MAGNETISM, SPECIFIC HEAT, AND SURFACE TOPOGRAPHY OF OXIDE SUPERCONDUCTORS

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ABSTRACT

Samples of the composition $M Ba_2Cu_3O_{7-x}$ with M = Y, Eu, Er, and Gd have been prepared by the standard solid state reaction method. The magnetic susceptibility has been investigated above room temperature up to 1870 K in vacuum. Specific heat measurements have been performed with a differential scanning calorimeter (DSC) working at low temperatures in a differential mode using superconducting and non-superconducting samples. The surface topography of the high-T_c superconductors has been investigated at room temperature by scanning tunneling microscopy (STM).

INTRODUCTION

The discovery of a new class of materials showing superconductivity at temperatures above 30 K by J.G.Bednorz and K.A.Müller [1] has stimulated a worldwide competition in exploring their physical properties and possible applications. We contribute to the research of these new materials by applying our techniques where we have longstanding experience. In a previous work [2] we reported initial results including the preparation of the oxides, the characterization by X-ray diffraction, the electrical resistivity measurements, the magnetic properties above room temperature up to 770 K in air and results obtained by photoelectron spectroscopy. Here we present magnetic susceptibility measurements up to temperatures of 1870 K at which the oxide superconductors are already partially molten. Specific heat data measured for various high-T_c superconductors between 85 K and 110 K using differential scanning calorimetry are also presented. As far as we know, superconductivity transitions were observed for the first time by this method in the new materials. We also show our first results of surface investigations by scanning tunneling microscopy.

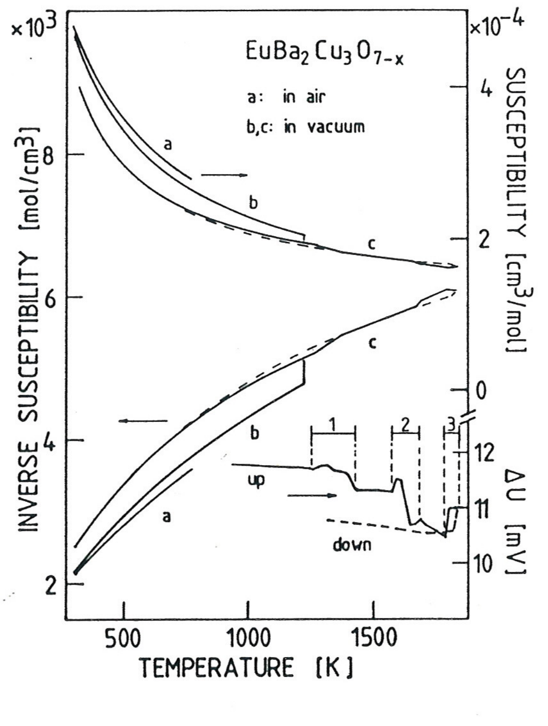

Fig. 1. The magnetic susceptibility of $EuBa_2Cu_3O_{7-x}$ ($x \sim 0.1$) above room temperature. solid line: heating; dashed line: cooling. Inset: Voltage applied to keep sample in balance as a function of temperature.

MAGNETIC PROPERTIES

The magnetic behavior of $M Ba_2Cu_3O_{7-x}$ has already been extensively investigated below room temperature both in the superconducting and normal states [3,4]. Here we present magnetic susceptibility data of these materials above room temperature up to 1870 K. The measurements were performed using the Faraday method.

The following topics can be

addressed: How is the susceptibility affected by different heating environments such as air or vacuum? Is there a visible change at the orthorhombic to tetragonal phase transition? Are the magnetic moments affected by the heating? What can we learn about melting from susceptibility measurements?

The magnetic susceptibility of $EuBa_2Cu_3O_{7-x}$ is shown in Fig. 1. The Curie-Weiss behavior known from low temperature measurements [5] is also observed above room temperature. It is evident that a small difference exists between the susceptibilities measured in air and in vacuum. In vacuum the susceptibility decreases more rapidly with increasing temperature. This indicates that the Pauli susceptibility and thus the density of states at the Fermi level are dependent on oxygen content. No change in susceptibility is observed at the orthorhombic to tetragonal phase transition. However, an unexpected decrease occurs around 1220 K, which is not reversible. After its completion, the Curie-Weiss behavior is still present. When the sample is heated up to 1870 K, three additional transitions occur which slightly affect the susceptibility. They can be better discerned by looking at the voltage ΔU necessary to keep the sample in balance. As ΔU is sensitive to changes in sample geometry, one can conclude that above 1220 K the material decomposes into different phases which may exhibit individual melting temperatures.

