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<sup>57</sup>Fe MOSSBAUER STUDY OF THE SUPERCONDUCTOR



by

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

## ABSTRACT

$^{57}\text{Fe}$  Mossbauer Spectroscopy measurements were made on the  $\text{YBa}_2(\text{Fe}_x\text{Cu}_{1-x})_3\text{O}_y$  superconducting compounds, for the Fe concentrations of 0.1%, 0.5%, 3.0% and 10%. The Mossbauer spectra, obtained at room temperature and at 4.2 K, are dependent on concentration and show several doublets that can be related to different Cu sites, to the number of oxygen vacancies, and to the presence of a high temperature tetragonal phase. This analysis is based on the values of the quadrupole interactions and on the ratio of the absorption areas. Two Mossbauer doublets in the dilute samples (up to 1.0% Fe) are associated to  $^{57}\text{Fe}$  in the  $\text{Cu}_1$  site of the compound.

The 4.2 K spectra of the more concentrated samples (3.0% and 10% Fe) show spin relaxation effects indicating that iron has a magnetic moment.

Magnetic susceptibility measurements show, with increasing iron concentration, a decrease in  $|\chi_g|$  at 77 K and in  $\left|\frac{d\chi_g}{dT}\right|$  near  $T_c$ .

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

## 1. INTRODUCTION

Since the discovery of high- $T_c$  superconductivity in Y-Ba-Cu-O and La-Ba-Cu-O systems, intense efforts have been made to understand and characterize the structure and composition of the phase responsible for the superconductivity [1,2]. It is already accepted that this phase has the composition  $YBa_2Cu_3O_y$  ( $y \approx 6.9$ ), with an oxygen deficient perovskite-like crystal structure [3,4]; this structure is orthorhombic (space group  $Pnmm$ ) and it is stable up to 943 K, undergoing a phase transition to a tetragonal form ( $P4/mmm$ ) above this temperature [4]. The Y and Ba atoms form an ordered superlattice structure and the oxygen vacancies appear to play a critical role in stabilizing the new superconductor  $YBa_2Cu_3O_y$ . X-ray and neutron diffraction studies [5,6,7] have shown the existence of two distinct Cu sites derived from octahedral oxygen coordination:  $Cu_1$  has a square planar coordination due to the presence of two oxygen vacancies in the a axis, whereas the  $Cu_2$  sites have a tetragonal pyramidal coordination due to an oxygen vacancy in the c axis (Fig. 1). The presence of these oxygen vacancies determines the appropriate Cu-O equilibrium distances. The above structure has been recently disputed [8]; it has been proposed that there may exist disorder induced by partial occupation of Y sites by Cu ions and that oxygen vacancies may be located on the  $Cu_2$  planes, leaving the octahedral coordination in the  $Cu_1$  planes. Henceforth, we will use YBaCuO to mean the Yttrium Barium Copper compound with the 123 composition and structure.

Most of the structural studies in the YBaCuO compound were based on X-Ray and neutron diffraction techniques. Additional

information may be obtained from hyperfine (hf) interactions as revealed by local spectroscopies like Nuclear Magnetic Resonance (NMR), Mossbauer Spectroscopy (MS), Electron Paramagnetic Resonance (EPR) and Perturbed Angular Correlations (PAC). These techniques usually require the substitution of the constituent atoms in YBaCuO by appropriate probes. This process must be monitored in order to place the probe in a substitutional site and to avoid destruction of the superconductive behavior.

With the purpose of obtaining information on hf interactions, several samples of YBaCuO were prepared with Cu partially substituted by  $^{57}\text{Fe}$  (from 0.1% to 10%); the resulting Mossbauer spectra are discussed.

## 2. EXPERIMENTAL

The YBaCuO compounds were prepared from a mixture of pure  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$  (94.5% enriched in  $^{57}\text{Fe}$ ). Appropriate amounts of well mixed constituents were pressed into disks (10 mm diameter), then heated to 970 C for about 15 hours in an oxygen atmosphere. The furnace was cooled down at a rate of 50 C/h in order to achieve samples of better quality, following procedures described in the literature [6]. The samples, examined with the Cu K- $\alpha$  radiation, did not display any deviation from the 123 structure up to a concentration of 1.0% Fe (including the re-oxygenated samples). The samples that were quenched or heated under an argon flow showed the well known high temperature tetragonal structure. Above 1.0% iron there was a detectable change in the lattice parameter, this being very marked in the 10% sample. More than one batch was prepared for each Fe

concentration. The critical temperatures  $T_c$  and the superconducting behavior at each concentration was observed by DC magnetization measurements with a vibrating sample magnetometer. The samples were cooled to 77 K in zero magnetic field and then studied under a field of about 60 G, with increasing temperatures.

