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MAGNETIC ORDERING OF $YBa_2(Cu_{1-x}Fe_x)_3O_7$**

by

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The Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ at room temperature show several doublets attributed to Fe in Cu(1) sites with different oxygen configurations. Here we present a systematic study performed at 4.2K for x=0.005, 0.01, 0.03, 0.05, 0.10,0.15. To obtain information about the magnetic ordered state two samples, with x=0.005 and x=0.15, have been studied at 4.2K under B_{ext}=5T. The Mössbauer spectra indicate that the iron moments are polarized for x=0.005, while in the ordered state (x=0.15) they have an antiferromagnetic or spin-glass-like arrangement with high anisotropy.

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

INTRODUCTION

The ^{57}Fe Mössbauer Spectra (MS) of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ at room temperature show several doublets attributed mainly to Fe in Cu(1) sites with different oxygen configurations[1]. This preferential occupation for Fe has been confirmed by electron and neutron diffraction experiments[2,3]. The relative intensities of these iron species depend on the oxygen content and iron concentration. Here we will discuss the 4.2K magnetically split patterns of the Mössbauer spectra which, as reported by several authors, is due to the existence of ordered iron magnetic moments. The aim of this study is to shed some light on the kind of magnetic ordering which takes place among the iron moments in the Cu(1) chains.

EXPERIMENTAL

Several samples of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ were prepared with Cu partially substituted by Fe(x=0.005,0.01,0.03,0.05,0.10 and 0.15). A mixture of appropriated amounts of Y_2O_3, $BaCO_3$, CuO and Fe_2O_3 (94,5% enriched in ^{57}Fe) has been used for sample preparation according to the usual procedure[1]. Special care was taken to obtain the proper oxygen content in order to avoid the presence of the iron species characteristic of $^{57}Fe:YBa_2Cu_3O_6$ oxides. The Mössbauer spectra were taken with source and absorber at 4.2K. For samples with x=0.005 and 0.15 the MS were taken at 4.2K in the presence of an external field of B_{ext} =5T, parallel to the direction of gama rays.

The analysis of the experimental data was performed with a complete Hamiltonian, allowing arbitrary angles between EFG tensor and B_{hf}. Line intensities were derived from the eigenvectors obtained after the diagonalization of the Hamiltonian. A slight distribution for B_{hf} of Lorentzian shape was allowed (a Gaussian gives fits of similar quality, the hyperfine parameters are the same for both shapes). An explicit distribution of the QS parameters was not introduced for the magnetic spectra.

RESULTS AND DISCUSSION:

The observation of split magnetic hyperfine spectra for $YBa_2(Cu_{1-x}Fe_x)_3O_7$ at 4.2K has been reported by several authors for samples with $0.02 < x < 0.10$, as a consequence of the ordering of the Fe magnetic moments in these systems. Here we present systematic results for several iron concentrations. The influence of iron concentration on the MS at 4.2K can be seen in fig.1. These spectra suggest that the ordering temperature increases with iron concentration. The broadening of the quadrupole doublets develops gradually into resolved magnetic spectra for $x \geq 0.10$. These spectra are formed by several magnetic components and the relative intensity of the iron species, with the highest hyperfine field, increases with iron concentration (see outermost resonance lines).

We concentrate now our study on the $YBa_2(Cu_{1-x}Fe_x)_3O_7$ samples corresponding to the two extreme values of the iron concentration range, $x = 0.005$ and $x = 0.15$, since they do not contain the same Fe species (see Table I) and display different behaviour at 4.2K. In order to get some information about the various Fe species we have studied the MS at 4.2K of both samples in the presence of an external magnetic field B_{ext} =5T. The comparison with the zero field MS at the same temperature is shown in fig.2(x =0.005) and fig.3 (x = 0.15); the magnetically split spectrum for x=0.15 seems to be quite insensitive to the B_{ext}, while dramatic effect is observed in the case of x = 0.005. For the analysis of the magnetic split spectra, the relative intensities of the different magnetic sub-spectra, as well as the isomer shifts and the corresponding quadrupole splittings for the species A, B, C and D were fixed to the values obtained from the paramagnetic state.

