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^{57}Fe MÖSSBAUER STUDIES ON SEMICONDUCTING AND SUPERCONDUCTING La-Ba-Cu-O†

by

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ABSTRACT

$La_{2-x}Ba_xCuO_4$ samples substituted with ^{57}Fe (less than 1%) were studied for $0 \leq x \leq 0.35$. Despite the fact that there is only one Cu site which can be occupied by the iron-substituent, the ^{57}Fe Mössbauer spectra at room temperature show three quadrupole doublets whose intensities were followed in different steps of sample preparation. They are characteristic of Fe^{3+}, and their Mössbauer parameters depend on the Ba content. One of the iron species may be due to defects since it disappears by further heat treatment, while the others are present even in the undoped La_2CuO_4. Magnetic ordering has been found at 4.2 K for samples with 0.5% Fe even in the superconducting samples with $x = 0.15$.

1. INTRODUCTION

In both systems $La_{2-x}M_xCuO_4$ and $YBa_2Cu_3O_{6+\delta}$, the transition from the semiconducting to the superconducting state is induced by increasing x, and they are antiferromagnetically ordered in the semiconducting phase. The Tc values depend crucially on the doping with the metal impurities (M = Sr, Ba, Ca) and on the excess of oxygen.

The modification induced in the electronic structure of Cu ions by doping may help to understand the mechanism responsible for the establishment of the superconducting state. Local information based on Mössbauer spectroscopy for ^{57}Fe substituted compounds may contribute to this aim. Due to the atomic size and chemical similarities it is expected that iron ions may occupy the Cu sites in all the Cu based oxides.

The Mössbauer study of $^{57}Fe:YBa_2Cu_3O_7$ allowed us to establish a preferential occupation of Cu(1) site by iron which may have several different oxygen configurations [1]. In contrast, for $La_{2-x}Ba_xCuO_4$ the Mössbauer results are expected to be easier to interpret since there is only one site for Cu ions in a distorted oxygen octahedron.

The $La_{2-x}Ba_xCuO_4$ system has the crystal structure of K_2NiF_4 for x = 0, and by increasing the Ba concentration up to x = 0.15 it undergoes an orthorhombic to tetragonal phase transition [2]. From the X-ray studies it has been established that in the orthorhombic phase the 4-fold axis of the CuO_6 octahedron is tilted versus the a-b plane. This is not the case in the tetragonal phase [3]. Recent neutron diffraction data indicate that this tilting has two different

orientations in the orthorhombic phase [4]. The charge compen-
sation due to the doping with Ba metal is claimed to induce
holes which are responsible for the supercurrents. These holes
may influence the electronic configuration of ions in the Cu
site if they are localized nearby.

Some Mössbauer studies of Fe substituted La-M-Cu-O
[5] have already been published, but apart from the observation
of an asymmetric doublet at room temperature (RT), no detailed
correlation of the Mössbauer spectra with the M content has
been attempted.

In this work, we will address our interest towards
the sensittivity of the Fe ions in the $La_{2-x}Ba_xCuO_4$ to the
local structure and to the presence of magnetic ordering found
at 4.2 K for samples with 0.5% Fe concentration.

2. EXPERIMENTAL

Independent batches for samples of $La_{2-x}Ba_xCuO_4$ con-
taining 0.5% ^{57}Fe have been prepared in two steps: batch 1
(for x = 0.0, 0.15, 0.25 and 0.35) and batch 2 (for x = 0.0,
0.005, 0.02, 0.05, 0.07, 0.10 and 0.15). Firstly pellets of
appropriate amounts of La_2O_3, $BaCO_3$, CuO and $^{57}Fe_2O_3$ were
synthesized in air at 900°C for 20h, followed by regrinding and
sintering twice under the same conditions. Samples examinated at
this stage of preparation were indexed as samples I. The next
step involves the regrinding and heating at 1100°C for 20h and
cooling down to 600°C at a rate of 50°C/h; then the samples
were kept at this temperature for 50h, and cooled to RT at

the same rate. These samples were named II. Samples from batch 1 were analysed in steps I and II, while those from batch 2 were analysed only in step II.

The X-ray diffraction studies of these samples agree with the published data: for $x < 0.15$ they have the K_2NiF_4 orthorhombic structure, with degree of orthorhombicity decreasing with Ba content. For $x \geq 0.15$ all the samples have the tetragonal structure.