The magnetic susceptibility of $YBa_2Cu_3O_{7-x}$ shows a different behavior compared to $EuBa_2Cu_3O_{7-x}$ (Fig. 2). Here a clear change in slope is observed upon heating at the orthorhombic to tetragonal transition [6]. The strong decrease around 1220 K is also present in this compound. It is surprising that $YBa_2Cu_3O_{7-x}$ becomes diamagnetic at 1220 K and approaches a constant diamagnetic value upon further heating.

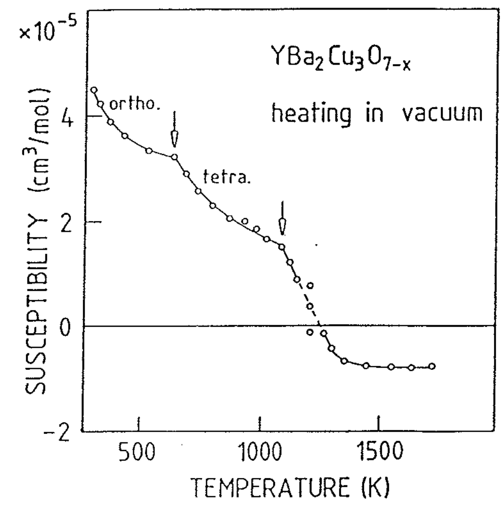

Fig. 2. The magnetic susceptibility of $YBa_2Cu_3O_{7-x}$ ($x \sim 0.1$) above room temperature.

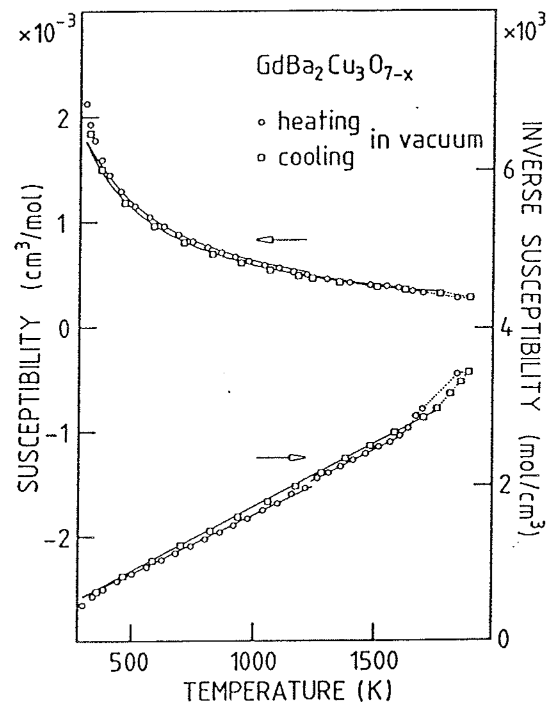

Fig. 3. The magnetic susceptibility of $GdBa_2Cu_3O_{7-x}$ ($x \sim 0.1$) above room temperature.

The susceptibility of $GdBa_2Cu_3O_{7-x}$ (Fig. 3) exhibits a Curie-Weiss like behavior up to high temperatures and shows no significant change at 1220 K.

SPECIFIC HEAT

Measurements of the specific heat were carried out in a conventional Perkin Elmer DSC-2. This provides direct access to the calorimetric properties of high-T_c oxides. In order to avoid thermal leaks at low temperatures, the whole sample holder was put in a Dewar, cooled to 77 K and flooded with pure Helium gas which was also precooled to liquid nitrogen temperature and passed through an air dryer. The temperature was calibrated using cyclopentane which shows three transitions between 120 K and 180 K. For the ordinate displacement calibration, gold and copper samples were used. All the measurements were performed with high reproducibility and, due to the differential measurement technique, provide an accurate determination of the electronic contribution to the specific heat. The DSC can be used to perform absolute specific heat measurements as well as differential measurements between superconducting and non-superconducting samples. In the differential mode the electronic contribution to the specific heat can be directly recorded. The non-superconducting samples were prepared by cutting a superconducting pellet into two pieces and destroying the superconductivity of one piece by further heat treatment. Both the superconducting and non-superconducting parts of the pellets gave exactly the same values for the specific heat above T_c.

