We have determined the various parameters of the electric field gradient (EFG) for different Fe-oxygen configurations. This was achieved by analyses of a variety of spectra using a procedure which allows fitting of all spectra of oriented 1-2-3 compounds obtained at different tilt angles \( \beta \) simultaneously, taking into account the degree of texture. The use of a point charge model is invalidated because of the high degree of estimated covalence. The Mössbauer parameters are rationalized. The absence of any observed anisotropy of the mean square displacement of the dopant at the Cu(1) site is rather intriguing.

1. Introduction

The structure of superconducting orthorhombic \( \text{YBa}_2\text{Cu}_3\text{O}_{6+y} \) (\( y = 0.4 \) to 1.0) contains two kinds of Cu with different stereochemistry. The chain or Cu(1) site has fourfold coplanar coordination in the \( (bc) \) plane with two oxygen neighbors, O(1) along the \( c \) axis at 1.86 Å and the other two O(4) at 1.94 Å along the \( b \) axis, giving a one-dimensional O(4)-Cu(1)-O(4) chain in that direction [1]. This chain has a zig-zag configuration, which is of a dynamic nature with O(4) ions oscillating between the two potential minima at about 0.15 Å on either side of the chain along the \( a \) axis [1–3]. The sheet or Cu(2) site is surrounded by a distorted square pyramid of five O atoms, four in the base of the pyramid at distances of 1.93 and 1.96 Å along the \( a \) and \( b \) axes, respectively, and the fifth O(1) at the apex in the \( c \) direction at a distance of 2.28 Å. The CuO\(_4\) sheets are not strictly planar as the Cu is shifted by about 0.25 Å out of the oxygen square-base towards the apical O(1) site, which links the Cu(1) site [4]. Yttrium cations are situated between the two Cu(2) sheets and are surrounded by eight oxygen anions in near-cubic coordination at a mean distance of 2.39 Å. The Ba atoms are found between the Cu(1) and Cu(2) layers with tenfold oxygen coordination, which is roughly cuboctahedral but with vacancies at two of the corners. The mean Ba-O distance is 2.86 Å.

There is general consensus that superconductivity resides mainly in the CuO\(_2\) sheets, while the CuO chains control the charge transfer into the sheets. When the oxygen from the chains is depleted and the overall oxygen content is below O\(_{5.4}\), the electron transfer into the sheets completely destroys superconductivity, and the 1-2-3 compound transforms into an insulating material.

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To gain an insight into the mechanism of superconductivity in the Cu-O compounds, it is essential to understand the nature of chemical bonding and the charge distribution between copper and oxygen. The Mössbauer quadrupole splitting is a measure of deviation from spherical symmetry of the electronic charge around the nuclear probe, and results from the interaction of the corresponding electric field gradient (EFG) with the quadrupole moment of the excited nucleus. Therefore, an experimental determination of the parameters of the EFG tensor viz. magnitude, sign, direction and asymmetry at different sites can give valuable information about the electronic charge distribution around the probe.

It would also be interesting to compare the Mössbauer parameters of configurations acquired by iron-57 versus cobalt-57. Generally, iron-57 substitution consists of 1% or more of copper sites, while cobalt-57 constitutes about 30 to 50 parts per million of replacement. Cobalt and iron substitute predominantly at the chain sites, especially at a relatively low level of substitution. This is shown by neutron and X-ray diffraction, EXAFS, IR, and rather unequivocally by Mössbauer studies [5–7]. Therefore, the aforementioned percentage substitutions are three times larger with respect to the chain only. Several researchers have observed magnetic hyperfine splitting in the Mössbauer absorption spectra of fully oxygenated $YBa_2(Cu_{1-x}^{57}Fe_x)O_7\gamma\delta$ at low temperatures [8–17]. This is indicative of localized magnetic ordering resulting from clustering of iron atoms [18,19], and can occur even at 0.8 to 1.5% level of iron-57 substitution [10,13]. The clustering of iron atoms in 1-2-3 compounds has also been investigated by X-ray, neutron and electron diffraction studies [18–22]. These observations are also supported by EXAFS and anomalous differential X-ray scattering studies [23,24]. An extra oxygen is picked up for every two atoms of Fe. The rearrangement of oxygen ions around an iron atom creates an environment at the neighboring site which already has the proper oxygen configuration. This leads to formation of linear clusters of iron along the (110) direction [19,21,22] with, presumably, a 5-coordinate configuration.

There are several reports in the literature on Mössbauer studies of $^{57}Fe(^{57}Co)$-doped 1-2-3 compounds using oriented powders [25–30], oriented films [31], and single crystals [32,33], with a view to determining the EFG parameters of different species present. The spectra is rather complex, with five of six species being present. The interpretation of the observations are rather contradictory and often controversial, despite the fact that there is fairly good agreement regarding the Mössbauer parameters of the different species. Some of the problems underlying the controversy are as follows.

First, in the case of magnetically aligned powders, one can not assume that the degree of orientation is close to 100%. The degree of orientation depends on the size of particles, viscosity of epoxy during the period of polymerization, and the magnitude of the impressed magnetic field. Moreover, a conventional powder diffractogram might be misleading in evaluating the degree of orientation, because of the relatively small number of crystallites contributing to the diffraction pattern [34]. Secondly, neglecting to take into account even a minor species can bring about a change not