Paramagnetism and Superconductivity in Eu$_{0.7}$Sm$_{0.3}$Ba$_2$Cu$_3$O$_{7-\delta}$

V. Sandu,$^1$ S. Popa,$^1$ D. Di Gioacchino,$^2$ and P. Tripodi$^{2,3}$

Received 1 July 2004; accepted 17 August 2004

Magnetic properties of sintered Eu$_{0.7}$Sm$_{0.3}$Ba$_2$Cu$_3$O$_{7-\delta}$ were investigated both in dc and ac magnetic fields. The dc response reflects the interplay between the rare earth ion paramagnetic and the superconducting charge carrier subsystems, respectively. The harmonic susceptibilities exhibit special features: the second harmonic is anomalously high and the third harmonic in zero dc-field has reversed temperature dependence with respect to the theoretical models. The magnetic relaxation at low fields is monotonous and occurs as a two-stage relaxation, each stage obeying logarithmical time dependence with different rates. At high fields, the relaxation is nonmonotonous with a peak at intermediate time suggesting a temporary re-entrance of irreversibility when the flux-line density increases in the center of the sample because of the redistribution of the vortices toward that region.

KEY WORDS: Eu$_{0.7}$Sm$_{0.3}$Ba$_2$Cu$_3$O$_{7-\delta}$; magnetic susceptibility; magnetic relaxation; multiharmonic susceptibility.

1. INTRODUCTION

The compounds with more than one rare-earth element in the R site of RBa$_2$Cu$_3$O$_{7-\delta}$ are still the subject of an active interest due to the possibility of the interplay between the paramagnetic moments corresponding to different oxidation states and Cooper pair system.

The conduction band of RBa$_2$Cu$_3$O$_{7-\delta}$ is primarily composed of Cu$3d$ and O$2p$ orbitals [1], with a negligible small contribution of the R-ions to the Fermi level. Therefore, the magnetic ordering of the Cu ions is sensitive to the charge carrier density, whereas the R ions remain rather unaffected. Moreover, due to the large distance between R sites their coupling is small, hence, save the long range magnetic order set in only below 2 K [2,3]. At high temperature in an applied magnetic field, the R subsystem shows a paramagnetic response with a natural tendency of the R spins to align along the field. In contrast with the low temperature superconductors, there is no pair breaking in high-$T_c$ cuprates produced by the exchange interaction between the conduction electrons and the localized $f$-shell spins of the R ions. This fact is the result of the large separation between the conducting CuO$_2$ layers and the R ion relative to the small coherence length $\xi$ of Cooper pairs in superconducting cuprates and very low $f$-shell radius of the R ions. Therefore, the R ions do not affect the superconductivity and their magnetic state is controlled barely by the crystalline electric field.

In an applied magnetic field the copper and rare-earth ions behaves very differently. Due to its particular interaction with the mobile holes from CuO$_2$ layers [4], the Cu ion subsystem, at optimally doping, is practically insensitive to moderately applied fields and only the R$^{3+}$ subsystem is responsible for paramagnetism. Although at the scale $\xi$ the effect of the R ions is less effective, at longer scale, of order

---

1National Institute of Materials Physics, Bucharest-Magurele, POB-MG-7, R-76900 Romania.
2INFN-LNF, National Laboratory of Frascati, Via E. Fermi 40, 00044 Frascati, Italy.
4Present address: Department of Physics, Kent State University, Kent, OH 44242.
of magnetic penetration length $\lambda_L$ it become important. Therefore, the interest in the investigation of the mixed state in systems with paramagnetism and superconductivity coexist [5–9]. A complete picture of the behavior of these systems in magnetic field must involve both dc and ac measurements. Concerning the latter, a special attention was paid in the last decade to the high harmonics of the magnetic susceptibility, considered as a valuable source of information. However, by our knowledge, there is no report concerning the multiharmonic response of a superconducting $RBA_2Cu_3O_{7-x}$ with $R$ different of yttrium. Due to the sensitivity of the high harmonics to the field, we expect to find the fingerprint in their dependence on temperature and applied field.