The  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_y$  Mossbauer absorbers with  $x = 0.001, 0.005, 0.010$  and  $0.100$ , of the appropriate thickness, were prepared from powder obtained by crushing the pressed disks. The Mossbauer measurements were performed in transmission geometry at temperatures of 4.2 K and 293 K, with a  $^{57}\text{Co/Rh}$  source at the same temperature of the absorber. The data were recorded in a 1024-channel analyser and computer fitted with several doublets, each formed by two lines of equal intensity and equal linewidth, without any other constraints.

To study the influence of the oxygen content on the Mossbauer spectra, samples of  $\text{YBaCuO}$  were submitted to several treatments after synthesis in high temperatures: a) sinterization at 700 C in  $\text{O}_2$  atmosphere, for 12 hours, to increase the oxygen content, b) quenching from 1000 C to liquid nitrogen temperatures, to stabilize the high temperature tetragonal phase, c) annealing at 700 C in Ar atmosphere for 2 hours to obtain the tetragonal phase, d) annealing at 350 C in Ar atmosphere for 5 minutes, to reduce the oxygen content and e) annealing at 400 C under  $\text{O}_2$  atmosphere the same sample studied in the tetragonal phase, in order to recover the orthorhombic phase.

### 3. RESULTS AND DISCUSSION

The values of the magnetic susceptibility  $\chi_g = M_g/H$

for different concentrations, as a function of temperature, are presented in Fig. 2. The superconducting transition temperature (here defined as the temperature at which the susceptibility crosses the  $\chi_g = 0$  line), for all concentrations  $c \leq 1.0\%$  Fe, are within 0.2 K of 91.6 K. For  $c = 3.0\%$ , we obtained  $T_c = 88$  K, showing that the superconductivity of YBaCuO is relatively insensitive to the substitution of copper for iron. It should be noted that both the absolute value of the (diamagnetic) susceptibility  $|\chi_g|$  at 77 K and  $|d\chi_g/dT|$  near  $T_c$  decrease with increasing iron concentration, as expected. The critical fields  $H_{C1}$  at 77 K are about 140 G; for samples submitted to a second oxygenation,  $H_{C1}$  is about 185 G. For applied magnetic fields above 150 G, time dependent magnetization effects were observed in some of the samples.

The Mossbauer spectra obtained for Fe-substituted YBaCuO are very dependent on Fe concentration (Figs. 3 and 4). The spectra with 0.1% and 0.5% are very similar and may be fitted with two doublets, with negative isomer shifts (IS) relative to the  $^{57}\text{Co/Rh}$  source. As the iron concentration increases, new doublets appear, and for samples containing 10% Fe ( $x = 0.10$ ) the  $^{57}\text{Fe}$  spectrum is completely different. The Mossbauer parameters obtained from computer fitting several doublets to the experimental data are shown in Table I. To try to understand the present Mossbauer results and in order to correlate them with the proposed structure, we will discuss separately the different species which may be associated to the doublets used in the computer fits.

From the chemical affinity between copper and iron, we expect that the  $^{57}\text{Fe}$  atoms will occupy the Cu sites in the

YBaCuO compound. Although there are only two distinct crystallographic sites for copper, according to the more widely accepted structure [6], we observe at least five species represented by the doublets  $D_1, \dots, D_5$ , corresponding to iron with different local environments. This fact must be related to the presence of oxygen vacancies, to mixed phases or to the occupation of other sites. The  $Y_2BaCuO_5$  compound known as the green phase has also been prepared. Since the corresponding Mossbauer lines do not coincide with any of the five doublets we may say that this phase is not present in detectable amounts in our samples.

A drastic modification is observed in the Mossbauer spectra with 10% Fe substitution, as compared to the less concentrated samples. This may be due to a phase transition from an orthorhombic to a tetragonal crystal structure which has been observed by X-ray analyses [9], this phase transition sets in at 2.0% and it is already complete for 10% of iron substitution. However, the X-ray analysis of our 10% sample revealed that it still has the orthorhombic structure with modified lattice parameters ( $a = 3.888 \text{ \AA}$ ,  $b = 3.865 \text{ \AA}$  and  $c = 11.664 \text{ \AA}$ ) tending to a tetragonal structure. The fact that the quadrupole splitting (QS) obtained for the doublet  $D_5$  in this phase is reduced to 70% of the value obtained for the sample with low iron concentration (Table I) is in agreement with the higher local symmetry of the Cu site in this phase.

