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MÖSSBAUER SPECTROSCOPIC STUDY OF Fe-DOPED SUPERCONDUCTING Cu-OXIDES

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Abstract. – Fe impurities preferentially substitute the Cu-I sites (chain) in superconducting $YBa_2Cu_3O_{7-y}$ and a magnetic order is stabilized if the Fe concentration increases. ^{57}Fe Mössbauer results on superconducting Cu-oxides and also related non-superconducting ones are presented.

In order to study the magnetic properties of high T_c superconducting oxides, the Mössbauer spectroscopy has been applied by many research groups. Smit *et al.* have measured ^{115}Gd spectra of $GdBa_2Cu_3O_7$ and confirmed the existence of magnetic order at low temperature [1]. Indeed, the two-dimensional rare earth lattice is an attractive subject in the field of basic magnetism but the role of rare earth ions in superconductivity is regarded to be less important. Measurements on Fe nuclei in the Cu oxides are of particular interest since Fe atoms may replace the Cu sites.

Besides ours [2], a number of papers have been published, presenting the results of Fe impurities in superconducting $REBa_2Cu_3O_{7-x}$ [3]. Roughly speaking, all results are similar. The room temperature spectra are explained as a superposition of three quadrupole doublets. The details of site assignment, however, are not yet settled. If the Fe content relative to Cu is more than about 3 % , a magnetic hyperfine splitting appears at 4.2 K, which indicates that Fe atoms are involved in a magnetically ordered state. The line profile is complicated (Fig. 2) and it is hard to claim the uniqueness of theoretical fitting.

In this paper, we summarize the Mössbauer results on the magnetic behaviors of Fe impurities in the Cu-oxides. Comparing with the data on related, non-superconducting oxides, the results on superconducting oxides are discussed.

Prepared samples are as follows.

YBCO (x %), which means superconducting $YBa_2(Cu_{1-x}{}^{57}Fe_x)_3\ O_{7-y}$, namely x % of Cu is substituted by ^{57}Fe.

n-YBCO (x %), means oxygen-deficient YBCO(x %), prepared by quenching.

LCO (x %), semiconducting $La_2Cu_{1-x}{}^{57}Fe_xO_4$.

LSCO (x %), $La_{1.85}Sr_{0.15}Cu_{1-x}{}^{57}Fe_xO_4$.

The temperature dependence of Mössbauer spectra for n-YBCO(x %) reveals that there are two types of Fe having different magnetic properties (Fig. 1). It is already known that n-YBCO has a rather high magnetic transition temperature (T_N) and the antiferromagnetic coupling in Cu – O_2 plane (Cu-II site) is very strong. Therefore the fraction of Fe atoms with bigger hyperfine fields is attributed to those substituting Cu-II sites. The value of T_N estimated from the temperature dependence of this fraction is 420 K, which agrees with the result of neutron diffraction [4].

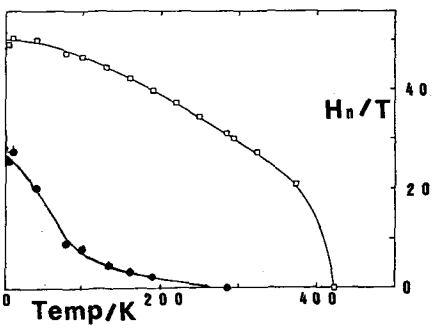

Fig. 1. – Two hyperfine fields in n-YBCO(8 %) as a function of temperature.

The other fraction with smaller hyperfine fields corresponds to Fe atoms in Cu-I sites (chain). The temperature dependence of the latter fraction is rather unusual, deviating remarkably from the Brillouin curve. It appears that T_N of Cu-I sites is much lower than that of Cu-II. This behavior is accounted for if we assume that the molecular field at Cu-I site is much weaker than that at Cu-II site. From this result, it is concluded that the high T_N of the oxygen-deficient (semiconducting) $YBa_2Cu_3O_{7-y}$ is due to the strong magnetic coupling in the planes (Cu-II) and the magnetic interactions in the chains (Cu-I) are relatively weak.