3. RESULTS AND DISCUSSION

3.1. Local Structure at Cu Sites in $La_{2-x}Ba_xCuO_4$ Compounds

Despite the fact that there is only one Cu site, the Mössbauer spectra at RT for the iron-substituent show the presence of three quadrupole doublets which we relate to species A, B and C, indicating different surroundings for iron; their Mössbauer parameters depend on the Ba content. In the case of batch 1 the samples were analysed also after several heat treatments as reported in reference [6]. From those results it was clear that species B is related with some defects present in badly formed samples, since it disappears with further heat treatment as can be seen in figure 1.

We report here a detailed Mössbauer study, mainly at RT, for well prepared $La_{2-x}Ba_xCuO_4$ samples II (batch 1 and 2). A wider concentration range is covered, allowing the study of the effect of Ba through the X-ray and Mössbauer spectra.

The Mössbauer spectra at RT for these samples

exhibit only the presence of species A and C, and their Möss-
bauer parameters are shown in Table I. Figure 2a shows that
the intensity of doublet C decreases with Ba content going to
zero for x = 0.15, when the tetragonal structure is stabilized
by the doping. In figure 2b the dependence of the quadrupole
splitting (QS) and of the relative intensities with composition
is shown. There is a smooth variation of the QS values with Ba
content suggesting that the Fe-substituent senses the change
in the lattice parameters induced by the doping.

The present result could be understood as a perturb-
ation of the local electronic structure at the Cu site due to
the presence of holes formed to compensate the difference of
charge of La^{3+} and Ba^{2+} ions. However, this attractive expla-
nation cannot be kept after the analysis of the Mössbauer
spectra obtained for the undoped La_2CuO_4. Even in this sample
the two Fe species (A, C) are observed.

The possible explanation for the presence of two
iron species in the $La_{2-x}Ba_xCuO_4$ series of compounds have to
be based on structural information available for this system.
The essential fact for the discussion is that the two species
are also observed for x = 0.0. For this reason, we have to
exclude the possibility that one of them is due to the loca-
lization of additional charges on the Cu site induced by the
Ba doping.

It is also possible to assume that the two iron
species reflect the two orientations for the tilting of the
oxygen octahedra. In this case, one has to conclude that only
one orientation remains when the tetragonal structure is
stabilized by the Ba doping. This interpretation is consistent

with the low temperature results, obtained from the neutron diffraction studies [4].

A further alternative would be the association of one species (A) with the occupation of the Cu site in a regular octahedron, while the other one (C) would be related with the presence of oxygen vacancies near to the Cu site. According to our results the concentration of such vacancies should decrease with the Ba content. Indeed, such a dependence of oxygen vacancies on the Ba content has been recently reported [7] showing different behavior for Ca and Sr doping. Mössbauer studies in $^{57}Fe:La_{2-x}M_xCuO_4$ samples (M = Ca, Sr) are in progress in order to test this assignment. However, in the pure La_2CuO_4, it is known that under special conditions, instead of oxygen vacancies, an excess of oxygen is present leading to a superconducting phase [8]. More experiments are necessary to decide for one of the possibilities discussed above.

3.2. Magnetic Ordering in La_2CuO_4 and $La_{1.85}Ba_{0.15}CuO_4$ at 4.2K

The phase diagram of $La_{2-x}Ba_xCuO_4$ [9] is known to range from an antiferromagnetic through a spin glass like region to the superconducting non magnetic region. However, the 4.2K Mössbauer spectra of the La_2CuO_4 and $La_{1.85}Ba_{0.15}CuO_4$ samples with 0.5% of ^{57}Fe exhibit magnetic hyperfine splitting in both cases as we have already reported [6].

The analysis of the experimental data was performed with a complete Hamiltonian allowing arbitrary angles between EFG tensor and B_{hf}. A distribution of Lorentzian shape for

B_{hf} was used, and the fit was tried, at first, by fixing the QS to RT values, and then leaving them free.