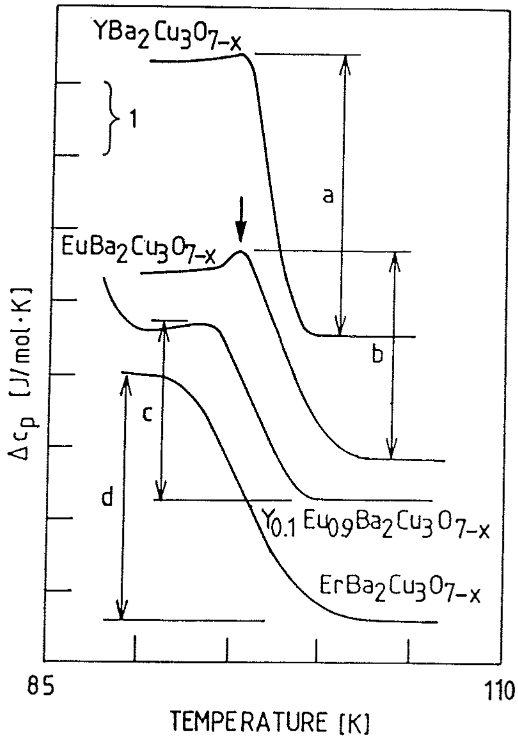

Fig. 4. Electronic specific heat of some oxide superconductors as a function of temperature. The values for $\Delta c_p/T_c$ are (in mJ/(K^2mol)): a: 37; b: 32; c: 32; d: 37.

The results obtained from the differential measurements are shown in Fig. 4. A clear step is observed at T_c for all the investigated concentrations. The step observed in $YBa_2Cu_3O_{7-x}$ is slightly smaller with respect to the values given in Ref. [7].

In the case of $EuBa_2Cu_3O_{7-x}$ an additional small peak can be seen at the lower temperature end of the superconductivity transition. At present we are looking for similar effects in the other samples by applying lower heating rates. In $Y_{0.1}Eu_{0.9}Ba_2Cu_3O_{7-x}$ we found evidence for a second superconductivity transition below 90 K.

SURFACE TOPOGRAPHY

It has already been pointed out that a detailed investigation of sample inhomogeneities in the new high-T_c superconductors is of particular importance for a better understanding of the superconductivity in these materials [8]. Therefore experimental techniques which can probe local properties of the samples are required.

Scanning tunneling microscopy offers the possibility to study local properties of a sample surface. This is a well known experimental technique for investigating superconducting materials. A large number of publications has already appeared [9-11] describing tunneling experiments performed with a STM at low temperatures where the STM tip and the surface of the high-T_c superconducting material are in contact. Although good local dI/dU versus U characteristics have been obtained [9-12], it was not possible so far to study local variations in the superconductivity of the high-T_c oxides by scanning the tip over the sample surface as it has already been demonstrated for other superconducting materials [13,14]. As a first step towards spatially resolved investigations of high-T_c superconductors by STM we have measured the surface topography as a function of the tunneling gap

Fig. 5. A Scanning electron microscopy (SEM) photograph of $EuBa_2Cu_3O_{7-x}$.

resistance at room temperature in air. Samples of $EuBa_2Cu_3O_{7-x}$ with T_c = 94 K were chosen for the STM measurements. The tunneling current I was held constant at 1 nA during the measurements. The tunneling gap resistance has been varied by changing the applied voltage U between tip and sample.

A tunneling gap resistance of about $10^9\ \Omega$ seems to be sufficiently high for getting reproducible topographic images with low noise scan traces. Reducing the tunneling gap resistance below $5 * 10^8\ \Omega$ results in difficulties to image the surface topography. We believe that a contact between tip and sample surface will then occur.

The topographic structures as imaged by STM on a nanometer scale agree well with similar topographic features as seen in electron micrographs of the same sample using secondary electrons (Fig. 5, Fig. 6). Both rounded and parallel structures are visible on top of the grains.

In Fig. 7 a 500 Å x 500 Å area of $EuBa_2Cu_3O_{7-x}$ is shown. The parallel structures which are about 150 Å apart might be related to the twinned, layered structure of the

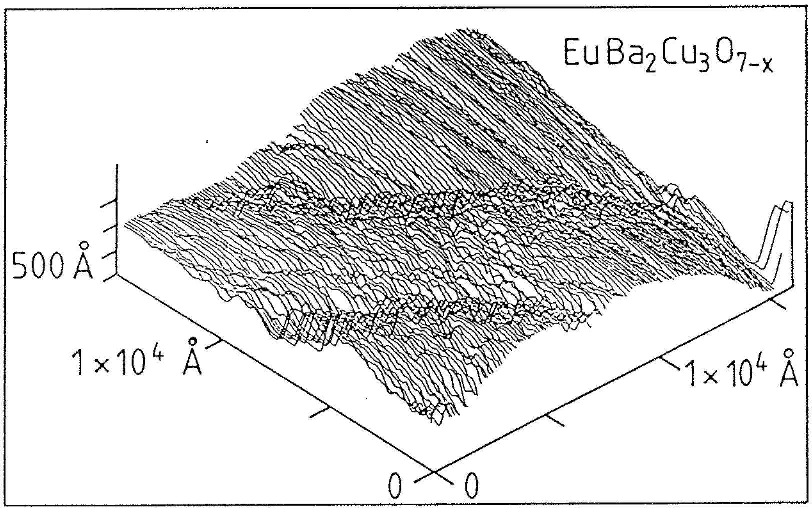

Fig. 6. Topographic STM image of a 15'000 Å x 15'000 Å area of $EuBa_2Cu_3O_{7-x}$ obtained with a tunneling current of 1 nA and a sample potential of -2.0 V.

high-T_c superconductors. The scan traces show alternating smooth and more irregular parts. The more irregular parts of the scan traces are probably related to less conducting "channels" within a single grain.

