High-pressure study on 60- and 90-K $EuBa_2Cu_3O_{7-\delta}$

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The 60- and 90-K superconductivity in $EuBa_2Cu_3O_{7-\delta}$ has been investigated under pressures up to 16 kbar. Unusually large pressure effects on the normal-state resistivity and the superconducting transition temperature of the 60-K compound were observed in contrast to the 90-K one. A subtle difference between the 30-, 60-, and 90-K superconductors is therefore proposed.

Recent discoveries of the 30- and 90-K superconductivity, respectively, in the single-layer ternaries[1] $(La_{1-x}M_x)_2CuO_{4-y}$ (M = Ba, Sr, and Ca; $0 \leq x \leq 0.2$; $y < 0.1$) and the triple-layer quaternaries[2] $ABa_2Cu_3O_{7-\delta}$ (A = rare-earth element; $\delta \leq 0.45$) have led to an avalanche of activity[3] in the study of these oxide compounds. Great experimental progress has been made on their physical and chemical properties both in the normal and superconducting states. At the same time, many theoretical models have also been advanced to explain the observations. In spite of the extensive efforts, the fundamental question concerning the mechanism responsible for superconductivity at such high temperatures, especially above 90 K, remains unsettled. One approach toward an answer to this question is to examine the possible dissimilarities between existing material systems with distinctly different superconducting transition temperatures T_c and/or to search for new material systems with high T_c. Although possible fundamental differences between the 30- and 90-K superconductivity has been suggested,[4] a formal address to the problem is yet to be made.

Recently, a 60-K superconducting phase has been proposed[5] to exist in $YBa_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O) when δ is near 0.4. Without disturbing the chemical characteristics, we have investigated the transport and superconducting properties of the 60-K $EuBa_2Cu_3O_{7-\delta}$ (Eu-Ba-Cu-O) compounds under hydrostatic pressures up to 16 kbar. A 90-K Eu-Ba-Cu-O sample was also studied for comparison. We observed a rapid T_c enhancement in the 60-K Eu-Ba-Cu-O with pressure at a rate of 0.9 K/kbar, about 100 times that of the conventional $A15$ high-T_c superconductors, in strong contrast to the 90-K Eu-Ba-Cu-O with a T_c enhancement rate of 0.1 K/kbar, while the sign of possible electron localization immediately above T_c and the overall resistivity of the 60-K Eu-Ba-Cu-O are suppressed. By examining these and existing results, we propose that a subtle difference exists between the 90- and 60-K superconductivity, and that similarity may persist between the 60- and 30-K superconductivity. The implications of this proposition will be given in comparison with some models previously suggested.[6]

We first synthesized the 90-K Eu-Ba-Cu-O compound by the standard solid-state reaction technique in four steps. First calcination of pellets of a thoroughly ground mixture of appropriate amounts of Eu_2O_3, $BaCu_3$, and CuO at 950 °C in air, rehomogenation of the calcinated pellets following their crushing and regrinding, sintering of the pellets of the rehomogenized material at 950 °C in an oxygen atmosphere, and finally cooling of the sintered pellets to room temperature slowly in an oxygen atmosphere. The 60-K Eu-Ba-Cu-O compound was then obtained by evacuating the 90-K Eu-Ba-Cu-O at temperatures between 300 and 500 °C for 30 min. Bar samples of dimensions $\sim$3 mm$\times$1 mm$\times$0.5 mm were cut from the pellets for measurements. Pt electrical leads were attached to the samples by Au paste. A standard four-probe technique was employed to measure at 17 Hz the resistivity ρ as a function of temperature. No difference was found between the ρ values determined at 0 and 17 Hz. The magnetization M of the samples at ambient pressure was measured in the presence of a field of 50 G with the PAR M155 vibrating sample magnetometer as the temperature varies. The high-pressure environment was provided by a Be-Cu clamp, using silicon oil as the pressure medium contained in a high-pressure cell. The pressure was determined at low temperature by a superconducting Pb manometer situated next to the sample. The temperature was measured by a chromel-alumel thermocouple attached to the sample inside the high-pressure cell above 20 K, and by a Ge thermometer mounted at the bottom of the Be-Cu high-pressure clamp outside the high-pressure area below 30 K.

