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MAGNETIC CHARACTERISTICS OF SUPERCONDUCTING $RBa_2Cu_3O_{6+y}$ (R = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb)

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Magnetic properties of superconducting $RBa_2Cu_3O_{6+y}$ compounds (R = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb) have been studied by using a SQUID magnetometer in the temperature range of 3 - 400 K. The susceptibility data of most of the samples can be well described by the Curie-Weiss relation. The rare earth ions exhibit essentially the full magnetic moments expected for the R^{3+} states, while the superconducting transition temperature remains in the 88 - 94 K range. The rare earth moments are generally found to interact antiferromagnetically. However, no magnetic order is observed in the temperature range studied. The Eu samples exhibited anomalous susceptibilities which we ascribe to the low-lying states of the ^7F_J manifold of Eu^{3+}.

ONE OF THE MOST REMARKABLE developments in condensed matter physics is the recent discovery of superconductivity in Y-Ba-Cu-O above 90 K [1, 2]. The single-phase compound responsible for the high T_c superconductivity was identified to be $YBa_2Cu_3O_{6+y}$ [3]. Surprisingly, superconductivity hardly deteriorates when Y is replaced by a rare earth, R, despite the large localized moments expected at the rare earth sites [4, 5]. In this work, we report the magnetic characteristics of superconducting $RBa_2Cu_3O_{6+y}$ compounds. We have found that the rare earth ions have large magnetic moments with values close to those expected for R^{3+} ions. The magnetic moments interact antiferromagnetically in most of the superconducting samples. However, no sign of magnetic ordering has been found. An anomalous behavior has been observed in the susceptibility of the Eu-containing compound; this can be accounted for by low-lying excited states.

The samples of $RBa_2Cu_3O_{6+y}$ where R = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb, were prepared under identical conditions by solid state reaction . Appropriate mixtures of R_2O_3, $BaCO_3$ and CuO were ground, pressed into pellets and sintered at 930 °C in an oxygen atmosphere. This process was repeated twice. X-ray diffraction showed that the materials are single phase, having the same structure as that of $YBa_2Cu_3O_{6+y}$ [3]. Resistance measurements were made using a four-wire method with both forward and reverse currents to eliminate any thermal voltage. Magnetic measurements were performed by using a SQUID magnetometer. In the superconducting state, diamagnetic signals were measured in an external field of about 10 Oe, whereas the susceptibility above T_c was measured in a field of a few hundred Oe.

Typical resistance data are shown in Fig.1. The values of T_c, defined as the midpoint of the resistance drop, are listed in Table 1. The width of the transition is generally only a few K. Superconductivity was also confirmed by magnetic measurements. Each sample exhibited a large Meissner effect as expected for bulk superconductivity. A typical example is also shown in Fig.1. The measured values of T_c agree well with those from the resistance measurements. It is clear from Table 1 that all of the $RBa_2Cu_3O_{6+y}$ samples have high transition temperatures (88 - 93.5 K). The presence of a rare earth element has at most a minimal effect on T_c.

The large magnetic moments on the R sites and their interactions were determined from the magnetic susceptibility in the normal state ($T > T_c$). The temperature dependence of the magnetic susceptibility (χ) for most of the samples can be well described by the Curie-Weiss relation,

$$\chi = \chi_0 + \frac{C}{T-\theta} = \chi_0 + \frac{n\, p_{eff}^2\, \mu_B^2}{3k_B\,(T-\theta)}, \qquad (1)$$

where χ_0 is the temperature-independent susceptibility arising from diamagnetic and Pauli

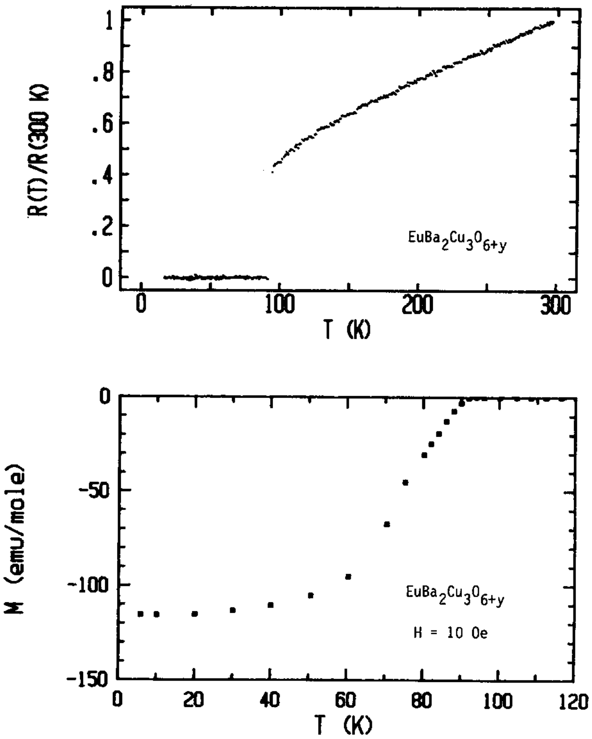

Fig.1 Resistivity and magnetization at H = 10 Oe as a function of temperature for $EuBa_2Cu_3O_{6+y}$

Table 1: Superconducting transition temperature (T_c), Curie-Weiss temperature (θ), effective magnetic moment (p_{eff}) and $g\sqrt{J(J+1)}$ of $RBa_2Cu_3O_{6+y}$.

