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Susceptibility Measurements Support High-T_c Superconductivity in the Ba-La-Cu-O System.

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Abstract. – The magnetic susceptibility of ceramic samples in the metallic BaLaCuO system has been measured as a function of temperature. This system had earlier shown characteristic sharp drops in resistivity at low temperatures. It is found that, for small magnetic fields of less than 0.1 T, the samples become diamagnetic at somewhat lower temperatures than the resistivity drop. The highest-temperature diamagnetic shift occurs at (33 ± 2) K, and may be related to shielding currents at the onset of percolative superconductivity. The diamagnetic susceptibility can be suppressed with external fields of 1 to 5 T.

In a recent search for high-T_c superconductivity, BEDNORZ and MÜLLER [1] reported resistivity measurements in the BaLaCuO system. This system was chosen because it exhibits a number of phases with mixed-valent copper constituents which exhibit itinerant electronic states between non–Jahn-Teller (JT) Cu^{3+} and JT Cu^{2+} ions. The existence of Jahn-Teller polarons in conducting crystals was postulated theoretically by HOECK *et al.* [2]. In general, polarons have large electron-phonon interactions, and therefore are favourable to the occurrence of high-T_c superconductivity [3].

Upon cooling BaLaCuO samples, first a linear metallike decrease in resistivity is measured, followed by an approximately logarithmic increase which was interpreted as the beginning of localization [1]. On further cooling samples of certain compositions and heat treatments, an abrupt decrease by up to three orders of magnitude is observed, reminiscent of the onset of percolative superconductivity. Possible 2D superconductivity fluctuations might also be present [1], because one of the three phases in the system is of the layerlike K_2NiF_4 type, *i.e.* it has the $La_{2-x}Ba_xCuO_{4-y}$ composition with $1 \gg x$, $y \geqslant 0$. The other two phases present are the nonconducting CuO and a nearly-cubic perovskite compound. To

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corroborate the existence of superconductivity, the susceptibility of BaLaCuO samples with various compositions and preparation histories was measured. It was expected that below T_c, grains coupled by Josephson junctions or the proximity effect might yield diamagnetic shielding currents and thus cause a change from Pauli paramagnetic to diamagnetic susceptibility [4]. The experiments described below have indeed borne out this property. A change of sign in susceptibility occurs slightly below the onset of the resistivity drop for all samples showing a drop.

The preparation of our oxygen-deficient compounds was detailed earlier [1]. In that case, the (La, Ba):Cu ratio in the starting composition was adjusted to be 1:1. Recently, our preparations have been extended to a series with (La, Ba):Cu ratios of 2:1, which is the composition of one of the three phases occurring in the original 1:1 series, namely, La_2CuO_4:Ba. Samples with varying BaO contents x were measured in the two series. Figures 1 and 2 display the resistivity of three typical representatives. The first with