The situation in superconducting YBCO is quite different. A spatially stable magnetic order does not exist in the planes. Therefore the magnetic properties of the whole system depend on the Fe concentration in the chains. As is shown in figure 2, the spectrum at 4.2 K for YBCO (1.5 %) has no magnetic splitting. By applying an external field (4.5 T), a significantly large

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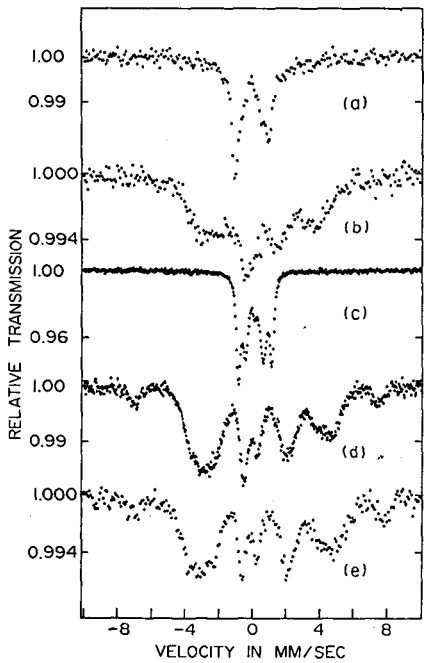

Fig. 2. – Mössbauer spectra, (a) YBCO(1.5 %) at 4.2 K without an external field, (b) with an external field of 4.5 T, (c) YBCO(8 %) at 25 K, (d) 4.2 K, (e) 0.1 K.

hyperfine field is induced, indicating that Fe atoms have magnetic moments. The value of hyperfine field ($\sim$ 25 T) corresponds to that of Fe in Cu-I site of n-YBCO(x %).

By increasing the Fe concentration, the magnetic interactions in the chains are enhanced. The spectrum for YBCO(8 %) has a magnetic splitting at 4.2 K and the profile is almost the same at 0.1 K. T_N is estimated to be about 15 K. From the profile of the spectrum, it can be judged that the major portion of impurity Fe occupies Cu-I sites. This preferential occupation seems to be the reason why T_c of YBCO does not drop very rapidly with the substitution of Cu sites by the magnetic impurity, Fe. In the case of $x = 8$ %, T_c ($R = 0$) is 34 K. T_N has been increased by Fe impurities in Cu-I sites but the concentration of Fe in Cu-II sites is not high enough to destroy the superconductivity. The temperature dependence in figure 2 indicates that Fe atoms in Cu-II sites also participate cooperatively in the magnetic order. However, it seems probable that superconducting Cu atoms in Cu-II sites are not taking part in the static magnetic order.

La_2CuO_4 is antiferromagnetic, as was evidenced by a neutron diffraction study [5], and a consistent result is obtained from the Mössbauer measurement on LCO(1.5 %). At 4.2 K, a fairly large hyperfine field (49 T) is obtained and the temperature dependence suggests that T_N is around 250 K. A similar result was already reported by Nishihara *et al.* [6].

It is well known that when a part of La is replaced by Sr or Ba, superconductivity appears and the magnetic order becomes unstable. With impurity Fe, T_c of LSCO(x %) decreases drastically since all Fe atoms enter into the $Cu - O_2$ network. Susceptibility and resistivity measurements indicate the transition is very broad, even when the Fe concentration is 1 % , and the sample cannot be regarded as a homogeneous superconductor. There is no proof that all Fe atoms in LSCO(x %) are involved in the superconducting phase. Nevertheless, interestingly, the Mössbauer result of LSCO(x %) at low temperature is quite different from LCO(x %). At 300 K, isomer shift and quadrupole splitting are the same for the two. At 4.2 K, the spectrum of LSCO(x %) is extremely broad and the profile of the spectrum cannot be distinguished. Possibly the magnitude and also the direction of hyperfine field are widely distributed. It seems also plausible that local magnetizations in LSCO are fluctuating in a rate near the Mössbauer characteristic frequency, 10^{-8} s. A future study will make clear this situation.

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