The Mossbauer doublet  $D_4$ , present only in the sample with 10% iron (Table I), decreases its intensity on further annealing in  $O_2$  atmosphere (Figs. 4b and 4c).  $D_4$  has also been observed in some other YBaCuO samples, even at low iron

concentration, from other preparations, as in batch 1 (the first set of samples). Therefore it is possible that the doublet  $D_4$  is due to a spurious YBaCuO phase like the tetragonal high temperature phase. In order to clarify this point we have prepared the tetragonal phase either by quenching two new samples ( $c = 0.5\%$  and  $1.0\%$ ) from 1000 C to liquid nitrogen temperatures, or by annealing at 700 C in Ar atmosphere and cooling slowly to room temperature the same samples already studied [4]. The main features of the Mossbauer spectra are independent of the method of preparation, in agreement with our X-Ray data which reveals that a tetragonal structure is obtained in both cases. If we compare the Mossbauer spectra for 0.5% iron concentration obtained from a quenched sample and a sample from batch 1 (Fig. 5), we may conclude that the doublet  $D_4$  belongs to the tetragonal phase of the YBaCuO compound. This doublet is then a signature of an improperly formed superconductor, i.e., lacking oxygen. However, the analysis of the Mossbauer spectra from several samples in the tetragonal phase shows that besides the  $D_4$  doublet, another iron species is present in a smaller proportion, with Mossbauer parameters depending on the method of preparation. The study of iron occupation in the tetragonal phase may help us understand the results obtained for the orthorhombic superconductor phase of YBaCuO compounds.

The neutron diffraction studies indicate that besides the higher symmetry expected for  $Cu_1$  and  $Cu_2$  sites in the tetragonal phase, as compared to the orthorhombic phase, there is a modification in the configuration of oxygen vacancies. The number of vacancies in the tetragonal phase increases markedly in the  $Cu_1$  plane and it is assumed that no oxygen atoms are left



in the x-y plane [10]. Consequently, an atom in the  $Cu_1$  site in the tetragonal phase will see a different local symmetry resulting from the axial coordination of oxygen atoms. The Fe ion that occupies the  $Cu_1$  site will have a quadrupole splitting of the same order in the tetragonal phase, as compared to the orthorhombic phase, despite the fact that the former crystal structure is more symmetrical. We therefore assume that  $D_4$  corresponds to iron in the site  $Cu_1$  in the tetragonal phase.

The assignement of iron species corresponding to the doublets  $D_1$  and  $D_5$  to copper sites in the orthorhombic phase is not easily done : these doublets may correspond either to the occupation of  $Cu_1$  and  $Cu_2$  sites or to the occupation of the same  $Cu_1$  site with different configurations of oxygen vacancies. The first hypothesis is in better agreement with the structure suggested by the neutron diffraction studies of Beno et al. [6], since they established an ordered oxygen vacancy superstructure in the  $Cu_1$  site which rules out the possibility of having more than one oxygen coordination configuration. If we assume (first hypothesis) that  $D_1$  and  $D_5$  are due to iron in  $Cu_1$  and  $Cu_2$  sites their correspondence may be made on the basis of the local symmetry and the corresponding values of the quadrupole splitting: the iron atoms in the  $Cu_1$  site, with square planar oxygen coordination, have a larger quadrupole interaction, according to a point charge calculation, than the Fe nuclei in the  $Cu_2$  site with tetragonal coordination. Therefore the doublet  $D_1$  would be due to iron in  $Cu_1$ , whereas doublet  $D_5$  to iron in the  $Cu_2$  site.