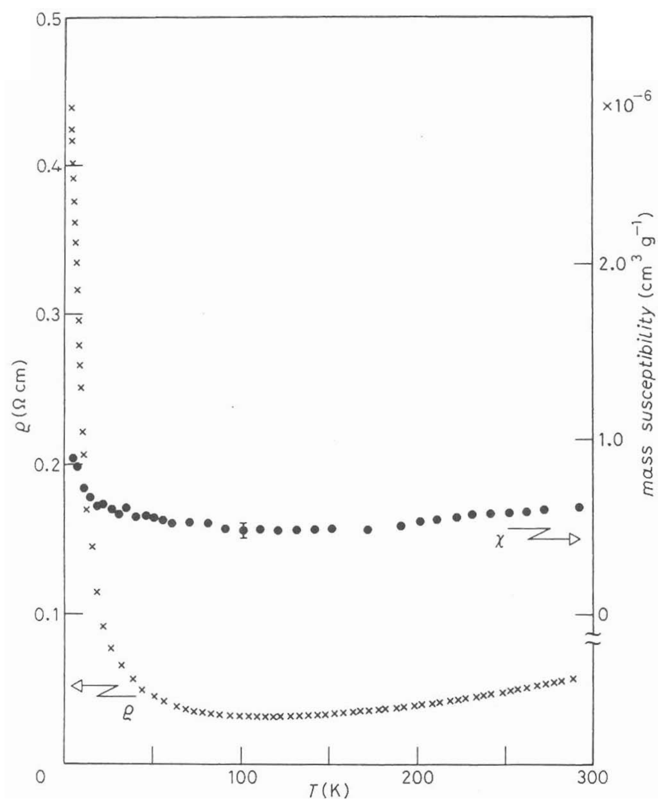

Fig. 1. – Temperature dependence of resistivity (×) and mass susceptibility (●) of sample 1.

nominal $x = 0.06$ and 1:1 clearly shows the onset to a localization transition. The second with $x = 0.6$ at 2:1 has a resistivity drop starting at 26 K, and in the third, $x = 0.15$ and 1:1, the drop occurs at the very high temperature of $T = 35$ K (fig. 2). Table I summarizes the details of the composition and firing temperatures of the three samples. A higher annealing temperature is allowed in the 2:1 series because in the absence of excess CuO, the melting point of these mixtures is increased.

The susceptibility of the samples was measured with a newly-installed BTI (Biomagnetic Technology Inc.) variable-temperature susceptometer VTS 905. Sample weights ranged

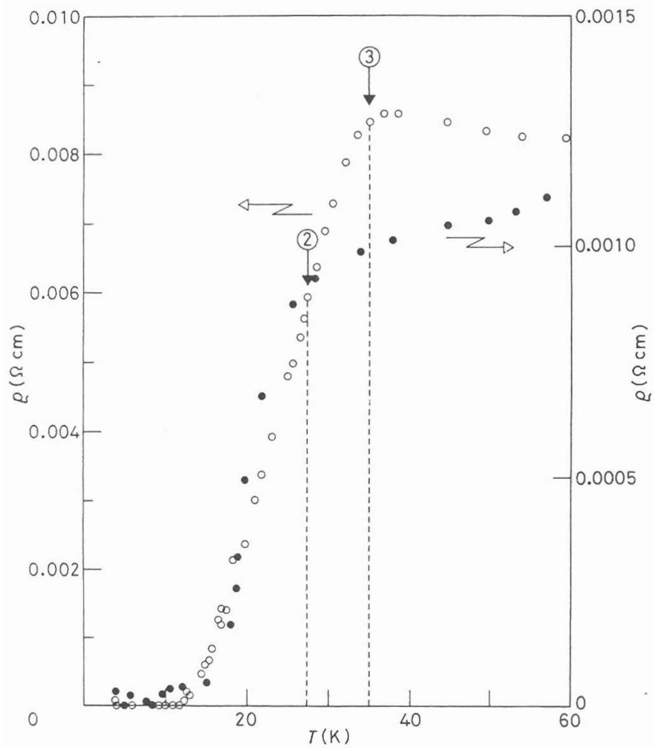

Fig. 2. – Low-temperature resistivity of samples 2 (●) and 3 (○). The onset of the resistivity drop is marked by vertical arrows. Temperature determined with a calibrated silicon diode sensor (DT-500, Lake Shore Cryotronics, Inc.).

TABLE I. – *Chemical composition, firing conditions, and sample weight for susceptibility measurements.*

Sample	(La, Ba) : Cu	Nominal composition Ba/La	Chemical analysis concentration Ba	Firing temperature (°C)	Sample weight χ-measurements (g)
1	1 : 1	0.06/0.94	0.01	900	0.355
2	2 : 1	0.6/1.4	0.12	1300	0.164
3	1 : 1	0.15/0.85	0.05	900	0.330

between 0.16 and 0.36 gram, see table I. Figure 1 displays the susceptibility of sample 1, and fig. 3 those of samples 2 and 3, all measured at 0.03 T. Each of them shows Pauli paramagnetic susceptibility at higher temperatures. In sample 1, with no drop in resistivity, this metallic susceptibility persists towards 20 K with Curie-Weiss enhancement starting there. However, samples 2 and 3 exhibit changes of χ to diamagnetism on cooling. This occurs several degrees below the onset of the resistivity drop as indicated by arrows in fig. 2 and 3. When the measuring magnetic field is increased, the diamagnetism is progressively reduced. Figure 4 reproduces such an experiment for sample 2. The inset gives the diamagnetic quenching at $T = 10$ K.

