Magnetic field dependence of the resistivity and susceptibility of the above-100-K Bi-Sr-Ca-Cu superconductor

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The magnetic field dependence of the resistivity and susceptibility of multiphase Bi-Sr-Ca-Cu-O compounds exhibiting transport and diamagnetic anomalies at $\simeq 115$ and $\simeq 75$ K are reported. The field dependence of the latter yields values of H_{c1} and $dH_{c2}/dT(T=T_c)$ very similar to those found for the $Y(R)Ba_2Cu_3O_{7-x}$ family of Cu perovskitelike superconductors. The field dependence of the above-100-K region strongly suggests that bulk superconductivity, as opposed to filamentary or fluctuation behavior, dominates at these temperatures.

Last year Michel *et al.*[1] found a new family of quaternary oxide superconductors containing Bi, Sr, and Cu cations. For compositions close to $Bi_2Sr_2Cu_2O_{7+\delta}$, they reported superconducting transition temperatures ranging from 7 to 22 K. Recently Maeda, Tanaka, Fukutomi, and Asano[2] and Chu *et al.*[3] have found resistive and diamagnetic anomalies near 110 K in the related quinary Bi-Sr-Ca-Cu oxide system, although the majority of the material becomes superconducting below $\simeq$80–90 K. In this paper, we present data on the magnetic field dependence of the resistive and diamagnetic transitions of multiphase, polycrystalline Bi-Sr-Ca-Cu oxide pellets which clearly demonstrate the existence of a phase displaying bulk superconductivity with a transition temperature of $\simeq 115$ K. Moreover, we postulate this superconductivity is associated with the existence of observed structural deviations[4,5] within a host single-phase lattice responsible for the lower temperature transition.

The samples used in this study were prepared using standard methods. Appropriate mixtures of Bi_2O_3, $SrCO_3$, and CuO were calcined at 800 °C for 6 h and subsequently reground, pressed into a pellet, and sintered in air at 855 °C for 15 h. For a number of multiphase samples prepared over a wide composition range we detected small diamagnetic anomalies below 115 K of magnitude typically only approximately 0.1% of the perfect diamagnetic response $(-1/4\pi)$. The largest diamagnetic anomalies in this temperature range were observed for samples prepared from starting mixtures of composition close to $Bi_2Sr_1Ca_2Cu_3O_x$. X-ray analysis showed that these samples contained large amounts of CuO which we found to be a common by-product in obtaining the high-temperature superconducting phase.

Diamagnetic shielding and Meissner curves are shown in Fig. 1 for a multiphase sample of composition, $Bi_{1.7}Sr_{1.3}Ca_2Cu_3O_x$. The bulk of the sample becomes superconducting below $\simeq 75$ K with diamagnetic shielding signals of approximately 40% of $-1/4\pi$ at 6.5 K. However, an abrupt diamagnetic anomaly of approximately 1% of the perfect diamagnetic response is found beginning at $\simeq 115$ K. The temperature dependences of the Meissner and shielding signals near the two respective transition temperatures are very similar. This is demonstrated in Fig. 1 by scaling the data at the higher-temperature transition by a factor of 40. The magnitude of the respective diamagnetic signals reflects the proportions of two distinct crystallographic phases with different transition temperatures. However, apart from CuO, only one phase could be identified from detailed x-ray studies. This phase, of composition $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_x$, was indexed to a tetragonal unit cell in the space group $I4/mmm$ with lattice parameters $a = 3.812$ Å and $c = 30.66$ Å.[6] The structure of this phase consists of an intergrowth of two BiO layers with a double perovskite layer. This double perovskite layer of the form Cu_2O_6 consists of corner sharing CuO_5 pyramids as in $La_2CaCu_2O_6$ (Ref. 7) and $YBa_2Cu_3O_{7-x}$. We believe that the Ca is between the Cu layers in analogy with $La_2CaCu_2O_6$ and that the site in between the Bi and Cu layers is predominantly occupied by Sr, in close agreement with the structures reported by Tarascon *et al.*[8] and Sunshine *et al.*[9]

The magnetic field dependence of the Meissner versus temperature curves for the same sample shown in Fig. 1 is given in Fig. 2 for fields ranging from 250 Oe to 10 kOe. These data were taken on cooling the sample in the corresponding magnetic field. Above $\simeq 115$ K, the observed

