

Magnetic and electronic properties of M -Ba-Cu-O ($M = Y, Er, Eu$)

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Various high- T_c superconductors of the La-(Ba,Sr)-Cu-O and the M -Ba-Cu-O systems with $M = Y, Er$, and Eu have been prepared by the solid-state reaction method. Single-phase samples with no additional diffraction peaks as verified by x-ray diffraction (XRD) measurements have been obtained. Measurements of the electrical resistivity and of the magnetization showed sharp superconducting transitions with a width of 1 K. The measurements of the magnetic susceptibility have been extended above room temperature up to 770 K. There is clear evidence for the formation of a magnetic moment in all M -Ba-Cu-O samples. Monochromated x-ray photoelectron spectroscopy (MXPS) valence band and x-ray photoelectron spectroscopy (XPS) core level spectra have been measured on various samples at room temperature and at liquid nitrogen temperature.

I. INTRODUCTION

Since the first publication by Bednorz and Müller¹ on the new high- T_c superconductors based on RE, Y-Ba(Sr)-Cu-oxides,^{2,3} this field has developed very rapidly by exploring new characteristics like high critical current densities.⁴ However, there is a need to understand the physics of these oxides; therefore it is our aim to study a variety of physical properties on these materials. We extend the field by applying our techniques to the new superconductors since we have longstanding experience in using various experimental analyses, such as scanning tunneling microscopy (STM) and rapid quenching. In the present work we report, as a first step, on the preparation of the oxides, the characterization by XRD, the electrical resistivity measurements, the magnetic properties, and the use of photoelectron spectroscopy. The studies by STM and rapid quenching have begun to show interesting results but are still under way.

II. EXPERIMENTS AND RESULTS

The M Ba₂Cu₃O_{7-x} samples were prepared by the solid-state reaction method with appropriate mixtures of starting powders of M_2O_3 , BaCO₃, and CuO. The mixtures were treated in a fashion similar to that already described in the literature.^{2,3,5} Table I gives a detailed listing of the sintering temperatures (with an accuracy of ± 10 K) and the annealing times used to obtain the superconducting samples. In contrast to the La-(Ba,Sr)-Cu oxides, the M -Ba-Cu oxides were fired only in oxygen flow. No decomposition was observed up to the maximum annealing temperatures indicated. It turned out that the M -Ba-Cu-O samples had to be cooled down slowly in oxygen flow to prevent them from losing their superconducting properties.

The electrical resistivity of the samples has been measured by a standard ac four-probe technique using a frequency of 983 Hz. The amplitude of the current through the samples was in the milliamper range. The temperature was measured with a Pt resistor above 77 K and with a Ge resistor below 77 K. Several of the measured resistivity versus temperature plots are summarized in Fig. 1.

In La-Sr-Cu-O compounds the onset of superconductivity is found at 36 K, and zero resistance is reached at 33.5 K. The single-phase M Ba₂Cu₃O_{7-x} samples showed onsets and midpoints of the superconducting transition above 90 K, with the exception of YBa₂Cu₃O_{7-x}, for which the midpoint was found around 81 K. The multiphase Y_{1.2}Ba_{0.8}Cu₃O_x sample becomes superconducting at a temperature that lies 5 K higher than in single-phase YBa₂Cu₃O_{7-x}. The width of transition of our samples is quite small, about 1 K. Only the Er-Ba-Cu-O sample showed a width of several degrees. This is caused by a tail in the lower part of the

TABLE I. Sintering conditions for various oxide superconductors.

Sample	T [°C]	Time [h]	Oxygen treatment	T_c^{onset} [K]
La _{1.85} Ba _{0.12} CuO _x	990	36	...	33
La _{1.8} Sr _{0.14} CuO _x	990	116	...	35
	900	+ 5.5	x	36
Y _{1.2} Ba _{0.8} CuO _x	1050	24	...	86.9
YBa ₂ Cu ₃ O _{7-x}	990	46	x	81.6
ErBa ₂ Cu ₃ O _{7-x}	950	69	x	91.7
EuBa ₂ Cu ₃ O _{7-x}	990	24	x	94.2
Y _{0.1} Eu _{0.9} Ba ₂ Cu ₃ O _{7-x}	990	46	x	86.9

