Superconductivity and magnetic order in the copper sublattices of the $YBa_2Cu_{3-x}Fe_xO_{7+y}$ ceramics

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The correlation between superconductivity suppression and magnetic ordering of copper atoms is determined in the $YBa_2Cu_{3-x}Fe_xO_{7+y}$ lattice by the $^{61}Cu(^{61}Ni)$ emission Mössbauer spectroscopy (EMS). © *1994 American Institute of Physics.*

It is known that the superconducting transition temperature T_c decreases as the oxygen content decreases in the $YBa_2Cu_3O_{7-z}$ superconductors with an orthorhombic lattice, and as the superconductivity disappears, the antiferromagnetic order appears in the Cu(2) sublattice and the lattice becomes tetragonal at $z>0.6$ (Refs. 1 and 2). When $YBa_2Cu_{3-x}Fe_xO_{7+y}$ solid solutions form, similar effects are observed: T_c decreases as x increases, the orthorhombic lattice transforms to the tetragonal lattice at $x>0.05$, and the superconductivity disappears at $x>0.45$ (Ref. 3). It is important that the superconductivity and the magnetic order of Fe ions at the Cu sites can coexist in the composition range $x=0.03$–0.45 (Refs. 4–7). However, it is still unknown whether the magnetic order of iron in $YBa_2Cu_{3-x}Fe_xO_{7+y}$ occurs as a result of the magnetic order of copper atoms (see, e.g., Ref. 8).

The $^{61}Cu(^{61}Ni)$ EMS used in this study can be used to solve this problem. In the above technique a decay of the ^{61}Cu parent nucleus, leading to the ^{61}Ni Mössbauer probe with nuclear parameters, provided a reliable determination of the magnetic order of copper sites.[9] Two pairs of compositions were investigated: $YBa_2Cu_3O_{6.96}$ (orthorhombic, $T_c=92$ K) and $YBa_2Cu_3O_{6.1}$ (tetragonal, $T_c<4.2$ K), $YBa_2Cu_{2.5}Fe_{0.5}O_{7.18}$ on the one hand, and $YBa_2Cu_{2.8}Fe_{0.2}O_{7.03}$ (tetragonal, $T_c=50$ K) and $YBa_2Cu_{2.5}Fe_{0.5}O_{7.18}$ (tetragonal, $T_c<4.2$ K), on the other.

The samples were prepared by a ceramic technique. The doping with ^{61}Cu was carried out by diffusion for 30 min at 650 °C under pumping-out for $YBa_2Cu_3O_{6.1}$ and at 450 °C for the other samples. According to Masterov *et al.*,[10] this treatment provides ^{61}Cu at the regular Cu sites and does not change the structure or T_c of the samples. The $^{61}Cu(^{61}Ni)$ emission Mössbauer spectra (MS) were recorded at 80 and 4.2 K. These spectra are shown in Figs. 1 and 2.

We considered the $^{61}Cu(^{61}Ni)$ MS as superpositions of two multiplets corresponding to Ni at the Cu(1) and Cu(2) sites. The multiplets were described by five or twelve lines for the pure quadrupole interaction and for the combined quadrupole and Zeeman interactions, respectively.

The calculated spectra were fitted to the measured spectra by the least-squares

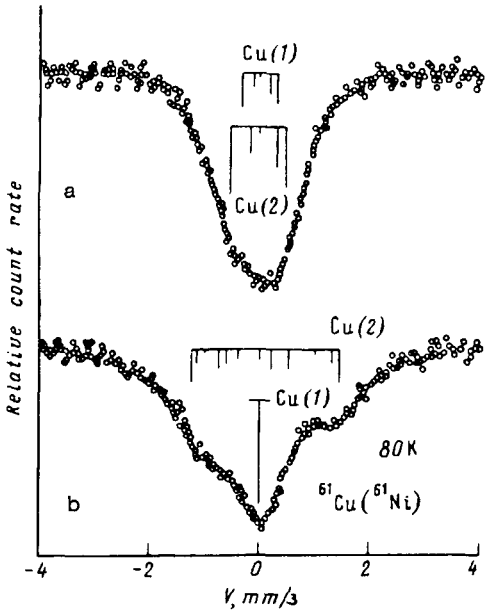

FIG. 1. ^{61}Cu(^{61}Ni) MS recorded at 80 K for the $YBa_2Cu_3O_{6.96}$ (a) and $YBa_2Cu_3O_{6.1}$ (b) ceramic samples. The positions and intensities of the components of the quadrupole multiplets are shown.

method. The fitting quantities were the Hamiltonian parameters H and $U_{zz}\{(3\cos^2\theta-1)/2\}$ [where H is the magnetic field, U_{zz} is the principal component of the electric field gradient (EFG) tensor (both are at the nucleus), and θ is the angle between the z axis of the EFG tensor and the magnetic field direction], as well as multiplet centroid positions, rather than the parameters of the separate lines. The fit was tested by