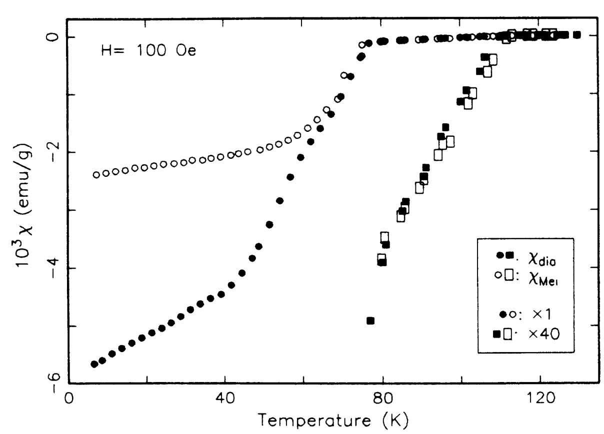

FIG. 1. Meissner (○,□) and diamagnetic shielding (●,■) signals as a function of temperature for a pellet of composition $Bi_{1.7}Sr_{1.3}Ca_2Cu_3O_x$, for an applied field of 0.1 kOe. The data shown as circles and squares are scaled by factors of 1 and 40, respectively.

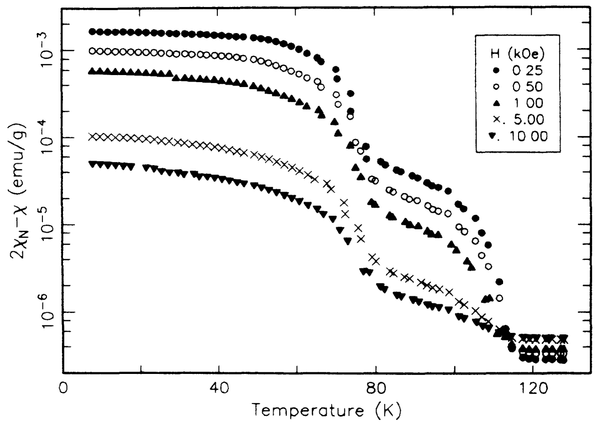

FIG. 2. Plots of $\log_{10}(2\chi_N - \chi)$ vs temperature at various fields shown in the figure (in kOe) for the same sample as in Fig. 1. Each curve was taken on cooling the sample from 130 K in a constant applied field.

susceptibility is independent of field and corresponds to a small paramagnetic susceptibility. In order to compare the behavior of the diamagnetic anomalies at the two distinct superconducting transition temperatures, Fig. 2 shows a semilogarithmic plot of the quantity, $2\chi_N - \chi$, where χ_N is the normal-state susceptibility above 120 K. This quantity is always positive and allows for a comparison of the magnitude of the diamagnetic susceptibility with that of the normal-state susceptibility. This figure graphically demonstrates the very similar magnetic field dependences of the anomalies, even though the magnitude of the diamagnetic signal is $\simeq 40$ times smaller at the higher transition temperature. The field dependence of the Meissner susceptibility at two constant temperatures, 8 and 85 K, is shown in the inset to Fig. 3. After scaling the 85-K data by a factor of 40 to take account of the smaller volume fraction of the high-temperature phase, the field dependences are very similar. We interpret this as direct evidence for bulk superconductivity above 100 K, as opposed to fluctuations or filamentary effects. Also in Fig. 3 is plotted the field dependence of the magnetization at a temperature of 7 K after cooling the sample in zero field. From these data, using the conventional method for determination of the lower-critical field H_{c1} as the point at which the magnetization curve deviates from a linear field dependence, we can estimate an upper limit for H_{c1} of $\simeq 300$ Oe.

Finally in Fig. 4 is shown the effect of magnetic field on the resistivity versus temperature curves. There is a marked drop in resistivity near 115 K with a second more pronounced drop below 85 K with the resistance only going to zero below 74 K. The data were taken using a standard low-frequency lock-in technique with silver paint contacts. The usual tests were made to ensure a uniform current distribution through the sample. A current of 10 μA was used and the field was applied transverse to the current direction. There is substantial broadening of the lower transition in small fields (data are shown in Fig. 4 for an applied field of 1 kOe). This type of behavior is similar to that found in inhomogeneous $YBa_2Cu_3O_{7-x}$. We can estimate $dH_{c2}/dT(T=T_c)$ from these data by considering the field dependence of the upper part of the transition near 75 K. We find this to be about 4 T/K.