However, the results reported by Izumi et al. [7] suggest that different configurations of oxygen vacancies may exist for  $Cu_1$  sites and, consequently, the Fe ion occupying this

site would feel more than one local symmetry. Due to partial occupation of the oxygen sites in the b axis (Fig. 1), the  $\text{Cu}_1$  planes may consist of alternate octahedral, tetragonal and square planar  $\text{Cu}_1$  sites, which could be associated to doublets  $\text{D}_5$  and  $\text{D}_1$ . This hypothesis requires a preferential occupation of the  $\text{Cu}_1$  site by iron, which may be understood on the basis of the allocation of  $\text{Cu}^{3+}$  and  $\text{Cu}^{2+}$  ions to  $\text{Cu}_1$  and  $\text{Cu}_2$  sites: it is claimed that  $\text{Cu}^{3+}$  is in the  $\text{Cu}_1$  plane and it may occupy 70% of this site; the  $\text{Cu}_2$  site is only occupied by  $\text{Cu}^{2+}$  [11]. Since in the oxide used to prepare the samples iron is in the 3+ state, it is expected that it will occupy preferentially  $\text{Cu}_1$  sites.

The analysis of the relative absorption areas of the Mossbauer doublets ( $\text{D}_1$ ,  $\text{D}_4$  and  $\text{D}_5$ ) for the same samples in the orthorhombic and tetragonal phase, may help towards the proper assignment of iron species to Cu sites. The relative absorption area of the doublet  $\text{D}_4$  (tetragonal phase) can only be formed from the simultaneous decrease in the intensity of doublets  $\text{D}_1$  and  $\text{D}_5$  (orthorhombic phase) as can be seen from the sample with 0.5% Fe (Table I). This assumption is also supported by the re-oxygenation at 400 C of the sample previously studied in the tetragonal phase, since the two doublets  $\text{D}_1$  and  $\text{D}_5$ , which characterize the orthorhombic phase, reappear. Thus, we may conclude that in our samples  $\text{D}_1$  and  $\text{D}_5$  are due to iron in the same  $\text{Cu}_1$  planes, both contributing to the formation of  $\text{D}_4$  in the tetragonal phase. More X-Ray and neutron diffraction studies are required to establish with confidence the structure of the compounds having different oxygen contents.

For some samples, in order to obtain good computer fits to the Mossbauer spectra, it is necessary to admit the presence of

the doublets  $D_2$  and  $D_3$ . The relative intensity of doublet  $D_2$  is always small, indicating that it is related to an iron species with low probability of formation. It can be associated with iron in  $Cu_2$  site or to iron in  $Cu_1$  site with a distorted octahedral coordination. This last hypothesis seems to be more probable since its Mossbauer parameters are comparable to those obtained for 1% iron in  $LaBaCuO_4$  [12], where the copper has a distorted octahedral symmetry without the oxygen vacancy. The doublet  $D_3$  probably belongs to phases with some un-reacted iron oxide or iron hydroxide.

Moreover, the  $YBaCuO$  samples were tested for aging effects by repeating both the magnetic susceptibility and the Mossbauer measurements within a two month period. The  $T_C$  values and the Mossbauer spectra did not show any appreciable modification, except for a small amount of precipitation of iron oxide or hydroxide, associated with the doublet  $D_3$ .

The  $^{57}Fe$  isomer shift values obtained for  $D_1$  and  $D_5$  in the  $YBaCuO$  compound (Table I) are far from the range for  $Fe^{3+}$  and cannot be attributed to iron in the high-spin configuration, which is usual in the oxides; the low-spin configuration for iron is not expected to occur in these systems. These IS results are consistent with a metallic character for the  $Cu_1$  and  $Cu_2$  sites obtained from local electronic density of states calculations [13].

The Mossbauer spectra obtained at 4.2 K for samples with 1.0%, 3.0% and 10% Fe are shown in Fig. 6. Samples with concentration of 3.0% Fe and above show spin-spin relaxation effects, indicating that iron in these cases has a magnetic moment which relaxes with a period comparable to the nuclear Larmor precession time. The static regime for the magnetic spectra has been looked for by

cooling the 10% sample to 1.6 K or by applying an external field of 40 kG (at  $T \sim 10$  K) without success. This experiment would allow the determination of the static magnetic interaction, to obtain the maximum effective field at the iron nucleus. The temperature dependence of the relaxation Mossbauer spectra suggests that the sign of the quadrupole splitting for the doublet  $D_5$  is positive [14]. This result cannot be easily correlated with the d-character electrons of the calculated band structure, reported for the YBaCuO compound [13], since the presence of iron ions as impurities strongly perturbs the local electronic structure.

The above results and discussion confirm that the investigation of hf interactions in the YBaCuO compounds can supplement structural studies employing other techniques, as neutron diffraction and X-Ray diffraction. However, the calculation of local electronic densities of states is important for the understanding of the hyperfine interactions and structural characteristics of these compounds. The present results do not show how the hf parameters and f factor change around the superconducting transition temperature; such studies are in progress.