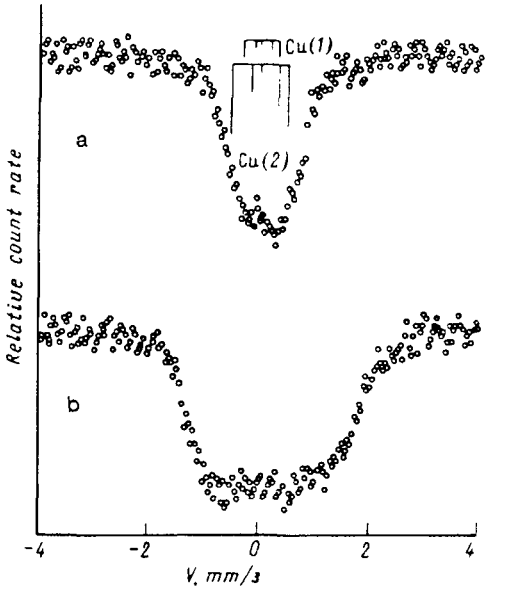

FIG. 2. ^{61}Cu(^{61}Ni) MS recorded at 4.2 K for the $YBa_2Cu_{2.8}Fe_{0.2}O_{7.03}$ (a) and $YBa_2Cu_{2.5}Fe_{0.5}O_{7.18}$ (b) ceramic samples. The positions and intensities of the components of the multiplets are shown.

the χ^2 criterion. In addition, we selected the multiplet centroids in the range ± 0.05 mm/s only because the isomer shift does not reveal itself in the ^{61}Ni MS.[11]

The ^{61}Cu(^{61}Ni) MS of a $YBa_2Cu_3O_{6.96}$ superconducting sample (Fig. 1) consists of two quadrupole multiplets corresponding to ^{61}Ni(2) and ^{61}Ni(1) centers. Their relative intensities $P=1.95(5)$ are quite close to the above relative populations of the Cu(2) to Cu(1) sites. The quadrupole coupling constants eQU_{zz}, as related to the ^{61}Ni ground state, were found to be 32(2) MHz and 54(2) MHz for Ni(1) and Ni(2), respectively.

The ^{61}Cu(^{61}Ni) MS of the $YBa_2Cu_3O_{6.1}$ semiconducting sample (Fig. 1) is a superposition of a narrow ($|eqU_{zz}|<30$ MHz) quadrupole multiplet, which is attributable to ^{61}Ni(1), and a multiplet, which arises from the combined quadrupole and Zeeman interaction of ^{61}Ni(2). The parameters are $H=85(5)$ kOe and $eQU_{zz}=-48(3)$ MHz, assuming[2] $\theta=90(10)°$. The relative intensity of the multiplets, $P=1.97(5)$, is also close to the relative population of the Cu(2) to Cu(1) sites. The magnetic field for Ni(2) is in good agreement with the magnetic order of the Cu(2) sublattice of the tetragonal $YBa_2Cu_3O_{7-z}$ phase, and thus supports the ability of the ^{61}Cu(^{61}Ni) EMS to determine the magnetic order of copper sublattices.

The ^{61}Cu(^{61}Ni) MS of the $YBa_2Cu_{2.8}Fe_{0.2}O_{7.03}$ superconducting sample (Fig. 2) consists of two quadrupole multiplets. Their parameters are very close to the parameters of the corresponding multiplets in the $YBa_2Cu_3O_{6.96}$ MS, but their relative intensity $P=4.0(4)$ differs considerably from the expected value 2.0. This discrepancy can be attributed to a decrease in the share of the regular Cu(1) sites when Fe occupies predominantly the Cu(1) sublattice. The intensity of the regular Ni(1) spectrum could be further reduced by the Ni(1) atoms with the Fe atoms in their nearest neighborhood.

The ^{61}Cu(^{61}Ni) MS of the $YBa_2Cu_{2.5}Fe_{0.5}O_{7.18}$ sample with the suppressed superconductivity (Fig. 2) reveals the presence of a Zeeman splitting. The resolution of the spectrum unfortunately is not enough to separate contributions from the Ni(1) and Ni(2) centers. Thus a clear correlation between the magnetic order in one of the copper sublattices and the superconductivity suppression is observed in both $YBa_2Cu_3Fe_xO_{7-z}$ and $YBa_2Cu_{3-x}O_{7+y}$ ceramics.

The ^{57}Fe MS were also recorded for the $YBa_2Cu_{3-x}Fe_xO_{7+y}$ samples. In accordance with Refs. 4–7, the spectra of $YBa_2Cu_{2.8}Fe_{0.2}O_{7.03}$ consist of four quadrupole doublets. At $T<50$ K one of them transforms in a badly resolved Zeeman sextet, which corresponds to a spin-glass-like Fe in the Cu(1) sublattice. Together with our ^{61}Cu(^{61}Ni) data, it shows that the magnetic field at ^{57}Fe does not arise from the magnetic order of copper. For the $YBa_2Cu_{2.5}Fe_{0.5}O_{7.18}$ sample the magnetic field at ^{57}Fe is observed in both copper sublattices.

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