2Cu_3O_x$. Higher field (4000 G) susceptibility measurements on the $x=6.0$ sample reveals a shoulder near 300 K that may be associated with ordering of copper moments, as recently detected in NQR [20] and neutron scattering [21] experiments. For oxygen concentrations less than 6.3 a small "Curie-like-tail" appears at temperatures below approximately 20 K that possibly is associated with the presence of a magnetic second phase; although, it could

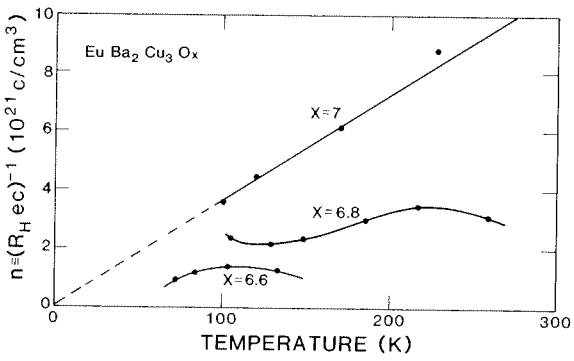

Fig. 6. Carrier concentration n, calculated from the single band expression $n=1/R_H ec$, where R_H is the Hall coefficient, as a function of temperature for various $EuBa_2Cu_3O_x$.

be intrinsic [10]. Finally we note that shielding-effect measurements on our sample in 100 G are in semiquantitative agreement with those reported by Tokumoto et al. [17].

4. Discussion

As a starting point for interpreting the data, it is useful to review what is known of the related system $La_{2-y}M_yCuO_4$, where M is a divalent atom. In undoped La_2CuO_4 there is a finite electronic specific heat [22,23] at low temperatures [$\gamma(T=0) \sim$ mJ/mol K^2], a highly anisotropic resistivity [16] which in the Cu–O planes has the form $\ln \rho \propto T^{-1/}$ characteristic of correlated variable-range hopping a small number of hole-like carriers [24], and a large positive thermoelectric power having a temperature dependence as expected from the resistivity [16]. Magnetic susceptibility [25] and neutron scattering experiments [26] show an antiferromagnetic transition in slightly oxygen deficient samples at $T_N \sim 26$K which decreases as oxygen stoichiometry is approached [27]. Upon substituting a divalent atom such as Ba or Sr for La, T_N is suppressed to zero (for $y \leqslant 0.06$) and for larger y superconductivity appears with T_c reaching a maximum near $y=0.15$ [28]. The addition of Sr increases the number of hole carriers linearly with y for $y \leqslant 0.15$ [24,29]. In superconducting samples, $\gamma(T=0)$ is 3–5 mJ/mol K^2 [22,30]. An analysis [31] of the magnetic susceptibility and $\gamma(T_c)$, determined from the specific heat jump at T_c, shows that both are enhanced, indicating the presence of Coulomb correlations.

We believe that the addition of oxygen in $RBa_2Cu_3O_x$ is analogous to divalent atom substitution in $La_{2-y}M_yCuO_4$. For strongly depleted ($x<6.4$) samples, we observe a temperature dependent resistivity and thermopower that suggest transport by variable-range hopping. Because of both the sintered nature of the sample and the fact that the temperature interval over which reliable transport measurements can be made was limited, it is not possible to distinguish unambiguously whether the hopping is correlated or not. However, as argued previously [11], there is evidence for strong electron–electron interactions in $x=7$ samples that presumably persists upon removing oxygen. In the non-supercon-

ducting regime ($x<6.4$), NQR [20] and neutron scattering [21] show antiferromagnetic ordering (of Cu $3d^9$ moments) at a transition temperature that depends strongly on oxygen content and goes to zero at a critical oxygen concentration ($x_c \simeq 6.4$) above which superconductivity appears. Such behavior is consistent with a Mott–Hubbard-like transition near x_c, with transport and magnetism arising from localized states ($x<x_c$) and superconductivity ($x>x_c$) from extended hole-like states produced by oxygen addition.

Recent measurements [32,33] of the low-temperature specific heat of $YBa_2Cu_3O_x$ ($6<x<7$) crystals show that the electronic contribution changes little in going from the superconducting to non-superconducting states and that it remains large, 5–9 mJ/mol K^2. In ref. [32] it was argued that $\gamma(T=0)$ arises, at least in part, from extended or localized states at the Fermi energy.Such a conclusion is consistent with the results of this study. Interestingly, Ayache et al. [34] find a similar result for $\gamma(T=0)$ versus x but also find that the specific heat jump at $T_c[\Delta C(T_c)]$, which is clearly detectable for $x=7$, becomes undetectably small for $x \leqslant 6.6$ samples that show superconductivity as detected through magnetic susceptibility. Because ΔC is directly related to $\gamma(T_c)$ (in BCS theory), these observations imply that $\gamma(T=0)$ and $\gamma(T_c)$ are not related directly. Assuming the dirty limit, we have calculated $\gamma(T_c)$ from the critical field slope and resistivity near T_c and find that $\gamma(T_c)$ for $x=6.6$ should be approximately 30 times smaller than for $x=7.0$, consistent with the specific heat measurements [34] at T_c. These results suggest that most of the electronic specific heat at T_c is associated with the integrity of the Cu–O chains, whereas that at $T=0$ is dominated by the Cu–O planes.