#### 4. ACKNOWLEDGEMENTS

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## FIGURE CAPTIONS

- FIG. 1** - Crystal structure of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_y$  compound.
- FIG. 2** - Temperature dependence of the magnetic susceptibility  $\chi_g = M_g/H$  (o). The crosses (+) represent samples submitted to a second oxygenation (see text).
- FIG. 3** - Room temperature  $^{57}\text{Fe}$  Mossbauer spectra of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_y$  samples with low iron concentration (0.1% Fe, 0.5% Fe and 1.0% Fe).
- FIG. 4** - Room temperature  $^{57}\text{Fe}$  Mossbauer spectra of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_y$  for a) 3.0% Fe; b) 10% Fe; c) 10% Fe after annealing in  $\text{O}_2$  atmosphere.
- FIG. 5** - Room temperature Mossbauer spectra of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_y$  with 0.5% Fe: a) sample from batch 1 (see text) and b) sample quenched from 1000 C.
- FIG. 6** -  $^{57}\text{Fe}$  Mossbauer spectra of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_y$  at 4.2 K, for a) 1.0% Fe; b) 3.0% Fe and c) 10.0% Fe.
- FIG. 7** -  $^{57}\text{Fe}$  Mossbauer spectra of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_y$  with 10% Fe at different temperatures, showing spin relaxation effects.

## TABLE CAPTIONS

- Table I** -  $^{57}\text{Fe}$  Mossbauer parameters isomer shift relative to iron metal ( $\delta$ ), quadrupole interaction ( $\Delta E$ ), linewidth ( $\Gamma$ ) and relative intensity (A) of the different doublets present in the  $\text{YBa}(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_y$  spectra at room temperature. Typical errors are:  $\delta$  ( $\pm 0.006$  mm/s),  $\Delta E$  ( $\pm 0.02$  mm/s),  $\Gamma$  ( $\pm 0.02$  mm/s) and A ( $\pm 4\%$ ).