Figure 3a displays the magnetically split pattern for La_2CuO_4 showing an additional weak paramagnetic impurity. The asymmetry of the outer line intensities is compatible with two sextets, having different quadrupole interactions consistent with the RT data. The fit of this data gave QS values of 1.5 mm/s and 1.72 mm/s for species A and C respectively. This result indicates that the species A is more sensitive to temperature than C. The B_{hf} values obtained with such a fit for species A and C were 47 T and 49 T respectively. Both fields are perpendicular to the principal component of the EFG which, according to the known crystal structure, should be in the c direction. Notably neutron diffraction data for the La_2CuO_4 system [10] show that also the Cu moments are perpendicular to the same direction. An additional information, which may be relevant for the understanding of the origin of both species is that only species C has a distribution in the B_{hf} values.

The broad absorption lines of the magnetically split Mössbauer spectra at 4.2 K obtained for $Fe:La_{1.85}Ba_{0.15}CuO_4$ sample (figure 3b) are typical for a distribution of B_{hf} at the iron site. Apart of this distribution, a clear change was observed in the angle θ between the principal axis of EFG and the B_{hf} direction. The best fit resulted in a small Lorentzian distribution of B_{hf} around an average value of 45 T and a QS = 1.30 mm/s and an angle θ of 70 degrees. This fit of the

data may not be unique, however the distribution of B_{hf} and the change of θ, as compared with $Fe:La_2CuO_4$, can be a consequence of a perturbation induced by the Ba atoms in the ordering of the Cu moments. Mössbauer measurements as a function of temperature and Ba concentration could give more information about the freezing mechanism of the Fe magnetic moments.

The analysis of the magnetically split spectra of La_2CuO_4 (figure 3a) and $La_{1.85}Ba_{0.15}CuO_4$ (figure 3b) may be understood on the basis of the following arguments. The Fe ions,in this low concentration limit, are sensitive to the magnetic ordering of Cu moments: in antiferromagnetic La_2CuO_4 the Fe moments are well aligned, whereas they are perturbed by the Ba doping in the $La_{1.85}Ba_{0.15}CuO_4$. However, it cannot be excluded that the presence of Fe ions may induce a long range order involving also the Cu moments. Another hypothesis is that B_{hf} is influenced by a local perturbation induced by the Fe moments. The choice among one of these possibilities cannot be decided only on the basis of Mössbauer spectroscopy alone.

From the μSR measurements in the $La_{2-x}Sr_xCuO_4$ compounds, the coexistence of superconductivity with magnetic ordering was found for $x \leq 0.08$ [11], which could still be understood on the basis of two separated phases. However, very recently, similar results were observed by μSR [12] measurements on a single crystal of $La_{2-x}Sr_xCuO_4$ with $x = 0.15$. On the basis of these results, we can conclude that Fe-substitution in a concentration of 0.5% is sensitive to the magnetic ordering of Cu moments, which can still be enhanced by the

Fe ions. This result implies that substituents can be taken as a good local probe for the coexistence of magnetic and super-conducting phases in the same oxide sample.

CAPTION FOR FIGURES AND TABLE

Fig. 1 - Mössbauer spectra at RT of samples from batch 1:

    a) samples I (treated twice at $900^\circ C$ for 20h);

    b) samples II (after the final treatment at $1100^\circ C$ for 20 h).

Fig. 2 - a) Quadrupole splittings of species A and C as a function of Ba concentration.

    b) Relative absorption areas of species C as a function of Ba concentration.

Fig. 3 - Mössbauer spectra at 4.2 K:

    a) La_2CuO_4 with 0.5% ^{57}Fe.

    b) $La_{1.85}Ba_{0.15}CuO_4$ with 0.5% ^{57}Fe.