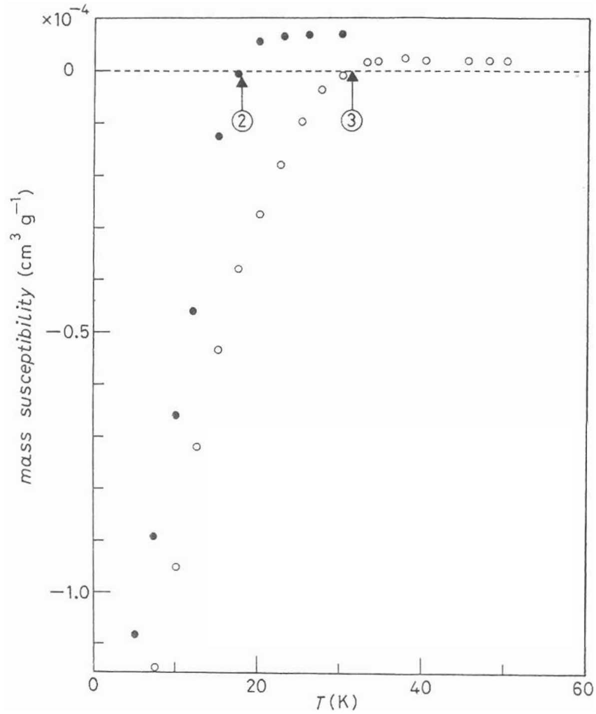

Fig. 3. – Low-temperature susceptibility of samples 2 (●) and 3 (○). Arrows indicate the temperature of the paramagnetic-to-diamagnetic transition. Temperature determined with a Rh/Fe thermometer calibrated *in situ* against Pt and Ge standard thermometers.

The behaviour of sample 1 is very remarkable in itself. The resistivity increases over an order of magnitude from 100 K down to 4.2 K, *i.e.* localization sets in, possibly owing to Jahn-Teller polarons [3]. The susceptibility is nearly constant and Pauli-like positive in the range 100 to 20 K. This is what ANDERSON predicted to occur for quasi-localized, weakly correlated $(U \simeq 0)\, s = 1/2$ particles in disordered solids, and termed a Fermi glass [5]. First evidence of a Fermi glass resulted from electron spin resonance in the H-doped CaV_2O_6 whose conductivity followed Mott's law of variable range hopping for random systems [6]. In the present case, the temperature-independent susceptibility is followed in the same range as in CaV_2O_6:H. The Curie-Weiss behaviour at low temperature can originate from localized spins as in the $Li_{1+x}Ti_{2-x}O_4$ spinel system [7]. Of course, it is important to well characterize the ceramic samples under study. This has been done recently with X-ray powder diffractometry by BEDNORZ *et al.* [8]. The three phases in the 1:1 series are the nonconducting CuO, the La_2CuO_4:Ba, and $LaCuO_{3-y}$:Ba. The latter two, the only ones to occur in the 2:1 series, are metallic conductors at high temperatures in the absence of Ba. $LaCuO_{3-y}$ is a metal like $LaNiO_3$ [9], and so is La_2CuO_{4-y} [10]. The presence of the latter phases has also been confirmed by X-ray single-crystal precession measurements [8]. Obviously, random doping with Ba^{2+} causes localization in at least one metallic phase.