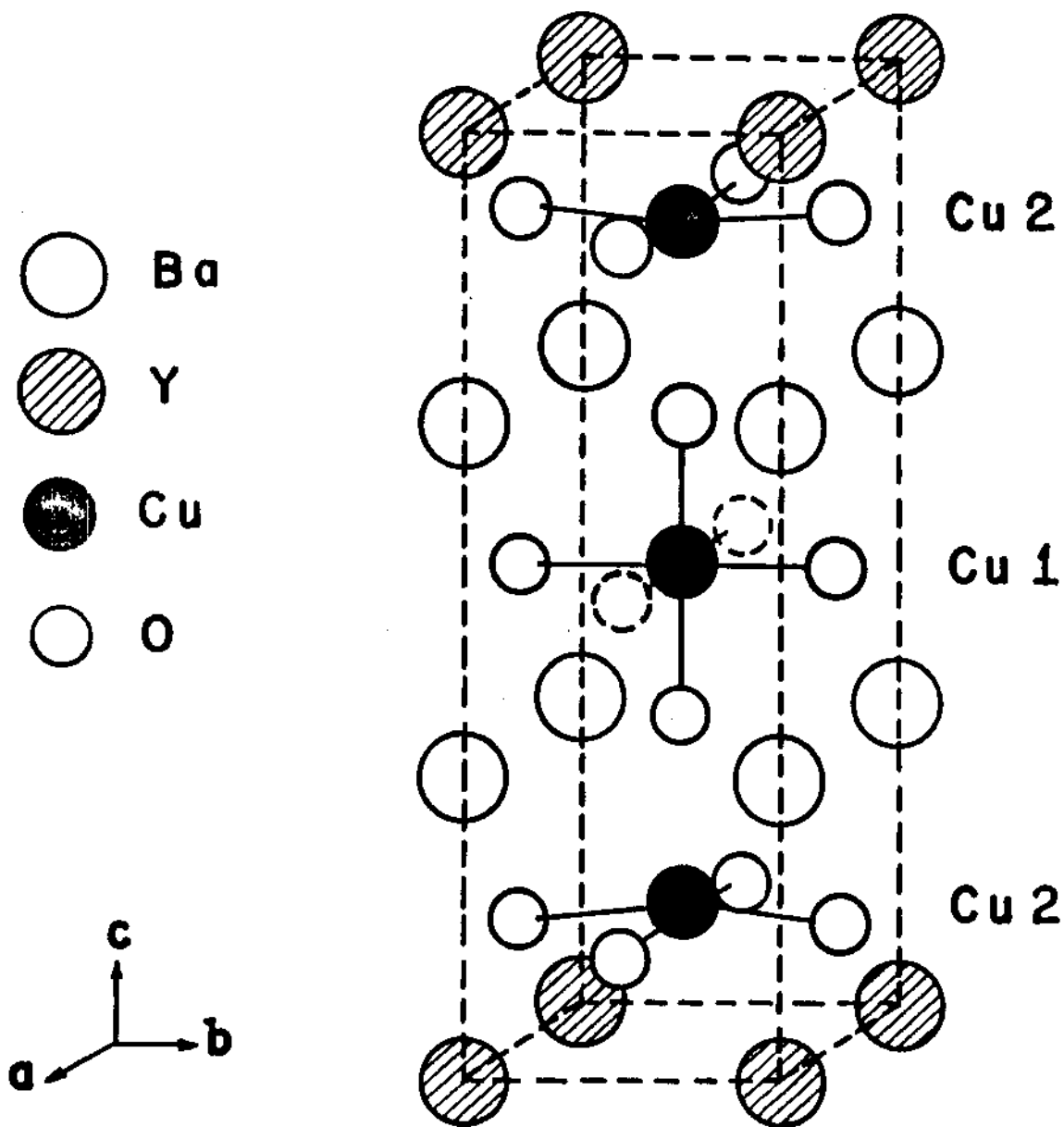
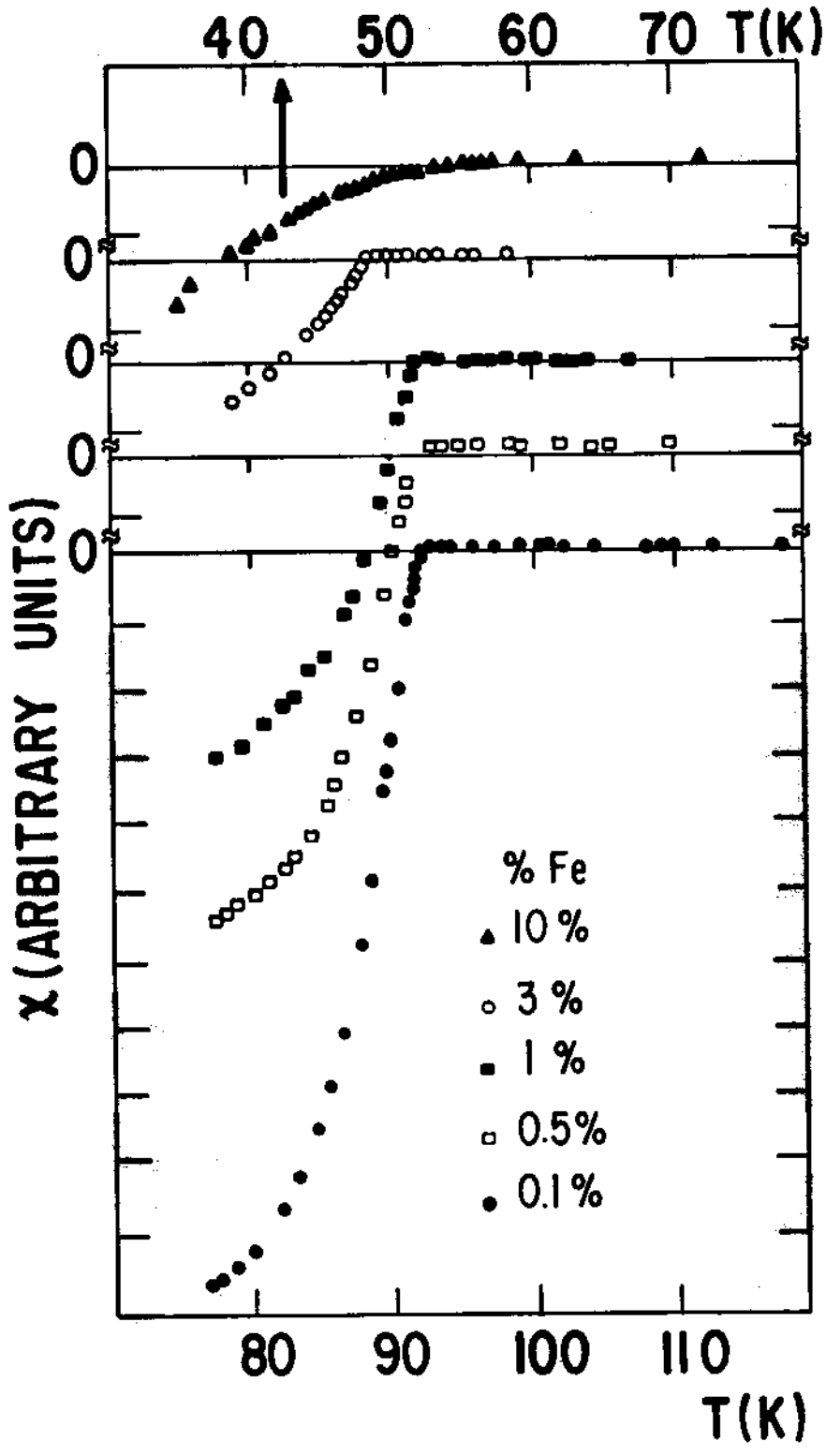


