MÖSSBAUER STUDIES OF ^{57}Fe SUBSTITUTION OF Cu IONS IN SUPERCONDUCTING OXIDES

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ABSTRACT

Since the discovery of high-T_c superconductivity in $YBa_2Cu_3O_7$ oxides several studies of metal ions substitutions were reported. The observed depression on T_c without a systematic correlation with the charge and magnetic moment of Cu substituents claims for more detailed information about its local properties as can be revealed by ^{57}Fe Mössbauer spectroscopy. The results for different iron concentrations combined with the modifications of the superconducting transition are discussed concerning the presence of magnetic moments on the Fe ions and the preferential occupation of Cu(1) sites, recently confirmed by neutron and electron diffraction experiments. The oxygen coordination for the different iron species are proposed on the basis of their dependence on Fe concentration, their behavior at high temperatures as well as the electron diffraction and electron microscopy measurements reported for Fe:$YBa_2Cu_3O_7$ samples.

Key-words: Superconductivity; Mössbauer spectroscopy; Iron in ceramics; Oxides; Magnetic ordering.

1 INTRODUCTION

Since the discovery of high T_c superconducting oxides intense efforts have been done to achieve a better understanding of the special properties of these oxides which could be responsible for superconducting materials. From the several theoretical models proposed until now it is still not possible to identify clearly which mechanism is the dominant interaction contributing to pairing formation.

From the phase diagrams of Y-Ba-Cu-O and La-B-Cu-O (B = Ca, Sr, Ba) the compositions of $YBa_2Cu_3O_7$ and $La_{1.85}B_{.15}CuO_4$ were established as responsible for the T_c values of 90 and 30-40K respectively. The effect of various substituents have been investigated mainly in the $YBa_2Cu_3O_7$ oxides in an attempt to enhance T_c further on. All the trivalent rare earths which substitute the Y ions do not induce modifications in the superconducting behavior[1]. The same is not true for the Cu substituents and several papers[2] described the results obtained for various metals, which in principle should occupy the Cu sites with, in some cases, dramatic effect on T_c [2]. This depression of T_c has no clear systematic correlation with the charge and magnetic moments of Cu substituents. However, the Cu substitution must be analysed very carefully, since it can induce modification on the oxygen content of the $YBa_2Cu_3O_7$ samples which has been widely proved to be essential for the H-T_c values.

Additional information for a better understanding of how the Cu substituents perturb the superconducting behavior of H-T_c oxides can be achieved from hyperfine interactions methods like Möss bauer effect and perturbed angular correlations since they reflect

the microscopic charge distribution at the substituent nucleus. However, this methods are restricted to some substituents which present appropriated isotopes. The combination of such experiments with usual macroscopic characterization methods can provide important pieces of information. Here we report the contribution obtained from Mössbauer spectroscopy to the understanding of Cu substitution by Fe in the superconducting oxides.

Since the first Mössbauer results were presented in the International Conference on Application of Mössbauer Effect (ICAME), in Melbourne, August 1988[3], different interpretations appeared. The main agreement corresponds to the magnetic patterns for the Mössbauer spectra of $Fe:YBa_2Cu_3O_7$ at 4.2K which indicate that iron has a magnetic moment. The presence of two crystallographic sites for copper, namely Cu(1), with square planar oxygen coordination, and Cu(2), with pyramidal coordination, together with the high sensitivity of ^{57}Fe to the oxygen content of the samples, induced many authors to analyse the Mössbauer spectra with two main asymmetric doublets[4] and propose, as wrong assignement, that the one with Quadrupole Splitting (QS) ≅ 2.0mm/s, is due to the occupation of Cu(2) sites[5]. Different interpretations are now emerging from more carefull experiments and in the recent papers[6] the number of iron species has increased. A general agreement established QS ≅ 2.0mm/s to be characteristic of iron species in the oxygen deficient phase, converging to our previous results[7].

2 EXPERIMENTAL

The $YBa_2(Cu_{1-x}Fe_x)_3O_7$ samples preparation has been previously reported[7]. Several treatments in O_2 flux at 500C were performed to achieve the best oxygen content for the samples. The X-ray analysis was made to determine the sample crystal structure.

The superconducting behavior was observed by DC magnetization measurements with vibrating sample magnetometer for sample cooled in zero magnetic field[7].

The Mössbauer spectra (MS) for several x values were obtained at 4.2K and 293K with $^{57}Co/Rh$ source, keeping the same temperature for source and absorber. The 293K MS were fitted assuming always doublets with symmetrical pairs of lines, while the 4.2K MS display complex magnetic splitted pattern which demand more elaborated fitting[8].