A STM topograph showing only a 100 Å x 100 Å surface area obtained with I = 1 nA and U = -1.0 V is shown in Fig. 8. In this image as well as in many other STM topographs we could detect steps being about 10 to 13 Å high. This agrees well with the known lattice constant along the c-axis of the material.

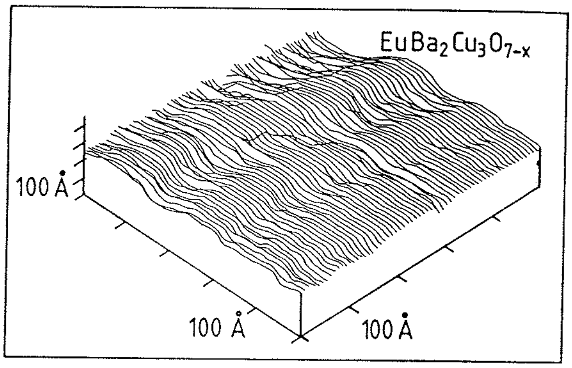

Fig. 7. Topographic STM image of a 500 Å x 500 Å area of a broken $EuBa_2Cu_3O_{7-x}$ sample surface obtained with a tunneling current of 1 nA and a sample potential of -1.0 V.

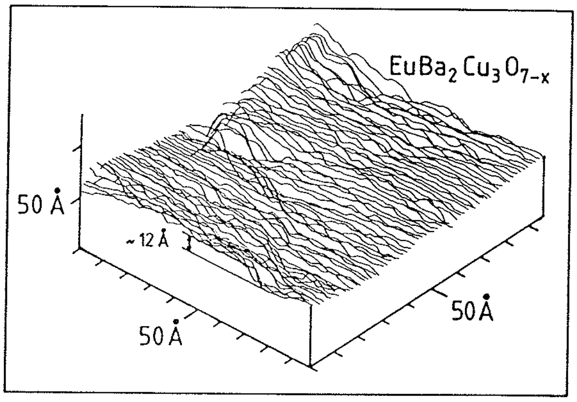

Fig. 8. Topographic STM image of a 100 Å x 100 Å surface area of $EuBa_2Cu_3O_{7-x}$ obtained with a tunneling current of 1 nA and a sample potential of -1.0 V.

DISCUSSION AND CONCLUSIONS

The presented results lead to propose two independent mechanisms responsible for paramagnetism in the 90 K superconductors. The first mechanism, which is dominant in $YBa_2Cu_3O_{7-x}$, is sensitive to the crystalline structure and lost above 1220 K together with the tetragonal structure [6]. It may originate from magnetic Cu^{3+} ions present in the orthorhombic and tetragonal structures [15]. The second contribution is closely related to M^{3+} in $MBa_2Cu_3O_{7-x}$. The measurements on $EuBa_2Cu_3O_{7-x}$ suggest that in this compound both contributions are present.

An estimate of the coupling strength in $YBa_2Cu_3O_{7-x}$ can be made by comparing the presented specific heat data to our normal state magnetic susceptibility data measured in air [2]. From the susceptibility behavior between 300 K and 600 K we calculate a Pauli susceptibility of χ_p = 38 x 10^{-6} cm^3/mol (Θ is taken to be -11.3 K [4]; Corrections for ionic diamagnetism are applied [16]). This value corresponds to γ = 11.6 mJ/(K^2mol-Cu). Together with the value for the specific heat jump at T_c which is $\Delta c_p/T_c$ = 12.3 mJ/(K^2mol-Cu), we get $\beta = \Delta c_p/\gamma T_c$ = 1.1. The result for β is smaller than what one would expect for BCS theory (β = 1.43). However, this does not necessarily imply that $YBa_2Cu_3O_{7-x}$ is a weak coupling superconductor, since a recent theoretical work claims that even in the very strong coupling limit, small β values can be obtained [17].

Finally, we have also demonstrated that tunneling on the new materials is possible, if relatively large voltages are applied between tip and sample. It has turned out that the STM is capable of resolving steps of a few Å in these new materials, and it will hopefully be possible to see even smaller steps which correspond to the a and b axis in the unit cell. Future STM measurements on high-T_c superconductors are planned at low temperatures in order to study the spatial variation of the superconducting energy gap.

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