R	Tc (K)	θ (K)	p_{eff}	$g\sqrt{J(J+1)}$
Nd	88	-14	3.07	3.62
Sm	93.5	+10	0.72	0.84
Eu	93.5	---	---	0 3.5*
Gd	93.5	+4	7.42	7.94
Dy	92.0	-7	9.66	10.63
Ho	92.5	-12	10.04	10.60
Er	89.5	-29	9.45	9.59
Tm	91.0	-40	7.61	7.57
Yb	89.5	-6	3.52	4.54

*Including contribution from excited states (Ref.6)

susceptibility, and n is the number of R ions with effective magnetic moment p_{eff}. The values of θ provide a measure of both the strength and nature of the magnetic interaction. For most of the samples studied χ_0 is small, of the order of 1-2 $\times 10^{-6}$ emu/g-Gauss. In such cases, a plot of $1/\chi$ vs T gives a linear relation from which the values of C, θ and p_{eff} can be determined. Two examples are shown in Fig. 2, $GdBa_2Cu_3O_{6+y}$ and $DyBa_2Cu_3O_{6+y}$. For R = Nd, Yb and particularly Sm, the temperature-dependent susceptibility is comparable to χ_0 due to their smaller magnetic moments. In this case, $1/\chi$ does not display a linear temperature dependence but $1/(\chi-\chi_0)$ does.

In the analysis of the magnetic susceptibility data, we have assumed that only the R ions carry an appreciable moment. The data were fitted to Eq.(1). The determined values of p_{eff} and θ of $RBa_2Cu_3O_{6+y}$ are shown in Table 1. Apart from $SmBa_2Cu_3O_{6+y}$ and $EuBa_2Cu_3O_{6+y}$, which will be discussed later, the magnetic characteristics can be summarized as follows: The value of p_{eff} is very close to $g\sqrt{J(J+1)}$, the value expected for the ground state of R^{3+} according to the Hund's rules. This confirms that the rare earth ions are indeed in the 3+ state [6]. Very remarkably, the R^{3+} ions have little or no effect on T_c. It has been found that superconductivity is severely affected if some of the Cu ions are replaced by magnetic transition ions [7]. These results support the conjecture that superconductivity occurs in the CuO_2-Ba-CuO_{2+z} -Ba - CuO_2 layers and not in the intervening layers

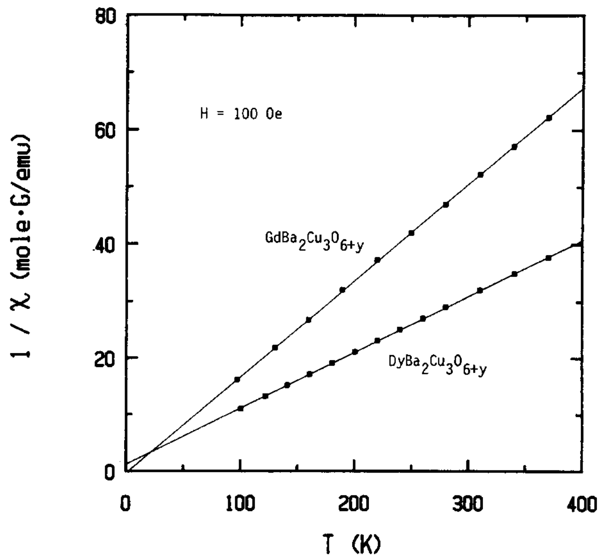

Fig.2 Linear temperature dependence of the inverse susceptibility (H = 100 Oe) for $GdBa_2Cu_3O_{y+6}$ and $DyBa_2Cu_3O_{6+y}$

containing R [4]. The magnetic interactions among the rare earth ions with large localized moments remain an intriguing aspect of these high T_c superconductors. As shown in Table 1, the susceptibility data indicate that θ is **negative** for most of the samples. The rare earth moments are therefore primarily interacting antiferromagnetically. Since the rare earth layers are far apart (~12Å), the interactions are essentially two-dimensional. It should be pointed out that we have observed no magnetic ordering in any of these samples at 3 K.