Table I. Fitted hyperfine parameters for samples II, batch 1 and 2: IS = isomer shift (ref. Fe metal); QS = quadrupole splitting.
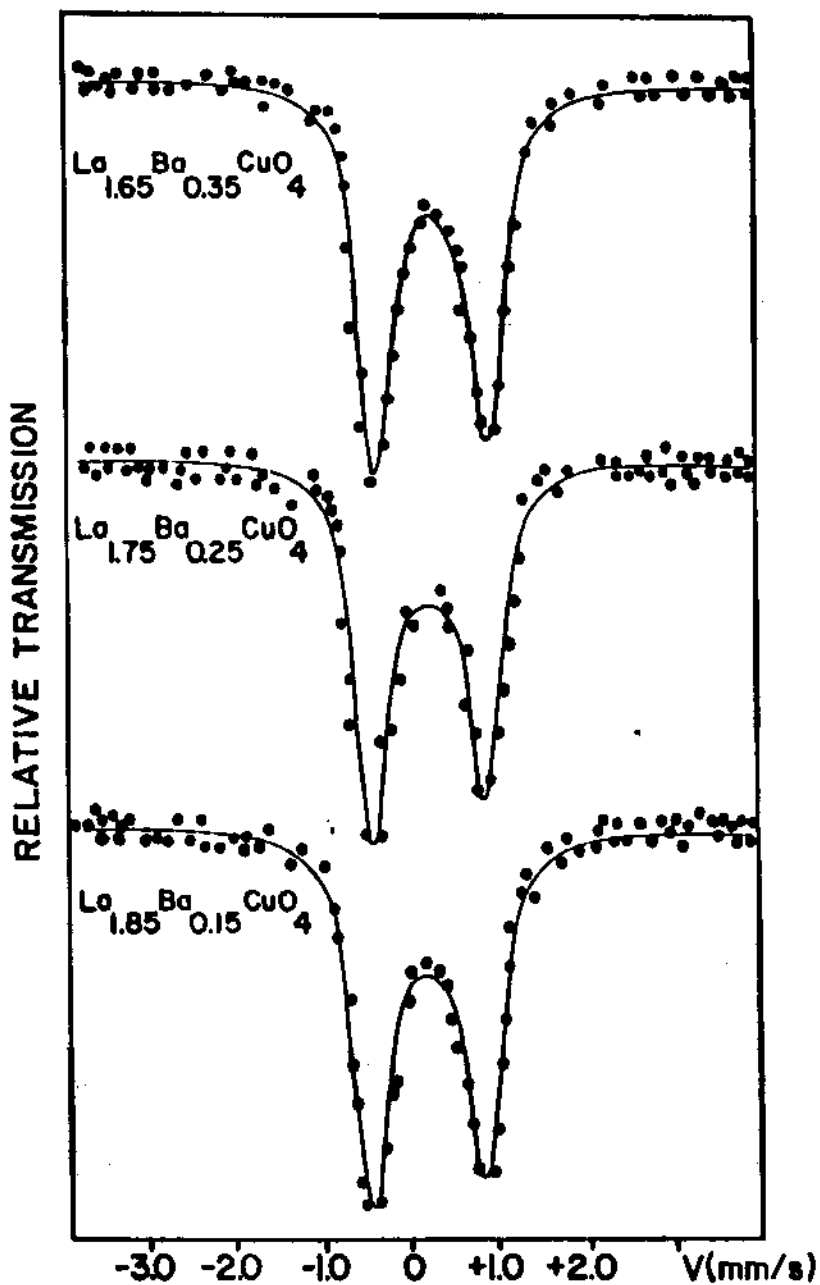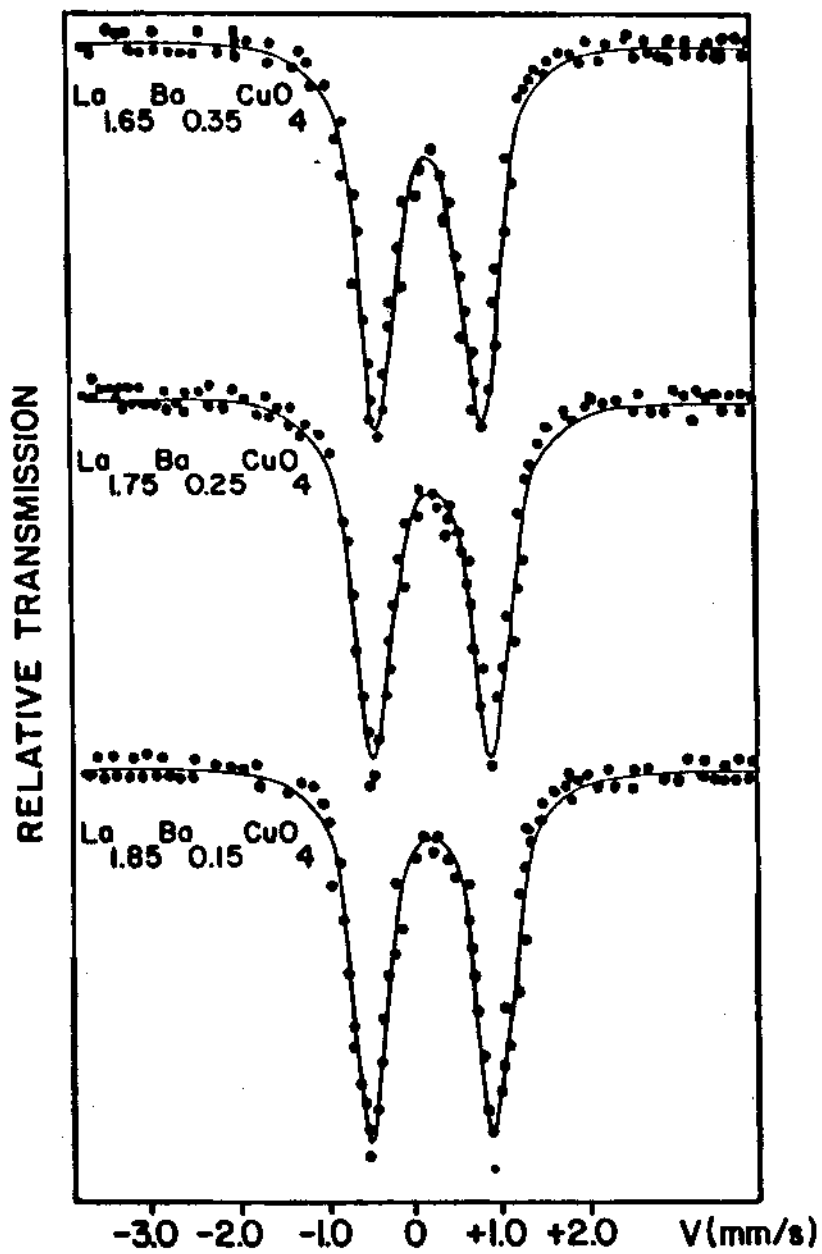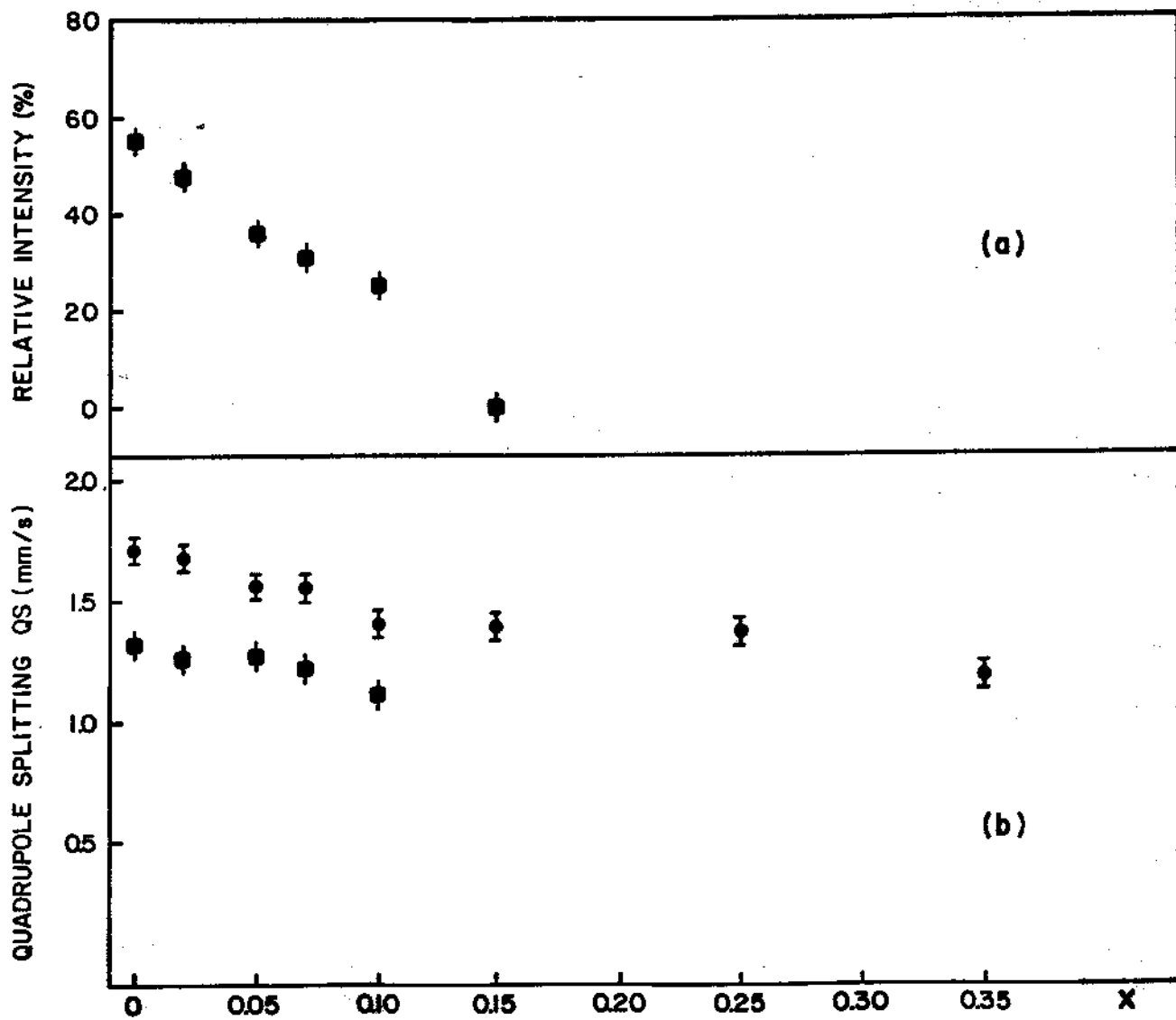
Fig. 1a