The following assumptions turn out to be the most appropriate ones for the data analysis (see fig. 2 and 3).

i) for x = 0.15 in zero field: The Fe moments are directed at fixed angles θ versus the EFG's for the various sites. η was kept zero.

ii) for x = 0.15 under applied field the assumption similar to i) turned out be to be the best; the external magnetic field has practically no effect on the alignment of Fe moments.

iii) for x = 0.005 under applied field: complete alignment of the iron magnetic moments along B_{ext} is achieved. This means that an average over random angles of the EFG versus $B_{eff} = B_{ext} + B_{hf}$ was performed. The asymmetry parameter η had to be kept < 0.2.

The various hyperfine parameters for the Fe species A, B, C and D, obtained from the fits are shown in Table I together with the distribution of B_{eff} and θ angle values.

The iron species associated to B (which dominates the MS at high concentrations) and D (characteristic for the oxygen deficient phase) have their magnetic moments perpendicular to the principal axis of the EFG. Their B_{hf} are 22T and 25T, respectively. The first species reveals a broader distribution in B_{hf}. This species also shows relative broad lines in the paramagnetic state. The negative sign of QS (see Table I) is not consistent with the results obtained from samples oriented in high magnetic field[4]. Using positive QS and small values for the angle θ, however, can not yield satisfactory fitts of our data. Also finite values of η as quoted in reference 5 give only poor agreament with our data.

The existence of magnetic moments at iron in samples with low x values can be derived from the Mössbauer spectrum in B_{ext} = 5T obtained for x = 0.005 (fig.3). They can be aligned by the external magnetic field and the B_{hf} induced by the external field is 16T. No information about θ for species A can be derived since it is present only in the sample with x = 0.005. There we had to performe an average over this angle in order to fit the Mössbauer spectrum in external field. The results revealed similar values for B_{hf} of the Fe in Cu(1) sites (A, B and D) of the order of 20T; while the B_{hf} values for C' species,

without clear attribution, is close to 45T and does not reach the saturation value in the x = 0.005 sample under external field. Another Fe species(C") with similar value for B_{hf} is observed in the x = 0.15 sample, having a different value of QS.

CONCLUSION:

From our results we can conclude that even for samples with x = 0.005 the iron has a magnetic moment, which can be aligned by the external magnetic field. The fact that the magnetic patterns (x=0.15) are hardly influenced by the external field (main effect is only a slight broadening of the spectrum) can be explained by a strong local anisotropy which cannot be overcome by the dipolar energy caused by the external field. The origin of this anisotropy is not yet clear. One may trace it to some kind of spin-glass - like moment arrangement with high frustation, which may well occur by formation of iron clusters[2].

Despite the proposed evaluation of the data turned out to be consistent with the relative fractions of Fe species derived from the paramagnetic phase, there remain still some questions concerning the uniqueness of the analysis of such complex spectra. Essentially the shape of the spectra for iron concentration x = 0.03 at 4.2K, and also the very similar spectra for x = 0.10 at 13K (not shown here)[1], could indicate that dynamic effects play a role. Such relaxation effects may be connected with the blocking behaviour of the magnetization of clusters.

There is hope that this kind of information combined with the values of isomer shift and quadrupole interaction can help to make a proper assignment for the oxygen coordination due to the different iron species which occupy Cu(1) sites in the $YBa_2(Cu_{1-x}Fe_x)_3O_y$ oxides.

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FIGURE CAPTION

Fig.1 - 4.2K Mössbauer spectra for $YBa_2Cu_3O_7$ with the indicated iron concentration.

Fig.2 - 4.2K Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ for x =0.005. a) $B_{ext} = 0$; b) $B_{ext} = 5T$.

Fig.3 - 4.2K Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ for x = 0.15. a) $B_{ext} = 0$; b) $B_{ext} = 5T$.