The susceptibility of $EuBa_2Cu_3O_{6+y}$ is particularly unusual. The large value of θ (-260 K) extrapolated from the high temperature susceptibility data shown in Fig. 3 suggests a very strong antiferromagnetic interaction, possibly even an antiferromagnetic ordering in the superconducting state. However, possible magnetic ordering can not be revealed through magnetometry due to the overwhelming Meissner effect. Therefore, in order to probe the magnetic characteristics of the Eu-containing sample at low temperatures, a method is required to suppress the superconductivity while leaving the magnetic properties intact. We have found [7] that by replacing only 10% of the Cu by Zn, superconductivity can be completely suppressed due to the filling of the antibonding d band. Indeed, $EuBa_2(Cu_{0.9}Zn_{0.1})_3O_{6+y}$ does not exhibit superconductivity, and its magnetic susceptibility has been measured in the entire accessible temperature range as shown in Fig. 3. Above 94 K, the susceptibility of the Eu samples with and without Zn are virtually the same. The magnetic characteristics clearly are not appreciably altered by the Zn substitution. No signs of magnetic ordering have been detected for the Zn-substituted sample. However, the susceptibility data of the Zn-substituted sample can not be fitted by Eq.(1) over the entire temperature range. The high temperature data ($T \gtrsim 100$ K) have been fitted to Eq.(1), leading to a large moment ($\sim 5\ \mu_B$) and $\theta \simeq -260$ K, whereas the low temperature data ($T \lesssim 100$ K) were fitted to Eq.(1) with a small moment ($\sim 1.5\mu_B$) and $\theta \simeq -5$ K. We have considered the possibility that some of the Eu ions may exhibit mixed valence in which the Eu^{2+} ($4f^7$) configuration would exhibit a large moment. This, however, is unlikely because only the Eu^{3+} state has been found in preliminary Eu^{151} Mössbauer measurements. The most likely cause is that Eu remains in the trivalent state ($4f^6$) with a ground state of $^7F_0$, but the excited states ^7F_j (j=1, 2, ...), only a few hundred degree above, also contribute appreciably to the magnetic susceptibility. In this case, Eq.(1) must be modified by a sum of those contributions weighted by Boltzmann factors [6].

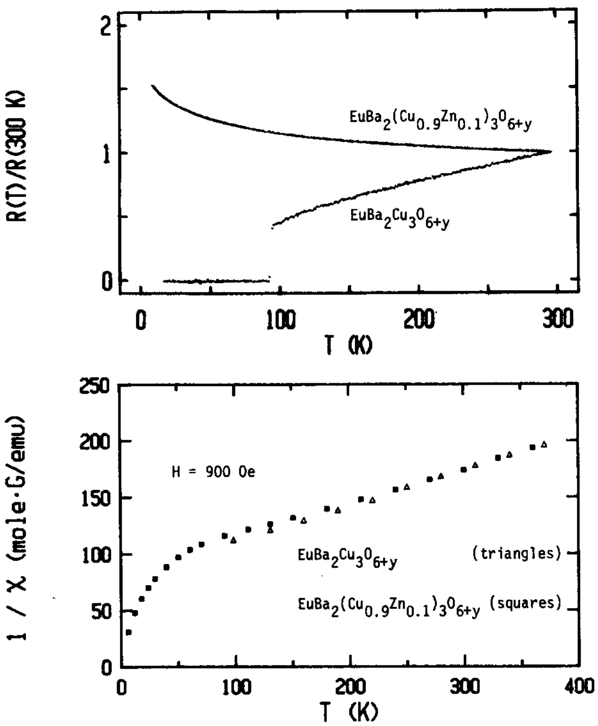

Fig.3 Resistivity versus temperature for $EuBa_2(Cu_{0.9}Zn_{0.1})_3O_{6+y}$, compared with $EuBa_2Cu_3O_{6+y}$. Note the complete suppression of superconductivity by 10% Zn-substitution. The squares and triangles are the inverse susceptibility data for $EuBa_2(Cu_{0.9}Zn_{0.1})_3O_{6+y}$ and $EuBa_2Cu_3O_{6+y}$ respectively. The magnetic behavior remains the same above T = 100 K.

Finally, it should be mentioned that three of the rare earth samples (R = Ce, Pr and Tb) could not be made superconducting. Whether this is due to starting materials of poor quality, or a need for a somewhat different reaction processes remains to be investigated.

In conclusion, $RBa_2Cu_3O_{6+y}$ exhibits high T_c superconductivity which is essentially unaffected by the presence of the rare earth ions. We have determined the magnetic moments of the rare earth ions, and the values are close to those expected from the trivalent state. The moments are generally found to interact antiferromagnetically, however no sign of magnetic order has been detected down to 3 K. The anomalously large negative values of the Curie-Weiss temperature (θ) for the Eu samples do not indicate a strong antiferromagnetic interaction, but merely a result from the contributions of the low lying excited states.

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