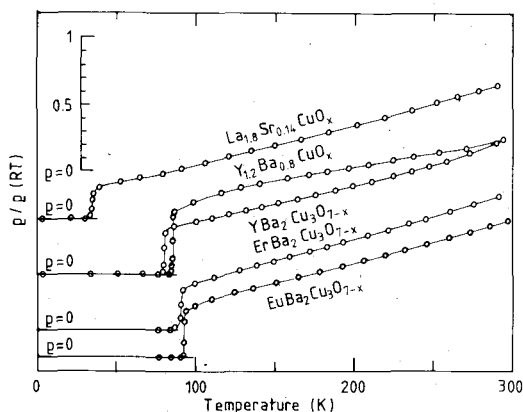


FIG. 1. Typical resistivity curves for various oxide superconductors.

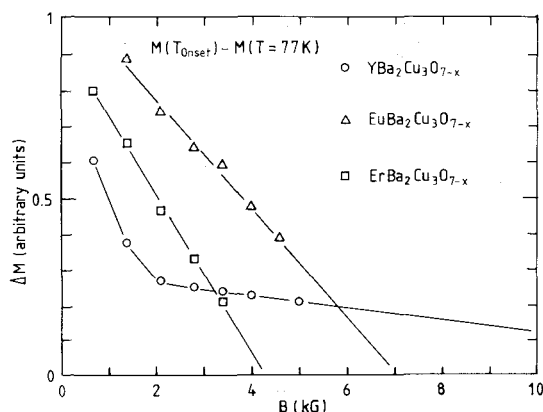


FIG. 2. Difference in the magnetization between onset temperature and 77 K as a function of the applied magnetic field.

transition. The absolute resistance of our single-phase $M\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ -type superconductors is of the order of $10^4 \mu\Omega \text{ cm}$ at room temperature. The resistance of $\text{Y}_{1.2}\text{Ba}_{0.8}\text{CuO}_x$ is approximately 1000 times larger.

The structures and phases of our samples were investigated by x-ray diffraction in the standard reflection geometry using monochromated $\text{Cu } K_\alpha$ radiation. The spectra showed that our $M\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ samples were single phased. The structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is of the same type as that found by Capponi *et al.*⁶ and is not affected by the substitution of Y by Er or Eu. We noticed a preferred orientation of the (001) planes parallel to the sample surface in $\text{ErBa}_2\text{Cu}_3\text{O}_{7-x}$.

The magnetic properties of our superconducting samples were investigated below room temperature with a vibrating sample magnetometer. A sharp drop from the paramagnetic into the diamagnetic state was observed at the normal to superconducting state transition. The measurements show that the diamagnetism is lowered as the magnetic field is increased. For $\text{ErBa}_2\text{Cu}_3\text{O}_{7-x}$ the drop in magnetization was not strong enough even to reach diamagnetism as soon as the field exceeded 0.2 T. This is due to the strong paramagnetism occurring in this material. The difference in magnetization between the onset temperature of superconductivity and 77 K is plotted versus magnetic field in Fig. 2. The oxides containing Er and Eu show a linear decrease of the superconductivity signal with increasing magnetic field, whereas for the Y sample two different slopes are observed, shifting the upper critical field to higher values.

The magnetic behavior of the La-(Ba,Sr)-Cu-O and *M*-Ba-Cu-O samples was also investigated above room temperature up to 770 K using a very sensitive Faraday balance working in air. The results are shown in Fig. 3. The oxygen content was taken to be about 7 for *M*Ba₂Cu₃ oxides⁷ and 4 for La-(Ba,Sr)-Cu oxides.² For $\text{La}_{1.85}\text{Ba}_{0.12}\text{CuO}_x$ we found that the susceptibility

first increased with increasing temperature, then showed a maximum at about 500 K and became smaller upon further heating. The decrease above 500 K is due to changes occurring in the sample and is not reproduced upon cooling. The susceptibility of $\text{La}_{1.8}\text{Sr}_{0.14}\text{CuO}_x$ is almost temperature independent with the exception of a small maximum at 500 K. For the *M*-Ba-Cu-O samples a Curie-Weiss-like behavior was observed for all the investigated compositions demonstrating the existence of magnetic moments in these materials. The susceptibilities of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and