X-ray powder-diffraction data showed the samples investigated were monophasic with lattice parameters $a = 3.859$ Å, $b = 3.904$ Å, and $c = 11.712$ Å for the 60-K Eu-Ba-Cu-O; and $a = 3.849$ Å, $b = 3.901$ Å, $c = 11.704$ Å for the 90-K Eu-Ba-Cu-O. Both types of samples clearly are orthorhombic, but the 60-K one has a lower orthorhombicity. Figures 1(a) and 1(b) show the temperature dependences of ρ and M for samples heat treated for 30 min in a vacuum at different temperatures. It is clear that the sample started to lose oxygen even at a vacuum-treatment temperature T_v as low as 100 °C, evident from the ρ increase following the vacuum treatment. In spite of this continuous ρ increase, T_c initially clusters around 90 K and then drops drastically to around 60 K when T_v increases to between 300 and 500 °C, similar to previous reports.[7,8] T_c rapidly decreases to 0 K when T_v exceeds 500 °C. In other words, there exists a plateau in the T_c-vs-δ plot. Coinciding with this drastic shift in T_c from 90 to 60 K, the temperature dependence of ρ also exhibits a marked change from simple metallic behavior to the ap-

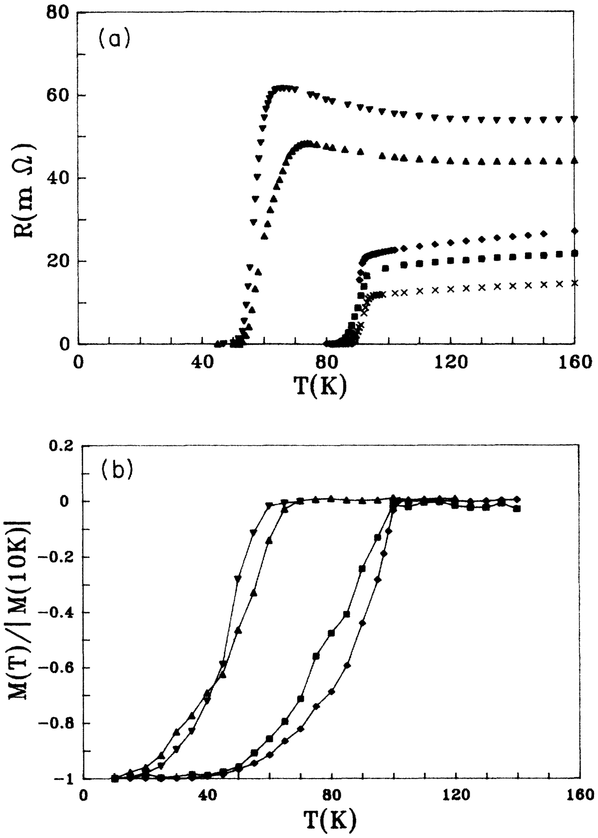

FIG. 1. (a) $\rho(T)$ and (b) $M(T)$ of Eu-Ba-Cu-O evacuated for 30 min at ×, 25; ■, 100; ♦, 200; ▲, 300; and ▼, 400 °C.

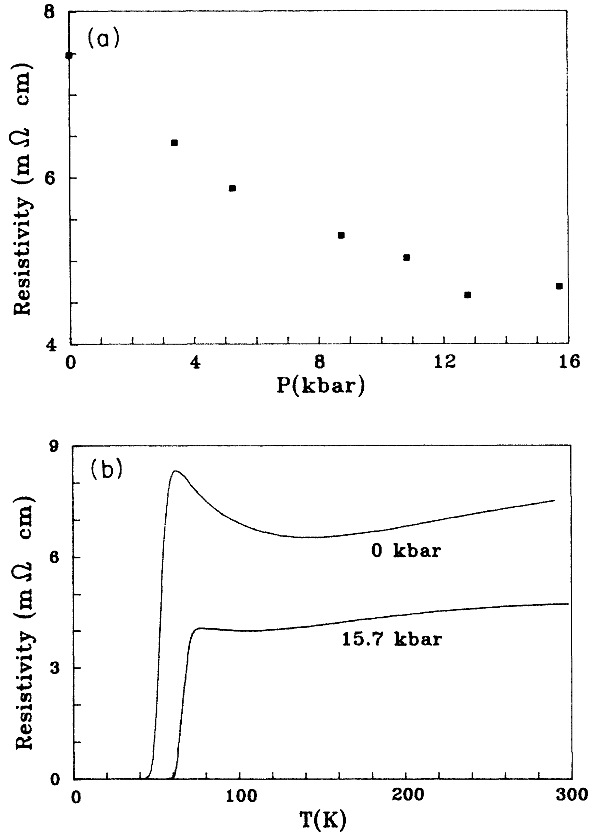

FIG. 2. (a) $\rho(P)$ at 300 K; (b) $\rho(T)$ at two pressures.