Fig. 1b

Fig. 2

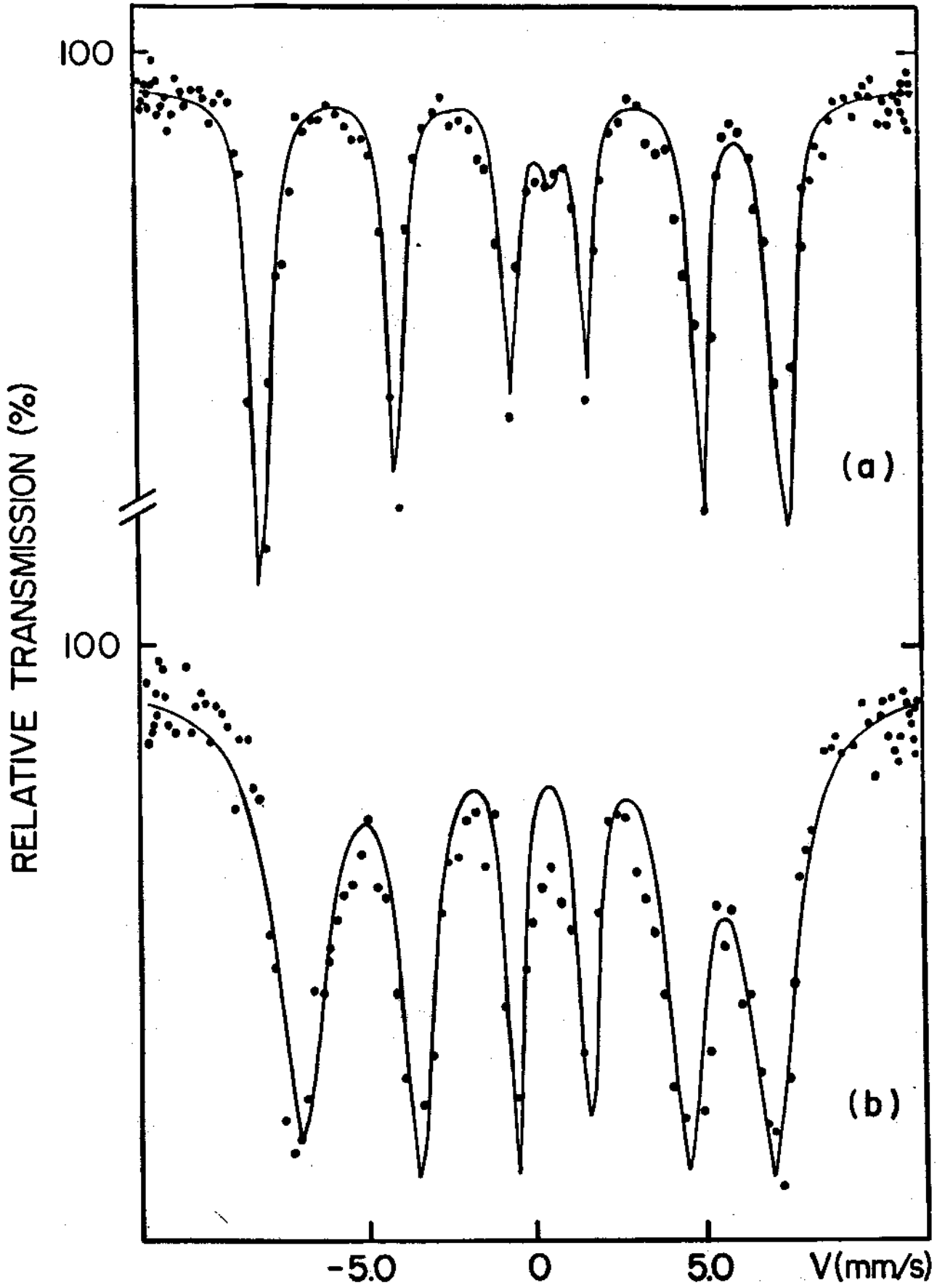Fig. 3

La$_{2-x}$Ba$_x$CuO$_4$	Species A		Species C	
	IS mm/s	QS mm/s	IS mm/s	QS mm/s
x = 0	0.30	1.71	0.31	1.33
x = 0.005	0.31	1.62	0.32	1.14
x = 0.02	0.31	1.69	0.30	1.26
x = 0.05	0.31	1.57	0.30	1.28
x = 0.07	0.30	1.56	0.32	1.22
x = 0.10	0.29	1.40	0.26	1.11
x = 0.12	0.29	1.39	0.28	0.89
x = 0.15	0.29	1.40	-	-
x = 0.25	0.29	1.37	-	-
x = 0.35	0.25	1.19	-	-

TABLE I

REFERENCES

[1] E. Baggio-Saitovitch, I. Souza Azevedo, R.B. Scorzelli, H. Saitovitch, S.F. da Cunha, A.P. Guimarães, P.R. Silva and A.Y. Takeuchi, Phys. Rev. B 37(13) (1988) 7967.

[2] T. Fujita, Y. Aoki, Y. Maeno, J. Sakurai, H. Fukuba and H. Fujii, Jpn. J. Appl. Phys. 26 (1987) L368.

[3] J.D. Jorgensen, H.B. Schüttler, D.G. Hinks, D.W. Capone,II, K. Zhang, M.B. Brodsky and D.J. Scalapino, Phys. Rev. Lett. 58 (1987) 1024.

[4] T. Egami, W. Dmowski, J.D. Jorgensen, D.G. Hinks, D. W. Capone, II, C.U. Segre and K. Zhang, Progress in High Tem - perature Superconductivity 3 (1988).