The onset of diamagnetism or its absence is systematic with respect to the resistivity behaviour, as fig. 1, 2 and 3 demonstrate. This is what one will expect if superconductivity with shielding currents exists. The statistical distribution of grain sizes is not known, nor is a possible variation in T_c's. The diamagnetic shift starts *below* what presumably is the highest superconducting T_c in a sample. Theories [4] on percolative superconductors yield such a behaviour. The diamagnetism in the superconducting layer compounds of $TaSe_3$ and

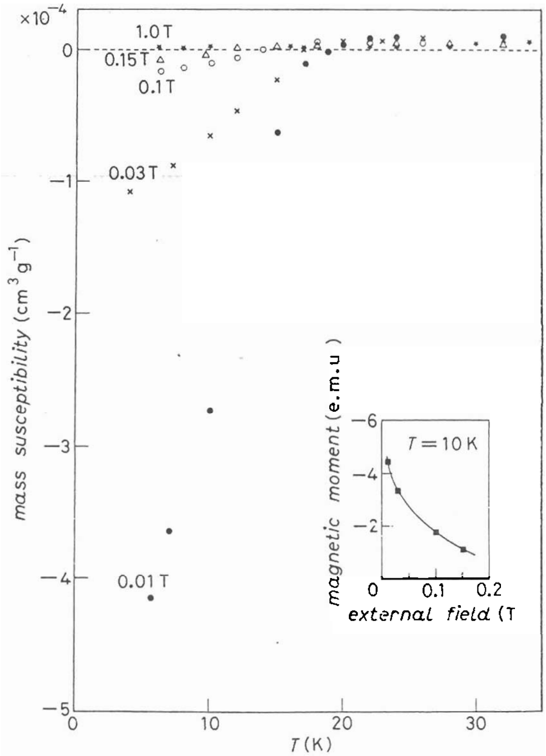

Fig. 4. – Low-temperature susceptibility of sample 2 recorded for different external magnetic fields. The inset shows the field dependence of the magnetic moment at 10 K (sample weight at 0.164 g).

$NbSe_3$ is qualitatively similar to our observations, but occurs quantitatively at quite different temperatures and fields [11]. It results from superconducting loops in the percolating network, and has been the subject of calculations where the diamagnetic χ is predicted to diverge at p_c as $-\chi = A[p_c - p/p_c]^{-b}$ with the most recent results of $b = 1.29$ in two, and $b = 0.34$ in three dimensions [4]. Therefore, $-\chi$ in principle allows determining the dimensionality of a system. In our measurements, $-\chi(T)$ is rounded at the onset. In the limit $p \simeq 0$, $-\chi = a_4 p^4 + a_6 p^6$ [4] theoretically, but a probable reason can also be a distribution in T_c's of the various grains, owing to an inhomogeneous Ba content. This requires a folding of the known analytic form of $-\chi(T)$ for a given T_c with the probability of different T_c's. More homogeneous samples may be obtained in the future. Although neither of these efforts has been carried out, the very fact of diamagnetism considerably supports the existence of superconductivity. This diamagnetism can be suppressed by application of high external magnetic fields. The Josephson or proximity junctions then become normal, and therefore interrupt the supercurrents. The result of fig. 4 gives evidence for this. From the inset, one sees that there is no peak in the susceptibility as it is found at H_{c1} in a single crystal, which is not expected to occur here, either.

The other two known oxide superconductors, the $Li_{1+x}Ti_{2-x}O_4$ spinel [7, 12] and the $BaPb_{1-x}Bi_xO_{3-y}$ perovskite [13], have T_c's near 11 and 13 K, respectively, quite lower than those probably found in the BaLaCuO. In the Li-Ti spinel, quite a clear Meissner effect, as in single crystals, has been reported for very small fields. A weak Meissner effect has also been measured on ceramic samples of $BaPb_{1-x}Bi_xO_{3-y}$ [14]. In our case, the diamagnetic shift is present, and reflects, as discussed above, the percolative character in our samples. From the onset in sample 3, this compound would become superconducting at (33 ± 2) K.