3 MÖSSBAUER RESULTS FOR DIFFERENT IRON CONCENTRATIONS

The MS obtained for the $YBa_2(Cu_{1-x}Fe_x)_3O_7$ samples at room temperature exhibit different results for x above and below some critical value $x \cong .01$. In the low concentration limit, $x = .001, .005, .01$, shown in Fig. 1, the MS present mainly three doublets (A,B,C) corresponding to iron species with quadrupole splittings(QS) of 1.56mm/s, 1.35mm/s, .30mm/s, respectively (see Table I). A fourth iron species (D) with QS = 1.97mm/s, characteristic of the $Fe:YBa_2Cu_2O_6$ insulator oxide, may be present in small proportion as a signature of an im

properly formed compound, (see Table I), even if the X-ray diffraction indicates a pure orthorhombic phase. The Mössbauer spectroscopy, in this case, is more sensitive than the X-ray analysis, since it can show the presence of oxigen deficient islands which are not big enough to be displayed as a crystallographic phase in the X-ray spectrum. The doublets A and B, which dominate the MS at low iron concentration, are sensitive to the sample oxygen content: they both transform reversible to D when the reduced oxyde in the tetragonal structure is prepared either by quenching or annealing in Ar atmosphere[7]. This leads to the conclusion that Fe occupies preferentially a Cu site which is very sensitive to the O_2 content, namely Cu(1) site[7]. This result has been recently confirmed by neutron and electron diffraction experiments[9,10]. The Fe species A,B and D are associated with the occupation of Cu(1) site albeit with different oxygen environments. However, the assignement of C is still to be established.

The increase of iron concentration produces modifications in the ^{57}Fe MS as can be seen in Fig. 2 compared with the Fig. 1. The spectra become more symmetrical due to the absence of the species corresponding to A related to the low iron concentration. Despite the fact that the samples with $.10 \lesssim x \leq .25$ exhibit similar MS spectra, the line width corresponding to B, with reduced QS ($\cong 1.1mm/s$), increases as well as the relative intensity of C. The MS for x=.25 (Fig. 2d) indicate the precipitation of a magnetic phase in agreement with the X-ray analysis which show the presence of extra reflection lines for $x \geq .20$, establishing the limit of solubility of Fe in $YBa_2(Cu_{1-x}Fe_x)_3O_7$. The preferential occupation of Cu(1) site by iron may be modified at higher concentration mainly if we consider that Cu(2) site is two times more abundant than Cu(1) site.

The iron species corresponding to Cu(2) site should have a different electronic configuration and consequently produce new absorption lines in the MS. However, they were not observed and consequently the possibility of such occupation needs to be discussed considering Fe species corresponding to C, or similar to B.

In order to shed some ligth on this question Mössbauer studies were performed on $YBa_2(Cu_{1-x}Fe_x)_3O_{6+\delta}$ samples, since the Cu(2) site is less sensitive to the oxygen content of the sample. The MS at 458K obtained for several Fe concentrations are shown in Fig. 3. They indicate that besides D, two new doublets E and F, with QS of $\cong .70mm/s$ and $.50mm/s$, are present, while the species corresponding to B and C disappeared. Thus it becomes difficult to associate them to occupation of Cu(2) site. F develops a magnetic spectrum at low temperatures[11].

From these experimental results the doublets A, B and C are assumed to be due to Fe species having higher oxygen coordination present in the orthorhombic structure of $Fe:YBa_2Cu_3O_7$. In order to test their relative stability the MS were obtained in air at high temperatures. An upper limit of 300C was taken since, even in air, at this temperature D was formed, probably due to the loss of oxygen.

The MS obtained in air for sample with $x = .005$ at the indicated temperatures are shown in Fig. 4. From these data it is possible to determine that the relative intensity of B increases at the expenses of A and that this effect is partially reversible with temperature[12]. The behavior of A is similar to that observed for the twin boundary in pure $YBa_2Cu_3O_7$ by TEM[13]. The observation of twin boundary in several small single crystals from

samples with x = .05 by electron microscopy[9] indicate that they are only present in the specimens with reduced iron concentration. This corresponds also to the concentration dependence of A which disappears at concentrations $0.01 \leq x \leq .05$, depending on preparation condition.

4 POSSIBLE MICROSCOPIC STRUCTURE FOR DIFFERENT IRON SPECIES IN $YBa_2(Cu_{1-x}Fe_x)_3O_7$ OXIDES

The understanding of the modification induced by iron substituents in the orthorhombic structure of $YBa_2Cu_3O_7$ as well as its different microscopic structures may be achieved by combining Mössbauer results with additional structural informations obtained by EXAFS, neutron X-ray and electron diffraction, electron microscopic and specific heat measurements. The critical Fe concentration, which stabilizes the tetragonal structure for $YBa_2(Cu_{1-x}Fe_x)_3O_7$, may have different values depending on the preparation condition.