Fig. 1



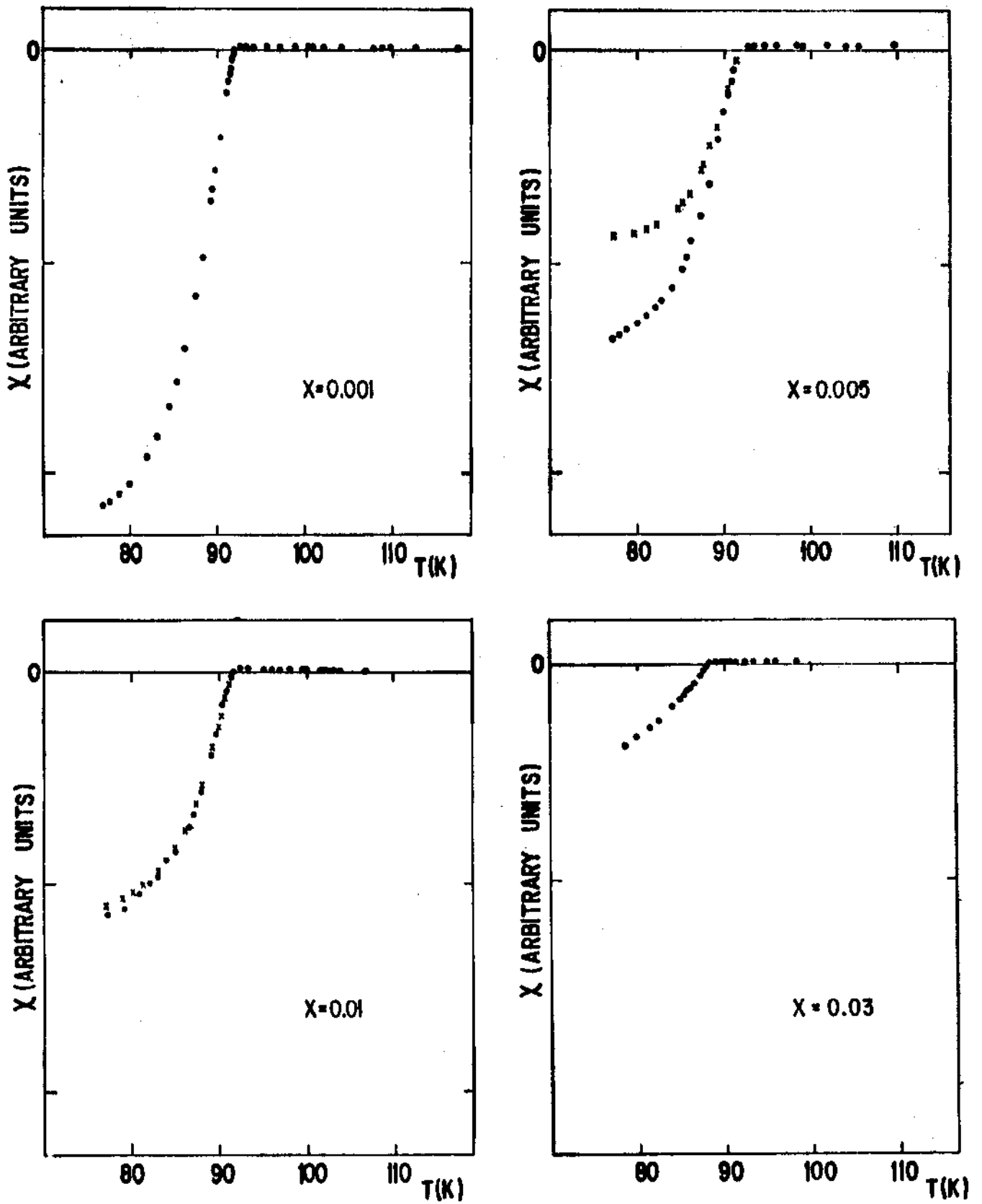