In our investigation, we have chosen a combination between two $R$ ions, europium (Eu) and samarium (Sm) for the following reasons: (i) Eu$^{3+}$ and Sm$^{3+}$ have the closest ionic radii $r$ among all rare earth elements with $r_{\text{Sm}} - r_{\text{Eu}} = 0.013$ Å, therefore, no lattice distortions are expected when substituting each other; (ii) the multiplet structure of the electronic levels is comparable with thermal energy for both elements; (iii) both elements can substitute barium and, subsequently, create the same type of disorder, and; (iv) the increasing magnetic moment of Sm$^{3+}$ at low temperature [10] compensates the saturation of the Eu$^{3+}$ [11]. The response of this system was investigated both in dc and ac magnetic field.

First, we analyze the dc behavior, which is better understood, and use the same as a reference for the multiharmonic ac data.

2. EXPERIMENTAL

Eu$_{0.7}$Sm$_{0.3}$Ba$_2$Cu$_3$O$_{7-\delta}$ polycrystalline samples were fabricated from reagent grade Eu$_2$O$_3$, Sm$_2$O$_3$, CuO, and BaCO$_3$ by solid-state reaction at 950°C for 24 h in flowing oxygen. The reacted samples were powdered and sifted. The powder was pressed into rectangular bar-like pellets, which were sintered, in flowing oxygen at 936°C for 16 h. Finally, the samples were slowly cooled for several hours down to the room temperature. The critical temperature is 90 K, as obtained from dc and ac susceptibility (see Figs. 3a and 6a below), and resistivity measurements (data not shown).

The structure, composition, and morphology of the samples were checked by scanning electron microscopy and exhibit good compactness with small pores and average grain sizes between 10 and 20 µm. The global electron dispersive spectroscopy (EDS) showed that all samples were essentially single phase with an average stoichiometry Eu$_{0.82}$Sm$_{0.23}$Ba$_{1.95}$Cu$_3$O$_{7-\delta}$. The slight excess of rare earth element and the deficit in barium could be the result of substitution of a small amount of Ba by R$^{2+}$ ions. The substitution should be possible because the ionic radius of both Sm$^{2+}$ and Eu$^{2+}$, 1.31 and 1.27 Å, respectively, are slightly lower than Ba$^{2+}$ radius (1.49 Å).

All the measurements reported later were made using standard techniques. The magnetic measurements, magnetization and dc-susceptibility, were measured using a Quantum Design SQUID magnetometer sweeping both temperature and magnetic field. The magnetization was measured from 2 to 86 K. The dc-susceptibility was measured both in zero-field-cooling (ZFC) regime, and field cooling (FC) regime, as the average on three successive measurements. The temperature was swept between 10 and 180 K at a constant magnetic field.

The ac-susceptibilities including the higher harmonics were measured with a homemade susceptometer [12] based on pick-up double coils surrounded by a driven coil. The sample was mounted on a sapphire holder inserted in one of the pick-up coils. The temperature was measured with a platinum thermometer (PT100) in a good thermal contact with the samples. The whole assembly was cooled in ZFC, in a thermally controlled He gas flow cryostat provided with an 8 T superconducting magnet. The measurements have been done on sweeping the temperature with a rate of 0.3 K/min up to a temperature greater than the zero field critical temperature of the samples (i.e. between 65 and 110 K). The ac driving magnetic field had an amplitude of $6 \times 10^4$ T at a frequency of $f = 1070$ Hz. The dc magnetic field was in the range from 0 to 1 T. The induced signal has been measured with a multi-harmonic EG&G lock-in amplifier. Both ac and dc fields were applied parallel to longest size of the sample.

Magnetic relaxation was measured in a dc-mode. A magnetic field higher than the full penetration field was applied at a constant temperature, and the time evolution of the magnetization was registered. After each set of data, the sample was warmed up above $T_c$ and then cooled down to the new temperature. The initial time $t = 0$ was defined as the time of the first data acquisition after the field was stabilized. Therefore, a certain time delay of about 50 s was necessary to set up before starting the measurement.