The crystallographic studies reported for samples with x=.05[9] and x = .10[10] revealed the preferential occupation of Cu(1) sites by iron, without an agreement concerning the relative occupation of Cu(2) sites. The combination of X-ray, neutron and electron diffraction with electron microscopy measurements in several small single crystals revealed the presence of orthorhombic microdomains even when an overall tetragonal structure is observed[9]. Only when domains predominate in the single crystals, the twin boundaries are observed. Structural studies and carefull analysis of electron microscopy for more concentrated samples (x=.10) allow to propose different oxygen coordinations for Fe ions and the forma-

tion of linear clusters separated by 10 to 20 $\overset{o}{A}$ domains of the orthorhombic structure with reduced iron concentration[10]. More over, the increase of oxygen content with iron concentration is consistent with the EXAFS results which suggest that iron has main ly five oxygen neighbors[14].

Recently a very carefull study was reported for samples with $0 \leq x \leq .04$ where specific heat measurements were combined with all the structural techniques already mentioned[15]. The critical iron concentration which induces tetragonal structure gives origin to a non homogeneous superconducting phase despite there is no iron segregation. The twinning observation depends also, as reported in the reference[9], from the iron concentration in the grains.

The ensemble of above results may lead to several conclusions, but the main one concerns with the homogeneity of iron distribution and the oxygen content. These two parameters can be responsible for the discrepancies obtained from the studies performed in samples with the same nominal concentration either by Mössbauer spectra or X-ray diffraction. The analysis with complementary techniques from microscopic to macroscopic level on the same sample is essential for the understanding of structural changes induced by iron.

In the following of this section we will propose microscopic assignements for some of the several iron species observed by Mössbauer spectroscopy, mainly based on the dependence of their relative intensities on iron concentration and oxygen content as well as the structural informations described above. Even for a fixed iron concentration several configurations may occur for Fe in Cu(1) site mainly due to disorder in the occupation of oxygen sites in

the Cu(1) plane established at the preparation conditions; the Fe coordination can range from 2 to 6 (Fig. 5) leading to different Mössbauer doublets.

The increase of oxygen content with Fe concentration may be due to progressive occupation of the oxygen vacancies resulting in the transition to the tetragonal structure. The assignement which we proposed to $A^{(12)}$, namely the occupation of twin boundary, is based on the temperature behavior and the x dependence of this iron species. Its relative intensity depends on the preparations, as observed for the twinnings, and both disappear when the tetragonal structure is estabilized. In this case we consider A to be the species most characteristic of the orthorhombic phase and which may have the configuration shown in Fig. 5d.

The doublet B dominates the MS for higher iron concentration, when the tetragonal structure is stabilized, and remains even for concentrations as high as x = .25. This species reflects a modification in the local structure of Cu(1) site as compared with the pure $YBa_2Cu_3O_7$. It is compatible with the configuration shown in Fig. 5e with an extra oxygen in Cu(1) plane resulting in the observed increase of oxygen content with iron. Similar configuration has been reported from EXAFS measurements on $YBa_2(Cu_{1-x}Fe_x)_3O_7$ samples[14].

The configurations assigned to the Fe species associated with A and B need to be consistent with the Mössbauer results at high temperatures since, as can be seen in Fig. 4, the relative intensity of B increases at expenses of A. Indeed the configuration attributed to A can transform in to B if an oxygen atom from a neighboring ion hopps to the 0(1) site and completes the 5th coordina-

tion as is shown in Fig. 5e.

The electron diffraction results[10] indicate the formation of iron clusters rich in oxygen content which could include an octahedral coordination for Fe in Cu(1) site as shown in Fig. 5f. This configuration has high local symmetry and its relative intensity should be small and increase with Fe concentration. It may be associated with C which displays similar features and, moreover, is absent in the MS of reduced samples.

The species corresponding to Fig. 5e, d and f are related to samples having high oxygen content. However in the process of preparing the reduced sample disorder may occur in the occupation of oxygen sites in the Cu(1) plane which will lead to other configurations. In such reduced samples with low iron concentration the MS is mainly formed by the doublet D, which can be attributed to axial coordination exhibited in Fig. 5a, similar to what is observed for Cu in $YBa_2Cu_3O_6$, or to configuration shown in Fig. 5b, if Fe binds an extra oxygen. This seems to be consistent with EXAFS measurements reported for Fe: $EuBa_2Cu_3O_6$ samples[16].