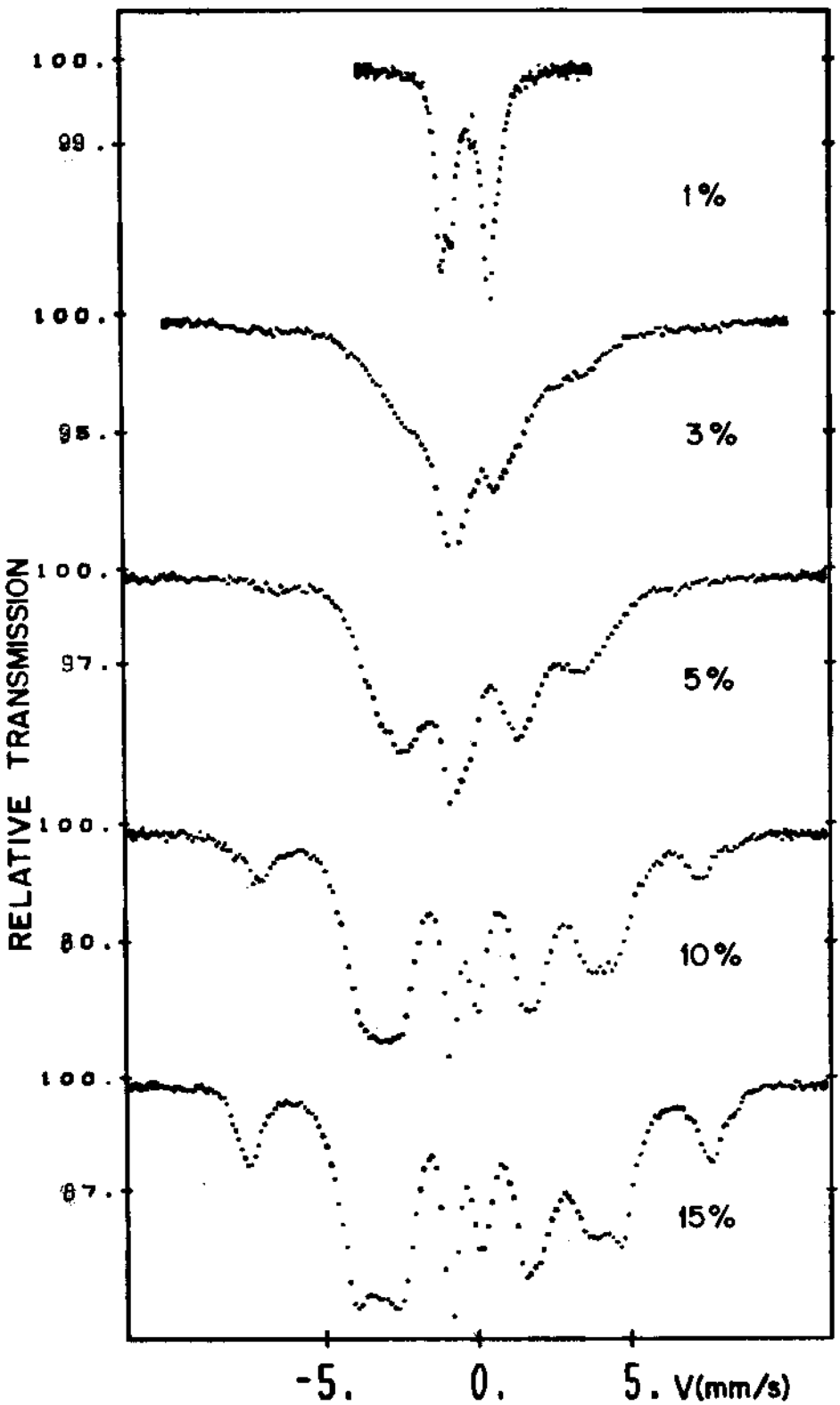
100.
99.
1%
100.
95.
3%
100.
97.
5%
100.
80.
10%
100.
87.
15%
RELATIVE TRANSMISSION
-5.
0.
5.
V(mm/s)