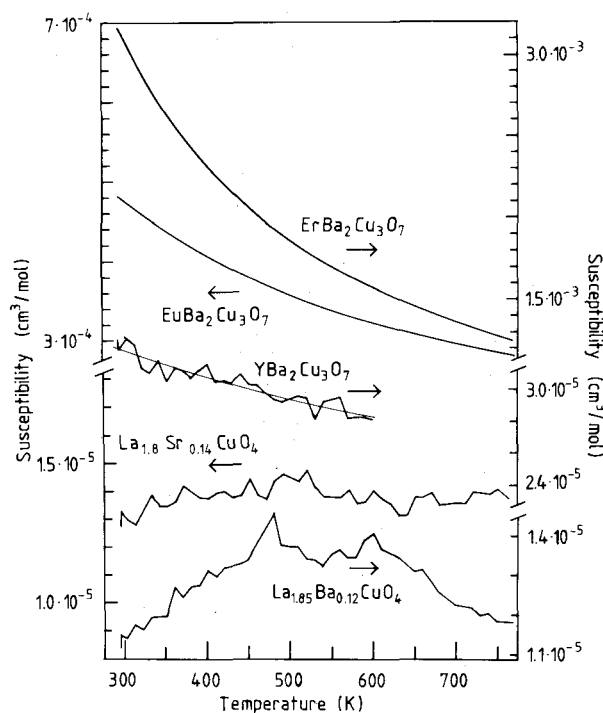


FIG. 3. Magnetic susceptibility above room temperature for various oxide superconductors.

ErBa₂Cu₃O_{7-x} were not affected by the heating. Also, *T_c* remained above 77 K for these two materials, indicating only small changes in the oxygen content of the samples. However, in EuBa₂Cu₃O_{7-x} superconductivity above liquid nitrogen temperature was lost during heating, and the susceptibility became slightly smaller. At room temperature the susceptibility curve of YBa₂Cu₃O_{7-x} joins the low-temperature values given by A. Junod *et al.*,⁸ whereas it is smaller by more than a factor of 2 compared to data published by Cava *et al.*⁷ This discrepancy is not yet understood. The susceptibility of EuBa₂Cu₃O_{7-x} is in good agreement with a curve published by Murphy *et al.*⁹; here the small difference can be explained by slightly differing preparation conditions.

Single-phase samples of La_{1.85}Ba_{0.12}CuO_x, YBa₂Cu₃O_{7-x}, and EuBa₂Cu₃O_{7-x} have also been investigated by x-ray photoelectron spectroscopy (XPS) and monochromated XPS (MXPS). Samples were carefully cleaned either by scraping *in situ* with a file or by scraping in N₂ flow and transferring them into the vacuum chamber immediately afterward. After cleaning, small shoulders occurring at the O 1s levels had disappeared, but small amounts of carbon could still be detected, probably due to absorption of CO and CO₂ gases at inner surfaces of these not completely dense samples.¹⁰ Figure 4 shows valence band spectra of La-Ba-Cu-O and Y-Ba-Cu-O taken at room temperature with monochromated Al K_α radiation. The spectra reveal broad features at binding energies of about 4 eV. Comparison with published data on the valence band structure of CuO¹¹ and recent calculations of the electronic bandstructure for La-Cu-O¹² show that this structure originates mainly from Cu 3*d* and O 2*p* electrons. These states almost determine the structure of the valence band. From our spectra we see that the density of states at the Fermi level (*E_f*) is quite small for both samples.

In Fig. 5 Cu 2*p*_{3/2} core levels for YBa₂Cu₃O_{7-x} are shown. They are identical to those obtained for Eu-Ba-

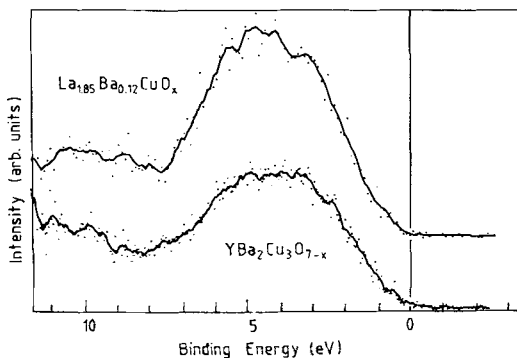


FIG. 4. The MXPS Al K_α valence bands of two different oxide superconductors at room temperature.

