The local magnetic, electronic, and structural properties of (RE)Ba$_2$Cu$_3$O$_{7-\delta}$ superconductors (RE = Gd, Dy, and Eu) were studied by Mössbauer spectroscopy using the resonances of $^{155}$Gd, $^{161}$Dy, $^{151}$Eu, and $^{57}$Eu. In GdBa$_2$Cu$_3$O$_{7-\delta}$, different magnetic ordering behaviors of the Gd sublattice are found for the orthorhombic (superconducting) and tetragonal (non-superconducting) phases. In DyBa$_2$Cu$_3$O$_{7-\delta}$, the magnetic moments of the respective CEF ground states in the orthorhombic and tetragonal phases are derived from paramagnetic hyperfine splittings at 1.4 K. In both DyBa$_2$Cu$_3$O$_{7-\delta}$ and EuBa$_2$Cu$_3$O$_{7-\delta}$, anomalies connected with the superconducting transitions in isomer shift, recoil-free fraction, and relaxation behavior were looked for, but not found. The electric-quadrupole splittings observed for both systems are discussed in connection with the lattice EFGs derived for the Gd system. In GdBa$_2$Cu$_3$O$_{7-\delta}$, the local properties of the various Fe sites are investigated over a wide temperature range in both the orthorhombic and tetragonal phase. The magnetic ordering of the Gd sublattice in the orthorhombic phase and of the Cu(2) sublattice in the tetragonal phase, respectively, is monitored via the magnetic splittings at the various Fe sites. Possible assignments of Cu(1) and Cu(2) sites as well as different oxygen configurations around the substituted Fe ions are discussed.

1. Introduction

The intimate connection between superconductivity and magnetism is one of the most fascinating properties of the new high-$T_c$ superconductors. In the YBa$_2$Cu$_3$O$_{7-\delta}$-type superconductors, a modest variation in oxygen stoichiometry changes the properties of the Cu-O layers from superconducting to magnetic. Replacing the Y$^{3+}$ ions by magnetic rare-earth ions like Gd$^{3+}$, Dy$^{3+}$, or Er$^{3+}$, on the other hand, does not change the superconducting properties of the system at all. At low temperatures one even observes magnetic order of the rare-earth sublattices [1–3]. This coexistence of superconductivity and magnetism in the new ceramic superconductors is different from the behavior of conventional metallic superconductors and of more complicated ternary systems like Chevrel phases or Rh-boride based systems [4].

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Mössbauer spectroscopy is well suited to study the interplay between magnetism and superconductivity [5]. In this contribution, we report on Mössbauer studies of YBa$_2$Cu$_3$O$_{7-\delta}$-type systems, where Y was replaced by Gd, Dy, and Eu. In the Gd system, we investigated the magnetic ordering behavior of the Gd sublattice between 1.2 and 2.4 K, both in the superconducting orthorhombic phase and in the non-superconducting tetragonal phase. In the Dy system, we observe paramagnetic hyperfine splittings already above the Néel temperature of 0.9 K, yielding valuable information on the groundstate magnetic moment of the 4f electrons in the orthorhombic and tetragonal phase. In the Dy and Eu systems we searched for anomalies connected with the superconducting properties in the isomer shift, recoil-free fraction, and relaxation behavior. We also performed Mössbauer studies of the Fe-substituted Gd system with the intention of observing magnetic interactions with the Gd sublattice (in the superconducting phase) and with the Cu(2)-O planes (in the tetragonal phase). It turned out that the various Fe sites, as evidenced by their different subspectra, monitor the respective magnetic orderings and, in their relative intensities, depend sensitively on oxygen stoichiometry.

2. Experimental

The preparation of the various samples followed the procedure described in the literature [1–3] and is outlined in detail in two previous publications of our group [6,7]. The samples were characterized by X-ray diffraction as single-phase orthorhombic (with $\delta \approx 0.1$) or tetragonal (with $\delta \approx 0.9$) systems. The tetragonal phases were prepared by annealing of the respective orthorhombic phase for 2 days in vacuum at $450^\circ$C. The superconducting transition temperatures $T_c$ were determined for all samples by four-point resistance measurements and, in selected cases, by magnetic susceptibility measurements [6–8]. In all studies presented here, the samples exhibit sharp superconducting transitions around 92.5 K with widths of $\approx 1.5$ K in the resistance curves. For the Fe-doped GdBa$_2$Cu$_3$O$_{7-\delta}$ samples, where 0.5 at% of Cu was replaced by $^{57}$Fe, no drop of $T_c$ or broadening of the transition curves was observed.

All Mössbauer experiments were performed in transmission geometry on powdered absorbers of appropriate thickness employing a sinusoidal velocity modulation of the source. The absorber were cooled in He-bath cryostats to defined temperatures ($\pm 0.01$ K for $T < 5$ K, and $\pm 0.2$ K to $\pm 1.0$ K for higher temperatures). In case of $^{57}$Fe studies, a vacuum oven was used for temperatures above 300 K. In the $^{155}$Gd studies, the source was kept at the same temperature as the absorber. In all other Mössbauer studies, the sources were at room temperature. The source matrices were SmPd$_3$, $(\text{DY}_{0.5}\text{Gd}_{0.5})F_3$, SmF$_3$, and Rh for the $^{155}$Gd(86.5 keV), $^{161}$Dy(25.6 keV), $^{151}$Eu(21.6 keV), and $^{57}$Fe(14.4 keV) resonances, respectively.