Fig. 1

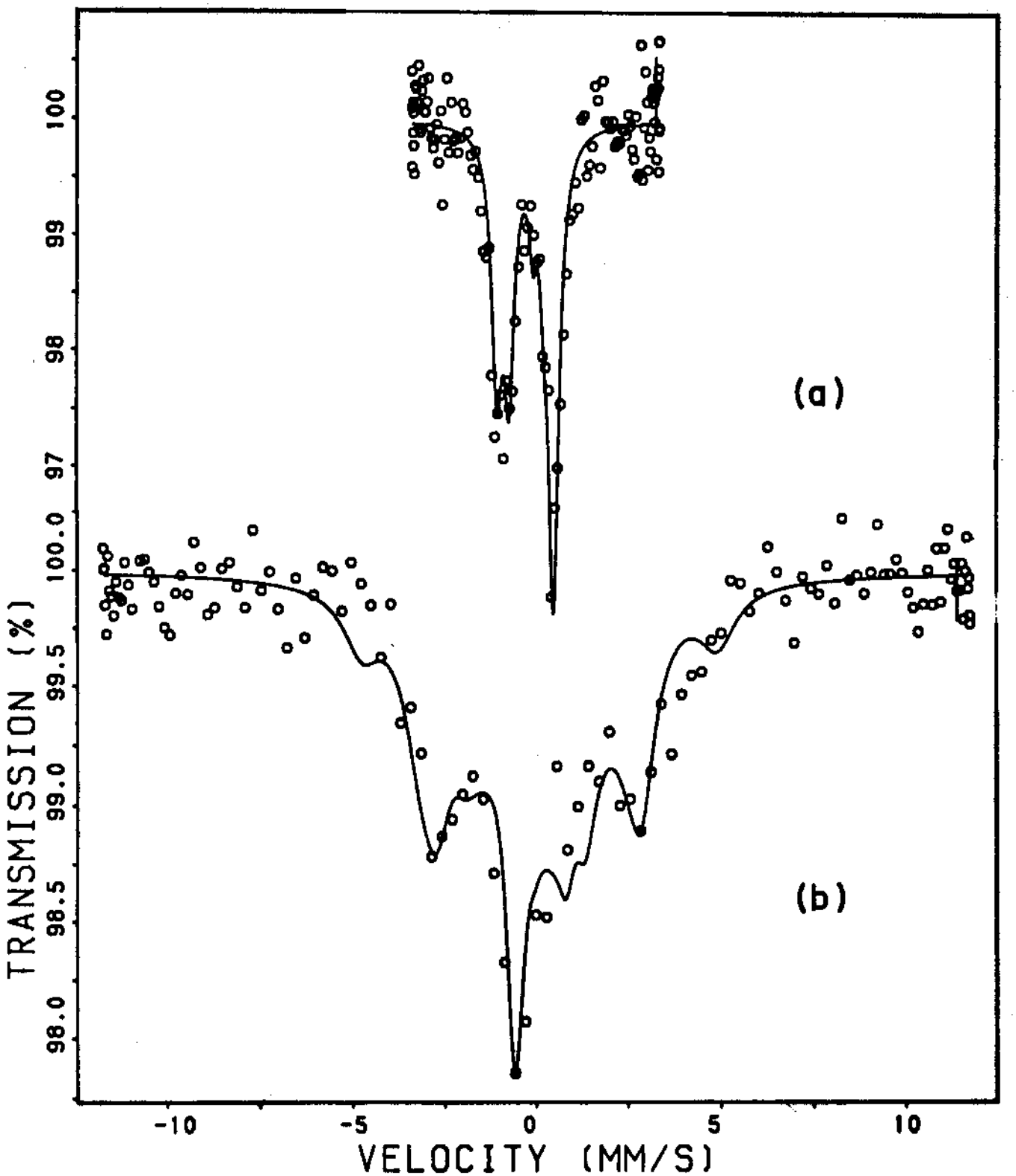
TRANSMISSION (%)
100
99
98
97
100.0
99.5
99.0
98.5
98.0
(a)
(b)
-10
-5
0
5
10
VELOCITY (MM/S)