pearance of a ρ peak immediately above T_c. Consequently, the 60-K plateau in the T_c-δ curve has been attributed[5,7] to the existence of a new superconducting phase with $\delta = 0.3 \sim 0.4$. This is consistent with the observation[9] of two differential-thermal-analysis peaks at 310 and 390 °C when oxidizing samples with $\delta = 0.6$, but only one at 390 °C when oxidizing samples with $\delta = 0.04$. The variation of carrier concentration with δ also supports the suggestion[10] of the existence of the 60-K phase. Recent model calculations[11] on the ordering of oxygen atoms in the two-dimensional CuO(1) layers between the BaO(4) layers indicate the possible formation of new oxygen-deficient phase by forming ordered CuO(1) chains and doubling the periodicity between chains.

In general, the overall ρ of both the 60- and 90-K Eu-Ba-Cu-O decreases with pressure. For the 60-K Eu-Ba-Cu-O, ρ is suppressed by 25% by a pressure of 12.4 kbar and the ρ peak is rapidly reduced as shown in Figs. 2(a) and 2(b), respectively. T_c is enhanced by pressure for both Eu-Ba-Cu-O phases. However, the rate of T_c increment dT_c/dP under pressure is 0.9 K/kbar for the 60-K Eu-Ba-Cu-O similar to the 30-K La-Ba-Cu-O (Ref. 12) and only $\sim$0.16 K/kbar for the 90 K Eu-Ba-Cu-O similar to the 90-K Y-Ba-Cu-O,[13] as displayed in Fig. 3. The slight decreases in dT_c/dP and $d\rho/dT$ above $\sim$8 kbar may be due to the presence of shear stress originating from the solidification of silicone-oil pressure medium at 300 K.

The application of pressure to matter inevitably generates a volume reduction. However, the effect of pressure[14] on the physical properties can be either a result of direct volume reduction or an associated change in the energy spectrum of the matter. Oxygen has been shown[15] to have a negative effective volume in Y-Ba-Cu-O and a positive effect on T_c, i.e., the unit-cell volume decreases and T_c increases as δ decreases. It would be natural to ascribe the large positive dT_c/dP to a direct volume reduction. On the other hand, the bulk modulii B of the 30- and 90-K superconductors have been previously determined[16] to be

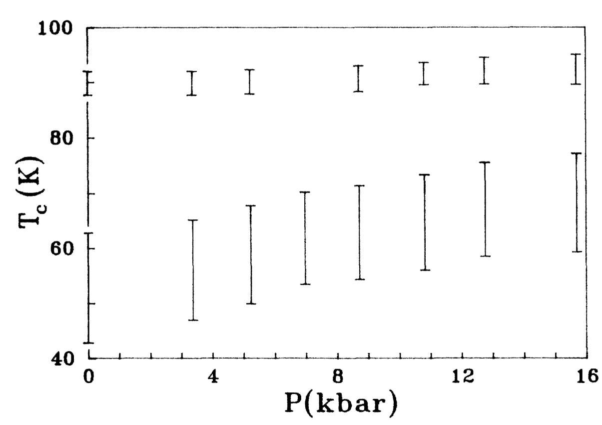

FIG. 3. $T_c(P)$ for the 60-K Eu-Ba-Cu-O and 90-K Eu-Ba-Cu-O.

1700 and 1800 kbar, respectively. It is therefore reasonable to assume a B between 1700 and 1800 kbar for the 60-K superconductor. Consequently, the drastic difference between the values of dT_c/dP for the 60- and 90-K superconductors cannot be caused by the straightforward volume reduction induced by pressure. Rather it may be associated with subtly different changes in the electron energy spectra of the two phases. The unusually large drop in ρ under pressure suggests that large charge transfer between the CuO(1) chains and the CuO(2) layers must have taken place more effectively in the 60-K Eu-Ba-Cu-O than in the 90-K Eu-Ba-Cu-O, perhaps due to the smaller chain density in the former. It is then very interesting to determine if the T_c of the 60-K Eu-Ba-Cu-O can be enhanced to above 90 K at an undiminishing rate. Studies to higher pressure under a better hydrostatic condition are under way.