The correlation between the onset of diamagnetic shifts and drop in resistivity in all BaLaCuO samples measured considerably increases the likelihood for the occurrence of superconductivity. If true, it is the system with the highest T_c's reported in any solid. The phase in which the probable superconductivity occurs is now identified as La_2CuO_{4-y} : Ba [8] and an effort to grow single crystals is underway. Specific-heat measurements presently planned on our ceramic samples may further confirm what the present work indicates.

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Additional remark.

After submission of the present manuscript, we became aware of the work in the Nb-Ge-Al-O system by T. OGUSHI and Y. OSONO, which shows features of high-T_c superconductivity [*Appl. Phys. Lett.*, 48 (1986) 1167].

Concerning the BaLaCuO system, an article appeared in *Asahi Shinbun, International Satellite Edition*, November 28, 1986, reporting efforts of Prof. S. TANAKA's group in the Department of Applied Physics, at the Faculty of Engineering, University of Tokyo, which in November confirmed a diamagnetic susceptibility in the 30 K range.

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Note added after acceptance

A detailed powder x-ray analysis combined with susceptibility measurements as in Fig. 3 shows that the phase becoming superconducting is the La_2CuO_4 layer-like oxide mentioned in the text. This phase has K_2NiF_4 structure [8], agreeing with a recent study by H. TAKAGI *et al.* [15]. This group also confirmed later, but independently, the diamagnetism with susceptibility measurements in their samples prepared by reacting the oxides. The onsets observed were in the same temperature range as in our case [16]. Our x-ray study was also conducted as a function of Ba content at 300 K, the La_2CuO_4 undergoing an orthorhombic-to-tetragonal structural phase transition (SPT) for higher Ba concentrations. It appears that this orthorhombic-to-tetragonal SPT is related to the high T_c superconductivity because it occurs near the Ba concentration where the highest onsets are observed. This view is supported by doping our La_2CuO_4 also with Sr^{2+} and Ca^{2+} where the same relationship between T_c and SPT on concentration of alkaline-earth ions was found [8].

In our investigations, the Sr^{2+}-containing samples showed the sharpest onsets of superconductivity and largest diamagnetism [17]. Our results on alkaline-earth doping prove the electronic origin of the superconductive enhancement, because the ionic radius of Sr^{2+} is nearly the same as that of La^{3+}, $r = 1.14$ Å, for which it presumably substitutes. The radius of Ba^{2+} is 0.22 Å larger, and the one of Ca^{2+} 0.15 Å smaller than that of La^{3+}. Thus, these two ions produce local stresses. The alkaline-earth doping creates Cu^{3+} ions with no e_g Jahn-Teller orbitals. Therefore, the absence of these J.-T. orbitals, i.e., J.-T. holes, near the Fermi energy probably plays an important role for the T_c enhancement as investigated theoretically [18].

The diamagnetism in our Sr^{2+}-doped La_2CuO_4 ceramics although being enhanced compared to Ba^{2+} and Ca^{2+}, is lower than that found by other groups [16, 19]. This results partially from different, applied probing magnetic fields, which in our case was 300 Oe, whereas it was presumably lower in other laboratories. For lower probing fields, the susceptibility χ is considerably enhanced as shown in the inset of Fig. 4. This is expected theoretically [20] in a superconductive glass. MÜLLER *et al.* [21] most recently proved the existence of such a superconductive glass state in La_2CuO_{4-y} : Ba from measurements of $\chi(T)$ and m(T) in zero-field and nonzero-field cooled states with the presence of metastability. Such a superconductive glass behavior is less manifest in the Sr samples with sharper onsets.

In the two-phase ceramics, the superconductivity is first enhanced by reduction because of the conversion of the perovskite $LaCuO_3$ to the La_2CuO_4 phase. However, for single-phase preparation, longer reduction times *destroy* the superconductivity, and a behavior like sample 1 of Fig. 1 is found. CHU's group at Houston University hopes to obtain onsets above 50 K under hydrostatic pressure [22]. If this is realized, then still higher T_c's may become possible in the future.