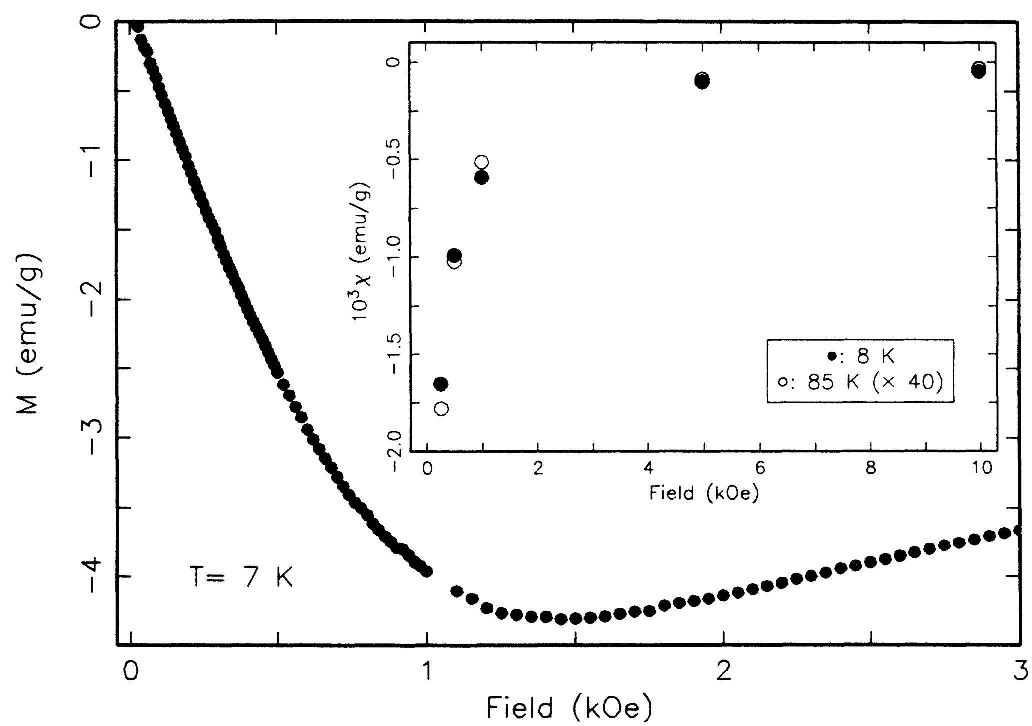

FIG. 3. Magnetization vs field for the same sample shown in Fig. 1 at 7 K, after cooling the sample from temperatures above 120 K in a field of $\simeq 10$ Oe. In the inset, the mass susceptibility is plotted vs applied field for fields up to 10 kOe. These data correspond to those in Fig. 2 and were taken by sequentially cooling the sample in various applied fields.