The simultaneous occurrence of superconductivity and antiferromagnetic ordering in the ternary La_2CuO_4 and related compounds,[9] depending on the O stoichiometry, prompts many to suggest the important role for the antiferromagnetic correlation in high-temperature superconductivity. If one assumes that antiferromagnetism in the system stems from the superexchange interaction with a dominant kinetic part, it can be obtained[17] that $T_N \sim zt^2/U$ and $dT_N/dP = \frac{10}{3}(T_N/B)$, where z is the number of the nearest magnetic neighbor ions, t the transfer integral, and U the intra-atomic Coulomb repulsion. The relations have been demonstrated to describe well the experimental data including the antiferromagnet of slightly oxygen-deficient La_2CuO_4. For optimal doping in the 30-K superconductors, where Cu^{3+} ions and thus holes are created, it was shown[18] based on a Hubbard Hamiltonian including the antiferromagnetic interaction that $T_c \sim t^2/U$. The similar dependence of T_N and T_c on t^2/U led to the suggestion[17] that dT_c/dP may also follow the same dependence and be equal to $\frac{10}{3}(T_c/B)$ as T_N, or $\phi \equiv (B/T_c)(dT_c/dP) = \frac{10}{3}$. From the present and previous work, the following values are obtained for ϕ: 3.2 (90-K Y-Ba-Cu-O, 90-K Eu-Ba-Cu-O); 30 (60-K Eu-Ba-Cu-O); and 14–40 (30-K La-Sr-Cu-O, 30-K La-Ba-Cu-O). The results suggest[18] that the model can explain the 90-K superconductivity but not the 60- or 30-K superconductivity.

Although all oxide superconductors with a $T_c > 10$ K are perovskite-related compounds, the crystal chemical details of the 90-K superconductors are very different from those of the 30-K superconductors: The former consist of loosely coupled triple Cu-O layers while the latter consist of loosely coupled single Cu-O layers. In fact the 90-K Y-Ba-Cu-O was the first true quaternary compound found in nature whose structure cannot be stabilized with less than four elements. This is in turn reflected in their superconducting properties. For instance, dT_c/dP for the 30-K superconductor is about 5 to 10 times that for the 90-K superconductor; a partial isotope effect[19] has been observed in the 30-K superconductor but only a negligibly small effect in the 90-K one; the positron lifetime[20] undergoes on cooling only a small increase in the 30-K superconductor but a large drop in the 90 K and general lattice softening[21] occurs upon cooling in the 30-K superconductor but not in the 90-K one. In view of the above differences, it should not be surprising to find different mechanisms giving rise to superconductivity in these different compound systems. The present high-pressure data clearly distinguish the 60-K Eu-Ba-Cu-O from the 90-K Eu-Ba-Cu-O and place it more closely to the 30-K superconductor. However, closer examination of the crystal chemistry may eventually classify the 60-K superconductor in a class of its own. The clustering of T_c of high-temperature oxide compounds on their equilibrium forms at 30, 60, and 90 K may not be accidental. This may be related to the specific active single, double, and triple Cu-O layers of the compounds noted earlier.[22] If this is true, the CuO(1) chains in the 60-K superconductors may play only a secondary role and not directly participate in the transport of the superconducting current, in contrast to the 90-K superconductors. By comparing the structural data of all high-T_c oxides, we would like to point out the importance of the O ions off the Cu-O layers, which have often been neglected in model calculations.

In conclusion, we have found that T_c of the 60-K Eu-Ba-Cu-O is enhanced at a rate 5 to 10 times that of the 90-K superconductor and in the range of that for the 30-K superconductors. By reviewing all existing data, possible grouping of high-T_c oxide superconductors has been proposed, implying different superconducting mechanisms in these different groups.

After writing this paper, we learned that a large pressure effect on T_c has also been observed by Borges *et al.* in $EuBa_2(Cu_{0.99}Zn_{0.01})_3O_x$ with a $T_c \sim 62$ K at ambient pressure.[23] The results do not change the conjecture raised in this paper since a phase can be reached in more than one route, i.e., doping and oxygen deficiency. The 60-K superconductor may situate near an inflection point of the density-of-state curve.

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