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ANOMALOUS BEHAVIOUR OF MOESSBAUER PARAMETERS OF A $YBa_2Cu_{2.875}Fe_{0.125}O_{\delta}$ SUPERCONDUCTOR AROUND 110 K.*

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Transmission Mössbauer spectra at various temperatures were obtained from $YBa_2Cu_{2.875}Fe_{0.125}O_{\delta}$ powder samples. The spectra displayed three quadrupole doublets, one of which behaves differently from the other two. The experimental data allows to infer that the Fe atoms occupy only Cu(1) sites with definite valence states and in three different environments. The model put forward here is consistent with previous experiments.

There has been a current discussion about the interpretation of Mössbauer spectra taken by different groups (1-4) in the 1-2-3 coumpounds. In order to contribute further to the knowledge of iron substituted samples, we have performed a detailed study of the Mössbauer spectra obtained from samples in which the Fe concentration is large enough to produce changes in the spectra, but sufficiently small as to prevent complete depletion of superconductivity. In a previous experiment with samples where the Fe concentration was aproximatelly half of the one in the present experiment, we found two quadrupole doublets that were associated with two distinct environments of the Fe atoms in the Cu(1) chains. When one adds up further dopant, the perturbation can be strong enough as to produce not only electronic change but structural transitions as well.

The resistance curve from the sample shows a semimetallic behavior above 240 K, a semiconductivity like behavior for temperatures below 240 K, an onset of superconductivity at 50 K and a zero resistance state reached at 35 K. Powder X-ray spectra showed that the sample is tetragonal with a c-lattice parameter shorter than either the orthorhombic or tetragoal (1-2-3) phase. The a-parameter is very similar to the one in the pure (1-2-3) tetragonal phase. It is worthwhile emphasizing that this tetragonal structure is quite different than the one found in pure compounds with oxygen deficiences. Unlike this latter one, the Fe tetragonal phase is superconducting (5).

Typical spectra at different temperatures are shown in Figure 1, in which one can distinguish three quadrupole doublets. The behaviour of the Mössbauer parameters as a function of temperature is shown in Figures 2A and 2B. The two central doublets, *a* and *b*, behave quite similarly to the ones obtained previously (1) in samples with half of the iron content. However, the external doublet *c* presents a large quadrupole splitting (2.0 mm/s) that does not change with temperature. This

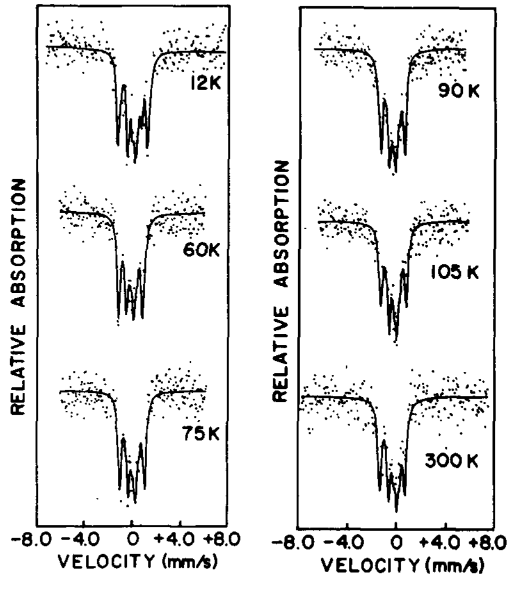

FIGURE 1
Mössbauer spectra at different temperatures.

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fact, together with the low value of the isomer shift, are characteristic of Fe^{3+} in a low spin state.

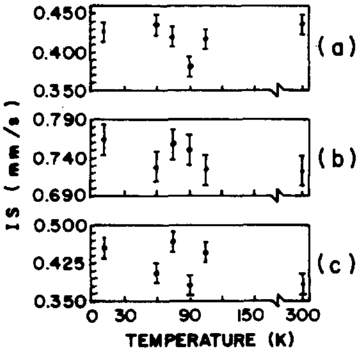

FIGURE 2A
Isomer shifts as a function of temperature.

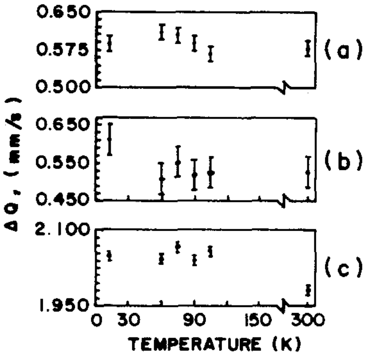

FIGURE 2B
Quadrupole splitting as a function of temperature.

The following interpretation of these experimental facts is based on a crude calculation assuming point charges and including the contribution of the valence electrons to the quadrupole splitting. Several configurations were examined. In all of them Fe^{2+} and Fe^{3+} were considered. From the chemical point of view there exists the possibility of finding Fe^{4+} (6) in the compound, although this further complication is not needed to explain the present data.

The results from this model show that the iron atoms only go to the Cu(1) sites in three different configurations: a) in the center of the oxygen octahedra with valence 3+, b) in the four-fold coordinated chain sites, also in a 3+ state, and c) in the two-coordinated axial symmetry in a 2+ state. This assigment is further supported by the strong temperature dependence of the external doublet *c* absorption (see Figure 3), which is explained by the fact that the iron atom is much less tightly bonded in the axial configuration.

A further fact is that this doublet *c* is asymmetric and that this asymmetry is inverted when varying the temperature. A rather good theoretical adjustment to this behaviour can be obtained by assuming the existence of a local magnetic field. At the moment, we have not an explanation for the origin of such fields, although there could be due to an antiferromagnetic ordering of the Cu atoms.

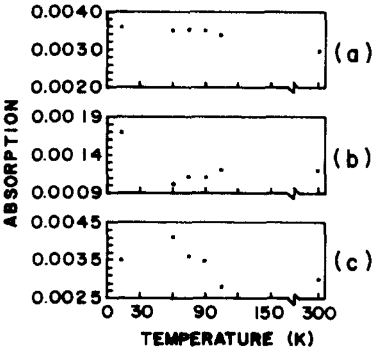

FIGURE 3
Absorption as a function of temperature.

In summary, the present work shows that a) iron substitutes copper in a low spin state, b) there are strong electric fields around the Cu(1) sites, where Fe atoms preferably set and c) according to the model, the valence states of iron are 3+ and 2+ and there is no need for higher iron valence states.

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