There are still two iron species, E and F, which are present in reduced samples whose relative intensities increase with iron concentration (see Fig. 3). It is possible that the configuration proposed for E and F need to take into account not only Fe-oxygen coordination in Cu(1) site but also the configuration of Fe and Cu as next neighbors. In this case more structural informations are necessary to understand them. However, the magnetic ordering temperature for F may indicate that it corresponds to occupation of Cu(2) or iron clustering at Cu(1) plane.

5 THE INFLUENCE OF IRON CONCENTRATION ON THE SUPERCONDUCTING TRANSITION OF $YBa_2(Cu_{1-x}Fe_x)_3O_7$

It is well established that Fe substituents depress T_c in $YBa_2Cu_3O_7$ compounds; initial studies compared 10% of Cu substitution by several transition metals Fe, Co, Ga and Zn. The latter induces the strongest effect[2] on T_c.

Fig. 6 shows how the superconducting transition, as seen by DC magnetization measurements[7], depends on iron concentration. The T_c onset stays constant until $x = .01$, but the fraction of Meissner effect decreases. Above $x = .01$ this last effect is enhanced and the T_c onset decreases further down until being supressed for $x = .15$. These two effects should be analysed with the information obtained from Mössbauer spectroscopy and X-ray diffraction. Since the magnetization measurements give a bulk information this result is an integration of part of the sample where no iron is present and parts where it gradually depresses T_c, resulting in a broadening of the transition. The observation of superconductivity until $x = .10$ is in agreement with the X-ray analysis of our sample which still sees part of the orthorhombic structure; only with $x = .15$ the tetragonal structure is established and no superconducting transition is observed. Consequently, as long as considerable fraction of the sample has an orthorhombic structure, T_c may still be observed. The measurements of T_c for samples which have already pure tetragonal structure, induced by iron substitution, may be understood on the basis of crystallographic studies[9] which indicate that this structure contains orthorhombic microdomains responsible for finite T_c values.

Consequently, the iron substitution always perturbs the su-

perconducting transition, but completely depresses T_c only when the concentration stabilizes the tetragonal structure.

6 CONCLUSION

The combination of Mössbauer results with several structural studies performed on $YBa_2(Cu_{1-x}Fe_x)_3O_y$ samples help to propose microscopic configurations for the several iron species observed in the Mössbauer spectra. This technique has proved to be very sensitive to the quality and oxygen content of the samples. Unhappily the complete structural studies were not performed on the same samples used for Mössbauer spectroscopy and their extreme dependence on preparation condition must be taken into account for the validity of our interpretation.

The observed preferential occupation of Cu(1) site may depend on the condition of the sample preparation, and we believe that this question needs further studies, because either no Fe is present in Cu(2) sites or it has similar hyperfine parameters as B since the line width of this doublet becomes broad with increasing Fe concentration. This, however, is inconsistent with the Fe species observed in the reduced samples[17].

The validity of the microscopic configuration for Fe in $YBa_2Cu_3O_y$ may be tested from first principles calculations of the hyperfine parameters, like preliminary results already reported[18]. The fact that the calculated isomer shift is in good agreement with the experimental values is an indication of the importance of d electron delocalization, through interaction with oxygen p elec-

trons. Consequently the ionic configuration model seems not to be appropriate for Fe in this compounds. The local d electron contribution to the electric field gradient (EFG) is too small compared with the observed values for the quadrupole interaction. This indicates that the lattice contribution to the EFG at Fe nucleus is important and may explain the good agreement reported between the experimental quadrupole interaction and the values obtained from point charge calculations[19].

It is still puzzling why the isomer shifts of several iron species, except A and F, stay in a very narrow range. One possible explanation is that only A reflects the metallic character of $YBa_2Cu_3O_7$ while the others species (B,C,D,E) correspond already to the semiconducting phase induced by Fe or by the reduced oxygen content. In order to confirm this explanation detailed calculations for the several configurations are necessary.

The combination of all structural, specific heat and DC magnetization measurements confirmed the early Mössbauer results[7], which indicated that above x = 0.01 the Fe substitution perturbs the orthorhombic structure of $YBa_2Cu_3O_7$ and proper studies should be done below this value.

With respect to the superconductivity we may conclude that iron always perturbs the transition, probably due to the modification in the local structure associated with the occupation of the oxygen vacancies in O(5) sites. The long range order of the oxygen vacancies is necessary to establish high T_c values in $YBa_2Cu_3O_7$ oxide and the Cu(1) substitution by iron supresses it with a dramatic effect on superconductivity.

ACKNOWLEDGEMENTS

FIGURE CAPTIONS

Fig. 1 - Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ at room tempera-
tures: a) $x = .001$, b) $x = .005$ and c) $x = .01$.