Fig. 2

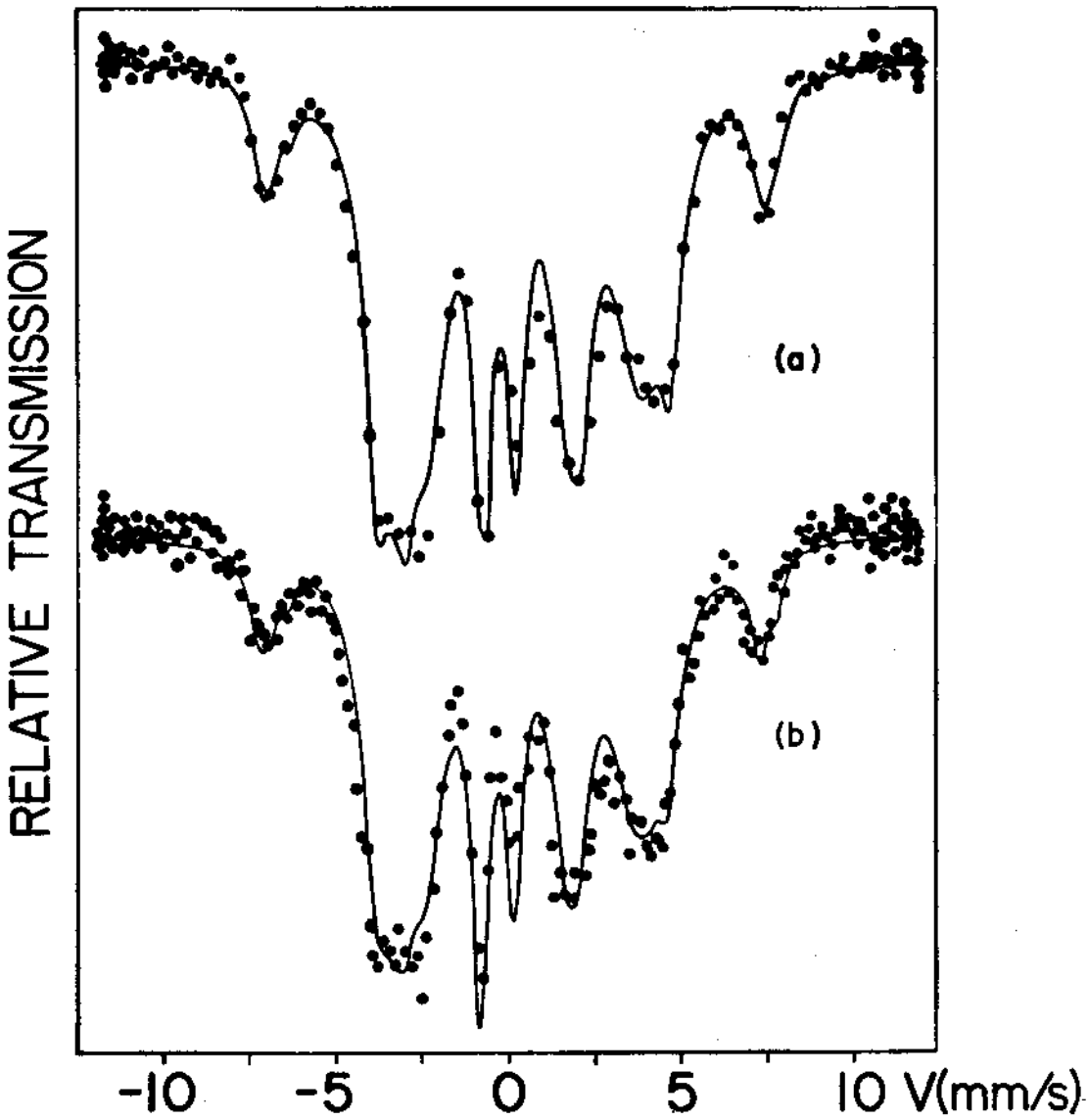

Fig. 3

$YBa_2(Cu_{1-x}Fe_x)_3O_7$	Fe Species	A %	IS (mm/s)	QS (mm/s)	B_{hf} (Tesla)	θ	Γ (mm/s)	RV (mm/s)
x = 0.005	A	49	-0.16	-1.58	-16(1)		0.35	0.95
	B	38	0.09	-1.20	21.5(5)		0.35	0.18
B_{ext} = 5T	C'	13	0.20	-0.30	35.0(5)		0.30	0.18
x = 0.15	B	70	0.02	-0.98	21.5(5)	90	0.50	0.31
	C'	16	0.20	-0.29	44.7(5)	0	0.85	-
B_{ext} = 5T	C''	3	0.41	+0.70	44.0(5)	0	0.46	-
	D	11	0.05	-1.89	25.3(5)	90	0.40	0.08
x = 0.15	B	70	0.02	-0.98	21.5(5)	90	0.40	0.32
	C'	16	0.30	-0.29	44.7(5)	0	0.80	-
B_{ext} = 0	C''	3	0.41	+0.70	44.0(5)	0	0.50	-
	D	11	0.05	-1.89	25.3(5)	90	0.40	0.00

TABLE I - ^{57}Fe Mössbauer parameters for $YBa_2(Fe_xCu_{1-x})_3O_7$: Isomer shift relative to iron metal (IS), Quadrupole splitting (QS), linewidth (Γ), magnetic effective hyperfine field (B_{hf}), angle between the EFG amd B_{hf} (θ), width of the Lorentzian distribution of B_{hf} (RV) and relative intensity (A %) of the different Fe species present in the Mössbauer spectra at 4.2K. η was assumed to be zero.

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