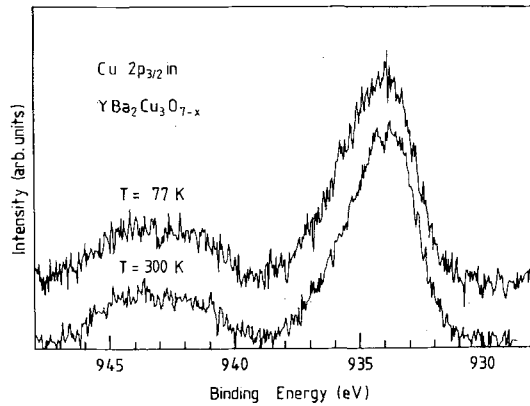


FIG. 5. The Cu 2*p*_{3/2} core levels of YBa₂Cu₃O_{7-x} measured at room temperature and at 77 K using Mg K_α radiation.

Cu-O and La-Ba-Cu-O. We observe that the core level shift with respect to metallic copper and the half width are nearly the same as in CuO.

The Cu 2*p* core levels show a pronounced satellite structure on the higher binding energy side. Such satellites are typical for paramagnetic copper ions.¹³ Here we find a small difference between superconducting oxides and CuO. The intensity of the satellite is slightly decreased in the superconductors, compared to CuO. Electron spectroscopy measurements taken at 77 K did not reveal dramatic changes in the spectra at all. Only a very small broadening of the Cu 2*p* core levels in Eu-Ba-Cu-O and Y-Ba-Cu-O was observed. Within the limit of our resolution of a few percent, we could not see indications for the existence of Cu³⁺ ions in the samples we investigated. This lack of Cu³⁺ ions has also been observed by Steiner *et al.*¹⁰

Figure 6 shows the Ba 3*d*_{5/2} core level at room temperature and at 77 K. We found that this level exhibits a shoulder at the lower binding energy side. The main peak is ascribed to BaO. The smaller peak, which gives

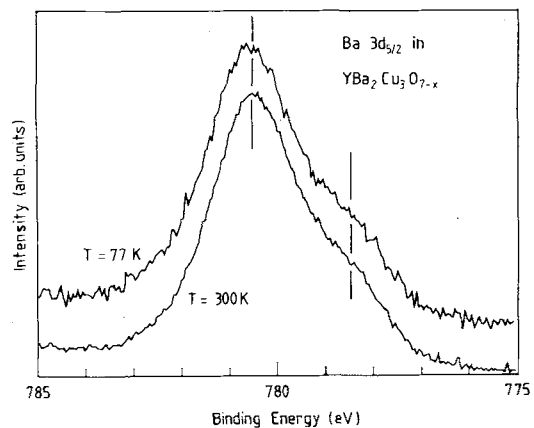


FIG. 6. The Ba 3*d*_{5/2} core levels of YBa₂Cu₃O_{7-x} measured at room temperature and at 77 K using Mg K_α radiation.

rise to the shoulder, is shifted in the direction of metallic Ba. From the determination of the structure of *M*-Ba-Cu-O we know that there are two Ba atoms per unit cell in Y-Ba-Cu-O and Eu-Ba-Cu-O. But as they are positioned at two equivalent sites, the shoulder of the $3d_{5/2}$ peak can not be explained by effects of different chemical environment. The shoulder can, however, be due to the oxygen vacancies near the Ba ions.

The spectra we have obtained for the Y, Eu, and La core levels do not differ from those expected for simple oxides. The oxygen 1s level is found to be split into two peaks. This splitting can be attributed to the inequivalent oxygen lattice sites existing in the unit cell.

III. CONCLUSIONS

In conclusion we can summarize the following observations for our high- T_c oxides: The width of the normal to superconducting state transition is as small as 1 K. The density of states at E_f is very small at room temperature. Although the core level spectra are not totally equivalent between the high- T_c oxides and CuO the spectra resemble those of CuO very much. We do not see Cu^{3+} ions. The occurring magnetic moments for the $M\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ samples make clear that for those materials magnetic moments in the normal state do not exclude the existence of superconductivity.

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