Fig. 2 - Mössbauer spectra of $YBa(Cu_{1-x}Fe_x)_3O_{7+\delta}$ at room tempera-
ture: a) $x = .10$, b) $x = .15$, c) $x = .20$ and d) $x = .25$.

Fig. 3 - Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ at 458K: a) $x=.05$,
b) $x = .10$ and c) $x = .15$.

Fig. 4 - Mössbauer spectra for $YBa_2(Cu_{.995}Fe_{.005})_3O_7$ at the indi-
cated temperatures.

Fig. 5 - Local environment of Fe at Cu(1) site.

Fig. 6 - Temperature dependence of the magnetic susceptibility χ
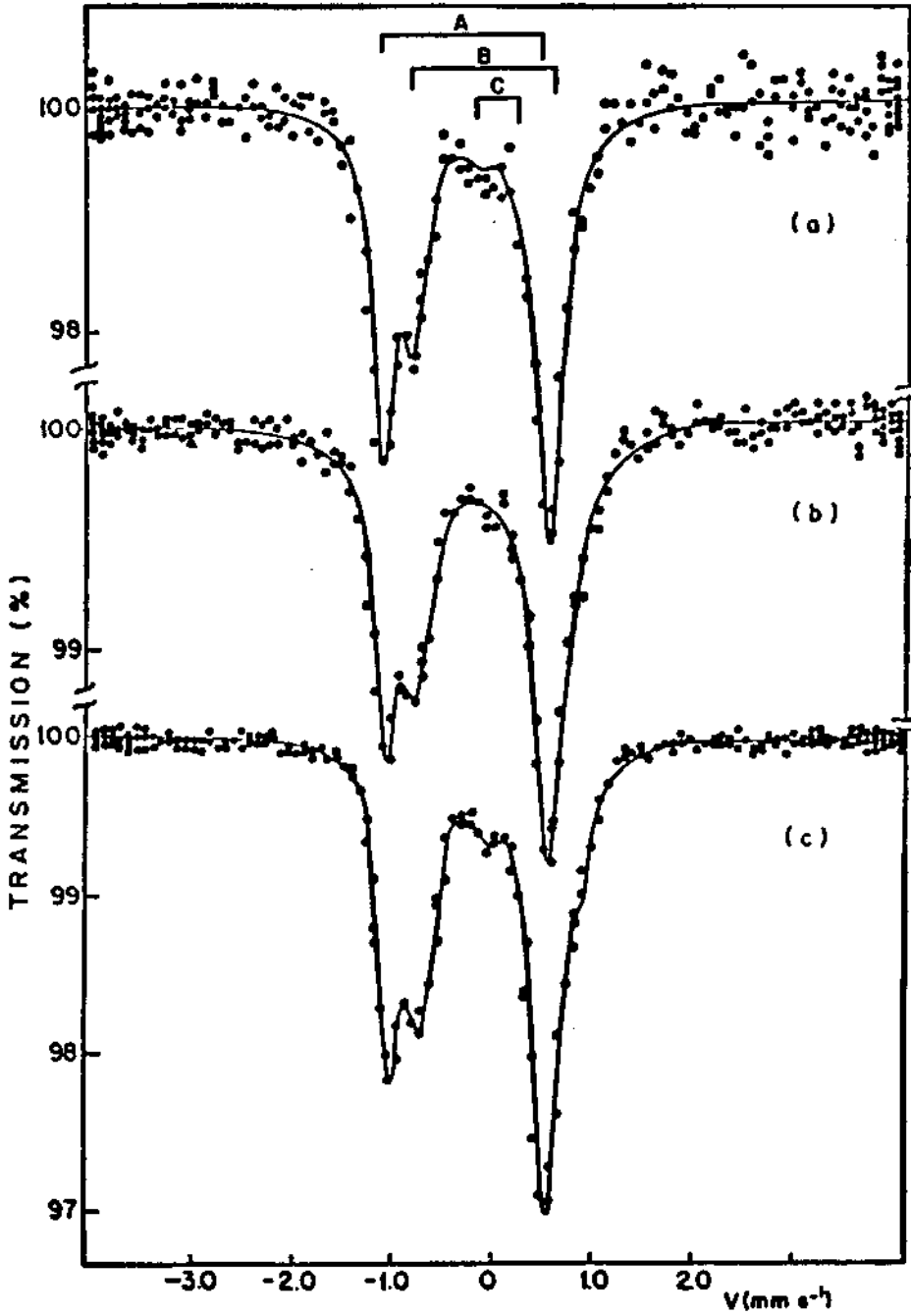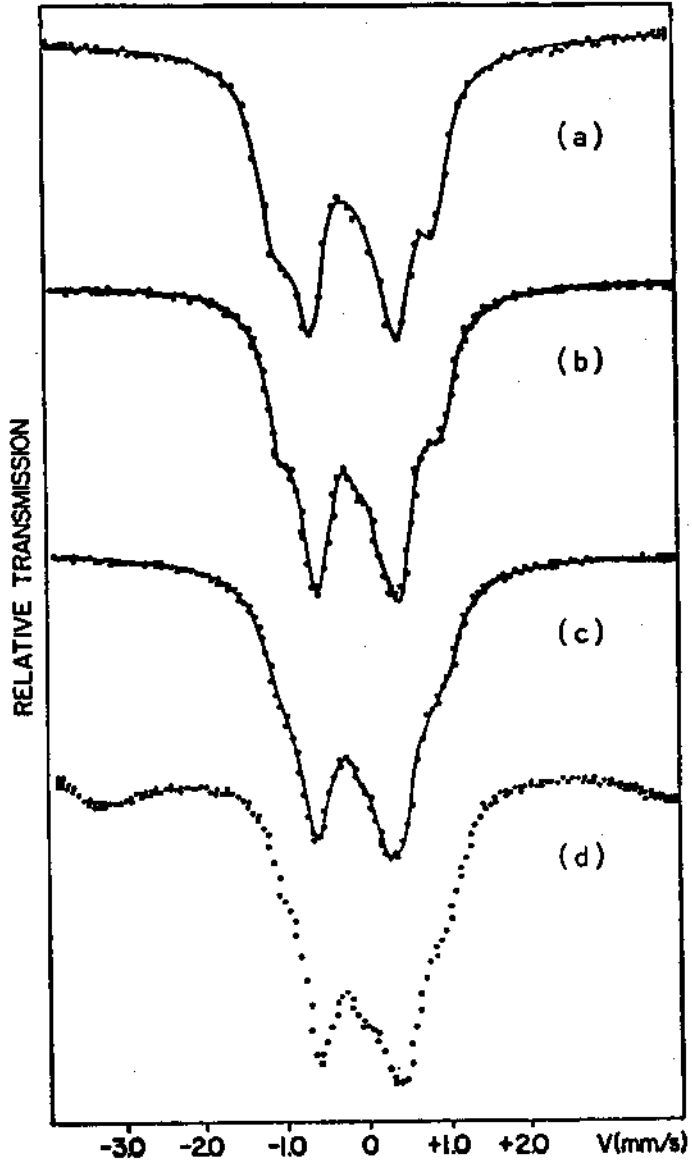for different Fe concentrations[7]. The upper scale re-
fers to the sample with 10% Fe.