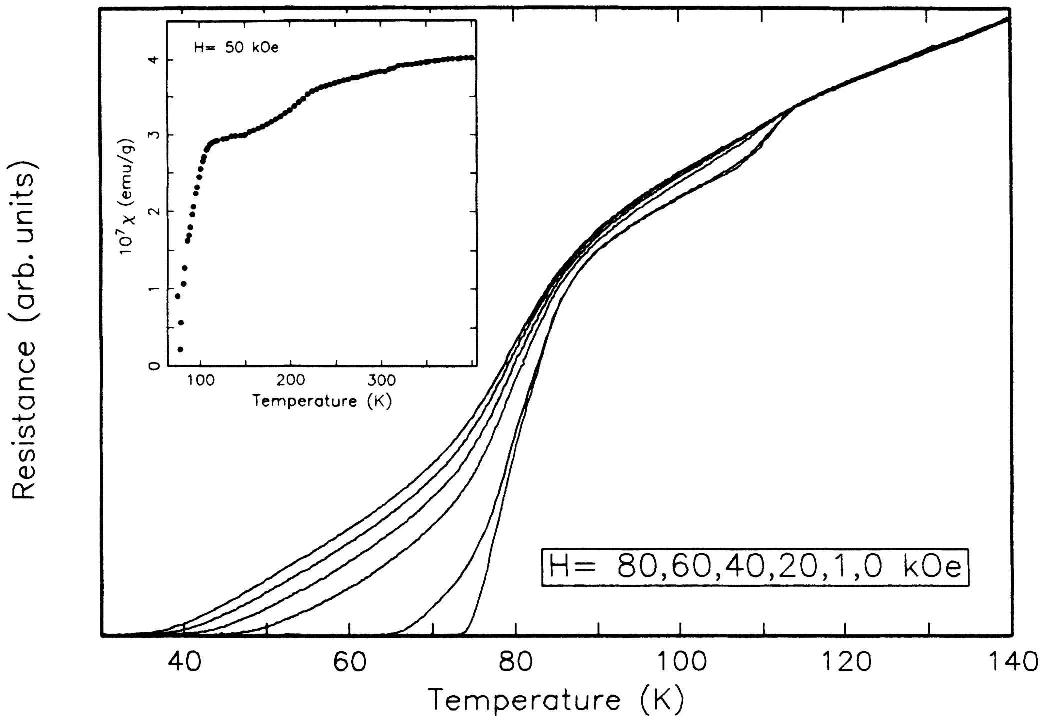

FIG. 4. Resistance vs temperature curves for various magnetic fields (0, 1, 20, 40, 60, and 80 kOe) for a sample of composition $Bi_{1.7}Sr_{1.3}Ca_2Cu_3O_x$. The magnetic field was applied perpendicular to the current through the sample. The inset shows the magnetic susceptibility of the same sample for temperatures in the range 80 to 400 K for an applied magnetic field of 50 kOe.

Since these values of H_{c1} and $dH_{c2}/dT(T=T_c)$ are very similar to those found in the $RBa_2Cu_3O_{7-x}$ family of materials,[10,11] similarly small values of the superconducting coherence length ξ are found using the Ginsberg-Landau-Abrikosov-Gor'kov (GLAG) equations.[12] The onset of the transition at 115 K is very little affected by the magnetic field, although the anomaly is largely washed out for fields above 20 kOe.

The inset to Fig. 4 shows the normal-state susceptibility versus temperature curve. These data indicate an anomaly near 220 K, which corresponds to CuO.[13] After correcting the data for this contribution, the susceptibility is approximately independent of temperature and has a value very similar to that for high-quality $YBa_2Cu_3O_{7-x}$ samples. For the Bi-Sr-Ca-Cu oxide system there seem to be no secondary phases with large Curie susceptibilities in contrast to the $YBa_2Cu_3O_{7-x}$ family for which the magnetic susceptibility is usually dominated by such phases.[13]

One possible origin of the superconducting behavior above 80 K extending to 115 K is that the region is a precursor fluctuation regime to the establishment of bulk superconductivity below 80 K. Our data show that this is clearly not the case. First, we observe two very sharp and independent diamagnetic onset cusps as a function of temperature. Second, the size of the diamagnetic susceptibility in this region is much larger than that expected for fluctuation-induced superconductivity; and finally, fluctuations are usually suppressed by small magnetic fields whereas we find a very similar field dependence of the diamagnetism in this temperature region to that at lower temperatures.

The substantial Meissner and shielding signals found in the 80–115-K temperature regions, namely 2.5% of the shielding observed at 6.5 K, are strong evidence for bulk superconductivity in an identifiable crystallographic phase. We find that both the thermopower and resistance remain finite in this temperature region which implies a distribution of this phase quite unlike that found in La_2CuO_4 material in which these properties vanish even when Meissner signals of about $\simeq 0.01\%$ of $-1/4\pi$ are found.[14] Indeed this behavior is quite consistent with the superconductivity being derived from a random distribution of unconnected three-dimensional regions which do not directly overlap. A promising candidate for such regions is the occasional occurrence of an extra Cu-O plane in addition to the two found between the Bi-O layers in the structure of the 75-K material, $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_x$, as seen in high-resolution transmission electron microscopy (TEM) images reported by Shaw *et al.*[4] and Veblen *et al.*[5] Depending on oxidation conditions, the local density of states in these excess Cu-O layers could be somewhat higher than in the bulk of the material, favoring a slightly increased transition temperature. Although only isolated excess layers have been reported, one would have to postulate the existence of extended regions of this type, since such isolated layers would not give rise to the substantial diamagnetic signals we have found.[15] These regions would thus comprise a new phase with a triple layer Cu-O perovskite structure. Since the low-T_c material discovered by Michel *et al.*[1] has a structure containing only one Cu-O plane between the BiO layers[6] this would make a pleasing progression of increasing transition temperatures with the increased size of the Cu-O network. It remains to be seen whether these domains containing additional perovskite planes can be grown as separate phases, or will remain as extrinsic defects in the host double-layer structure.

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