The Pauli susceptibility χ_P of $YBa_2Cu_3O_7$ is enhanced by electronic correlations, by over an order of magnitude relative to that calculated from the carrier density, to a value of $\sim 6\times10^{-7}$ emu/g [11]. Assuming a comparable χ_P in $EuBa_2Cu_3O_7$ means that it contributes only about 7% of the measured susceptibility at 100 K. The change in carrier concentration between $x=7.0$ and 6.8, assuming the correlation enhancement of χ remains constant in this interval, would give a reduction in χ_P (100 K) of 0.75×10^{-7} emu/g; whereas, we observe a decrease in χ (100 K) that is approximately one order-of-magnitude larger. This implies that either a single-band description is inappropriate or electronic correlations are suppressed with decreased oxygen content. The former is implicated from the substantial difference in the temperature dependences of n for these two samples. [We note that a two-band model can be constructed that adequately accounts for the temperature dependence of ρ, n and S, in a self-consistent way, for $EuBa_2Cu_3O_7$. This model assumes two conduction processes, one due to metallic-like carriers in parallel with an intrinsic, gaples semiconductor with temperature dependences characteristic of each process. The analogy here is to a half-filled Cu_{3d}–O_{2p} hybridized band and an almost completely filled O_{2p} band. Reasonably good fits of the data to this model, shown by the dashed lines in fig. 7, are obtained with physically reasonable parameters, one of which is a relatively large effective mass ($m^* \approx 10\ m_e$).] For oxygen concentrations less than 6.4, Ong et al. [18] found an approximately linear decrease in n versus x for $YBa_2Cu_3O_x$, such as was observed by Shafer et al. [29] for small Sr dopings in $La_{2-y}Sr_yCuO_4$. In that case it was argued that the linear dependence of n on Sr content was consistent with band filling of a single highly correlated Hubbard band. We suggest that similar arguments are appli-

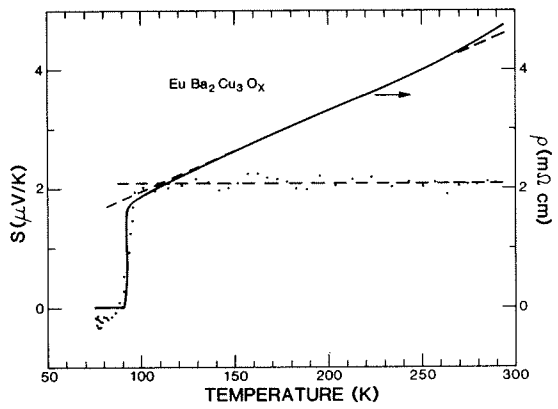

Fig. 7. Temperature dependence of the electrical resistivity and thermoelectric power of $EuBa_2Cu_3O_7$. Dashed lines are a fit to the data assuming a two-band model for transport (see text). Such a model is also consistent with the temperature dependence of the Hall coefficient R_H. We note that this model could not self-consistently explain the measured temperature dependencies of ρ, S and R_H for $x<7.0$.

cable to oxygen doping in $EuBa_2Cu_3O_x$ for $x<6.4$–6.5. In this regime, the susceptibility is enhanced by the presence of strong Coulomb and/or magnetic correlations.

5. Conclusions

The point of view suggested by our experiments, in conjunction with those reported elsewhere, is that the high-T_c superconductors $RBa_2Cu_3O_x$ should be regarded as Mott–Hubbard systems in which strong electron–electron correlations produce a metal–insulator transition near $x\sim 6.4$–6.5 that is accompanied by an orthorhombic-to-tetragonal transition. Reports [9,10] of superconductivity and an orthorhombic structure for $x<6.4$ may be associated [35] with a metastable phase. At small oxygen concentrations transport is by correlated variable-range hopping and the spin system is antiferromagnetic. For $6.6\lesssim x\lesssim 6.8$, an ordered oxygen defect structure produces $T_c\simeq 60$ K. the nature of this state remains unresolved. In samples with $x\gtrsim 6.8$, transport is not described simply but clearly must be affected by Coulomb correlations that could lead to magnetic excitations observed [36] recently in light-scattering experiments. The analogy between divalent atom substitution in $La_{2-y}M_yCuO_4$ materials and oxygen concentration in $RBa_2Cu_3O_x$ is striking and further suggests that the mechanism for superconductivity is the same in both. The most noteable difference, however, between these two systems is the presence of one-dimensional Cu–O chains in the 90 K superconductors. An extension of the analogy between these two systems leads to the conclusion that superconductivity is associated with the Cu–O planes in both, that the chains play a secondary but crucial role of providing the proper "environment", in much the same way as does the divalent atom in $La_{2-y}M_yCuO_4$, and that superconductivity arises primarily from electronic interactions.

Acknowledgements

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