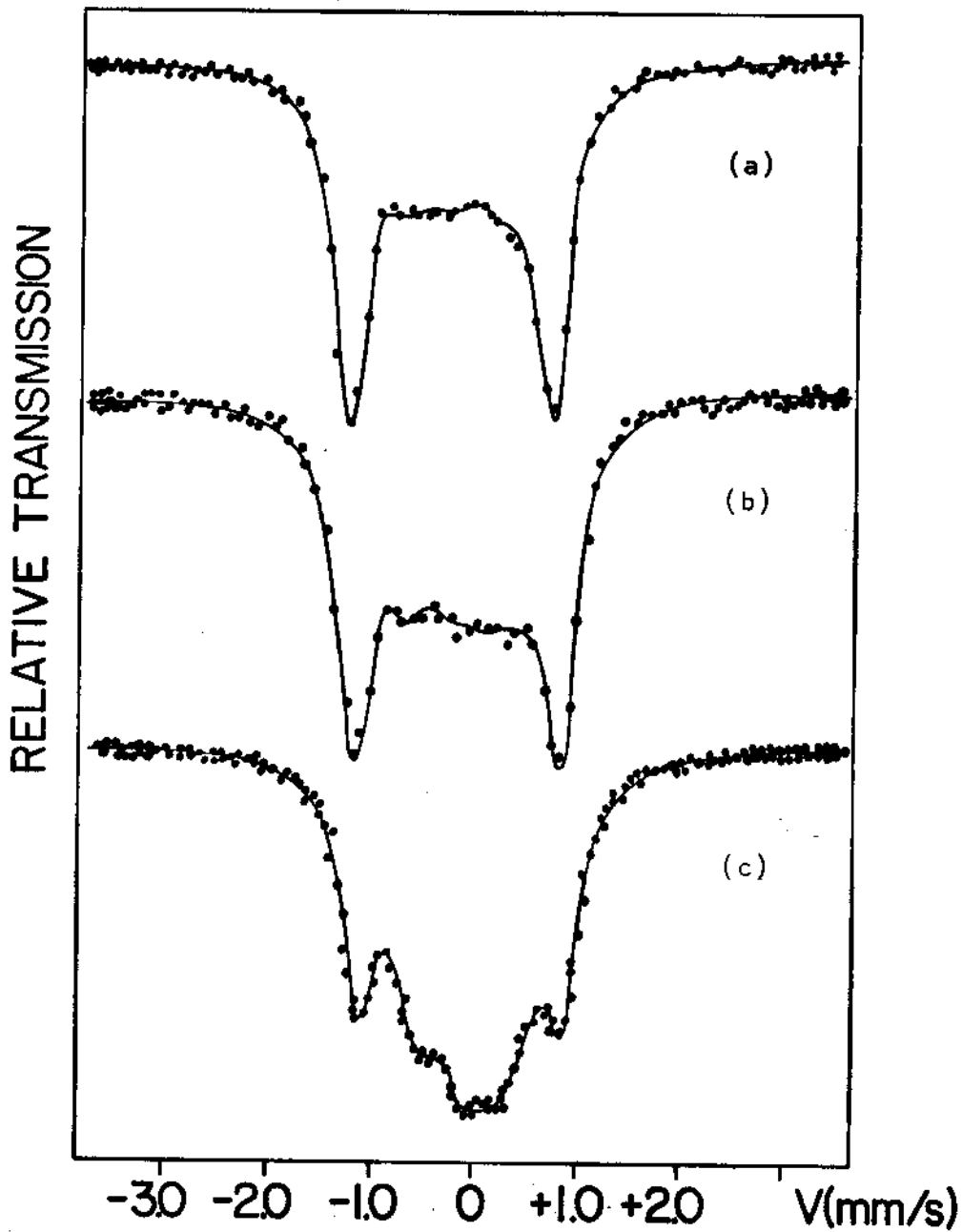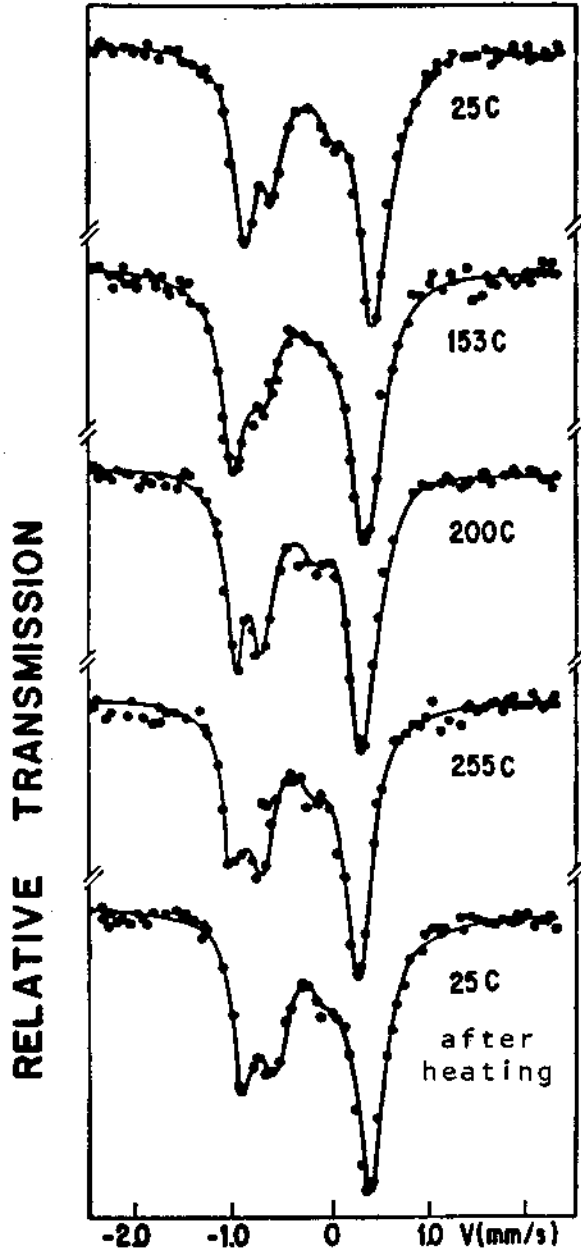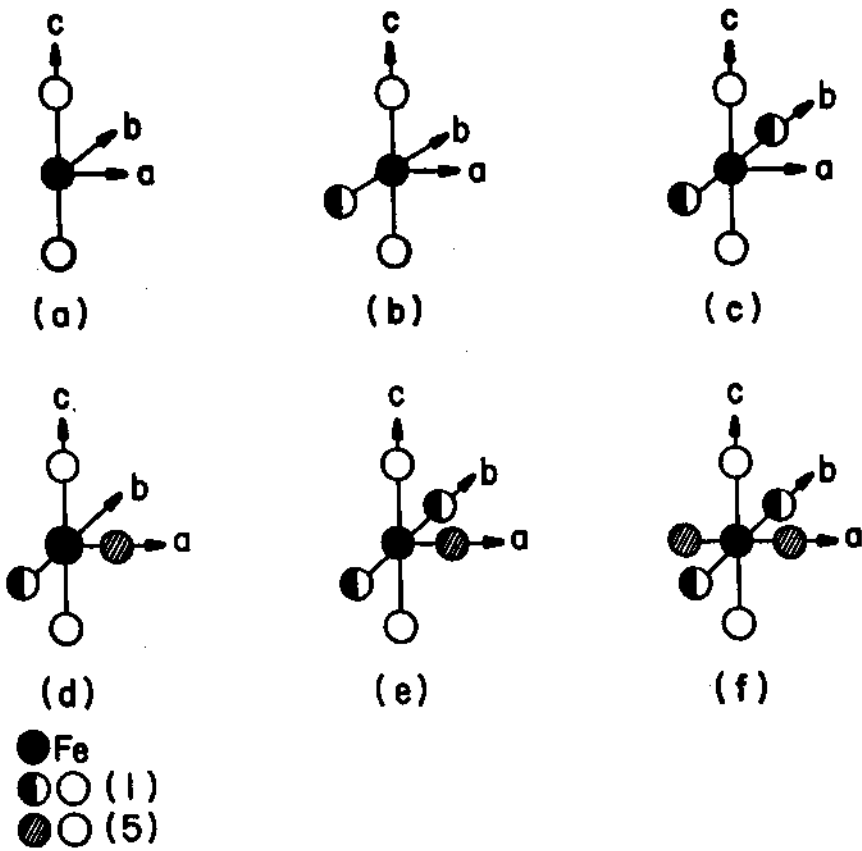Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5
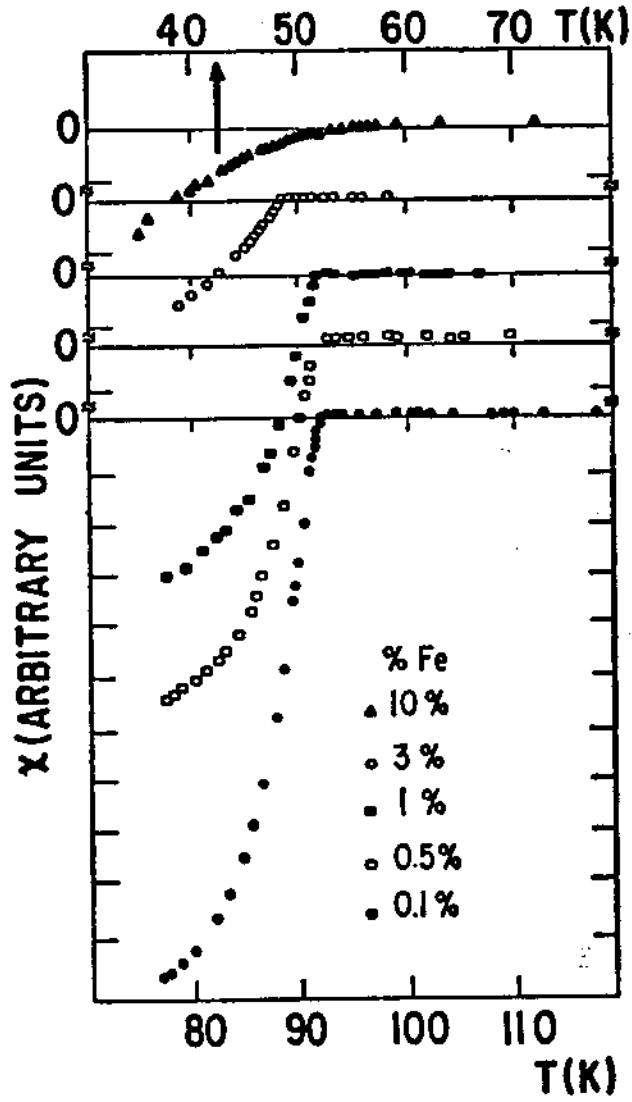
Fig. 6

TABLE I

	A	B	C	D	E	F
δ_{Fe}	-0.18	0.03	0.17	0.05	0.05	0.
QS	1.55	1.20	0.30	1.98	0.70	0.55

Isomer Shift (relative to metallic iron) and Quadrupole Splitting for Fe species present in the room temperature Mössbauer spectra of several $YBa_2(Cu_{1-x}Fe_x)_3O_7$ samples. The relative intensities of the corresponding quadrupole doublets depend on the x and y values.

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