[5] J.M. Matykiewicz, C.W. Kimball, J. Gianpintzakis, A.E.Dwight, M.B. Brodsky, B.D. Dunlap, M. Slaski and F.Y. Fradin, Phys. Lett. A 124 (1987) 453.

[6] E. Baggio-Saitovitch, I. Souza Azevedo, R.B. Scorzelli, H. Saitovitch, S.F. da Cunha, A.P. Guimarães, P.R. Silva and L.C. Sampaio, Progress in High Temperature Superconductivity 9 (1988) 368.

[7] Katsuyoshi Oh-Ishi, Masae Kikuchi, Yasuhiko Syono, Norio Kobayashi, Takaaki Sasaoka, Tomokazu Matsuhira, Yoshio Muto and Hiroshi Yamauchi, Jpn. J. Appl. Phys. 27 (1988) L1449.

[8] J.D. Jorgensen, B. Dabrowski, Shiyou Pei, D.G. Hinks, L. Soderholm, B. Morosin, J.E. Schirber, E.L. Venturini and D.S. Ginley, Phys. Rev. B 38 (1988) 11337.

[9] M. Kato, Y. Maeno and T. Fujita, Physica C 152 (1988) 116.

[10] D. Vaknin, S.K. Sinha, D.E. Moncton, D.C. Johnston, J. M. Newsam, C.R. Safinya and H.E. King Jr., Phys. Rev. Lett.58 (1987) 2802.

[11] H. Kitazawa, K. Katsumata, E. Torikai and K. Nagamine, Solid State Commun. 67 (1988) 1191.

[12] K. Nagamine, private communication.