Fig. 2



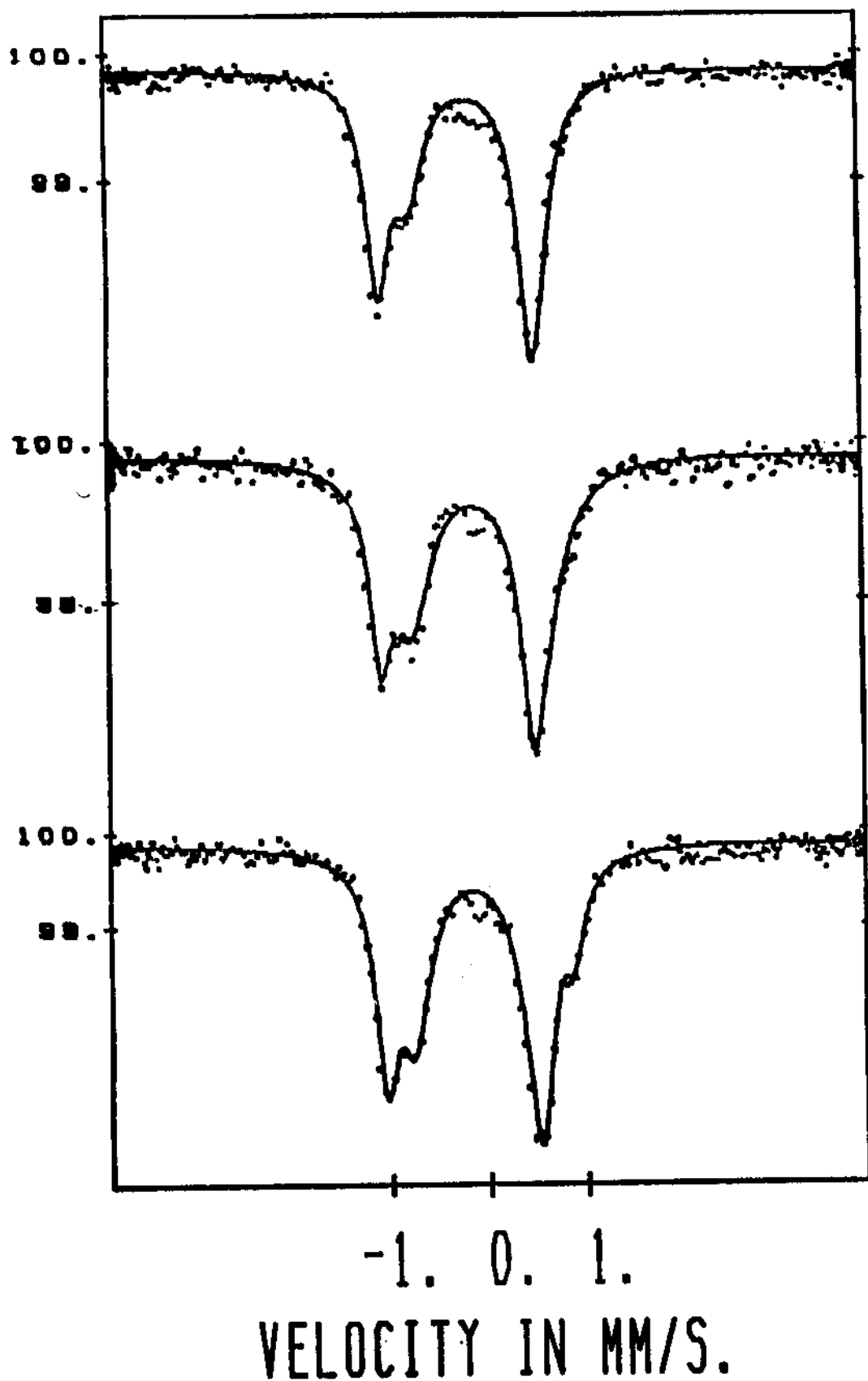


Fig. 3

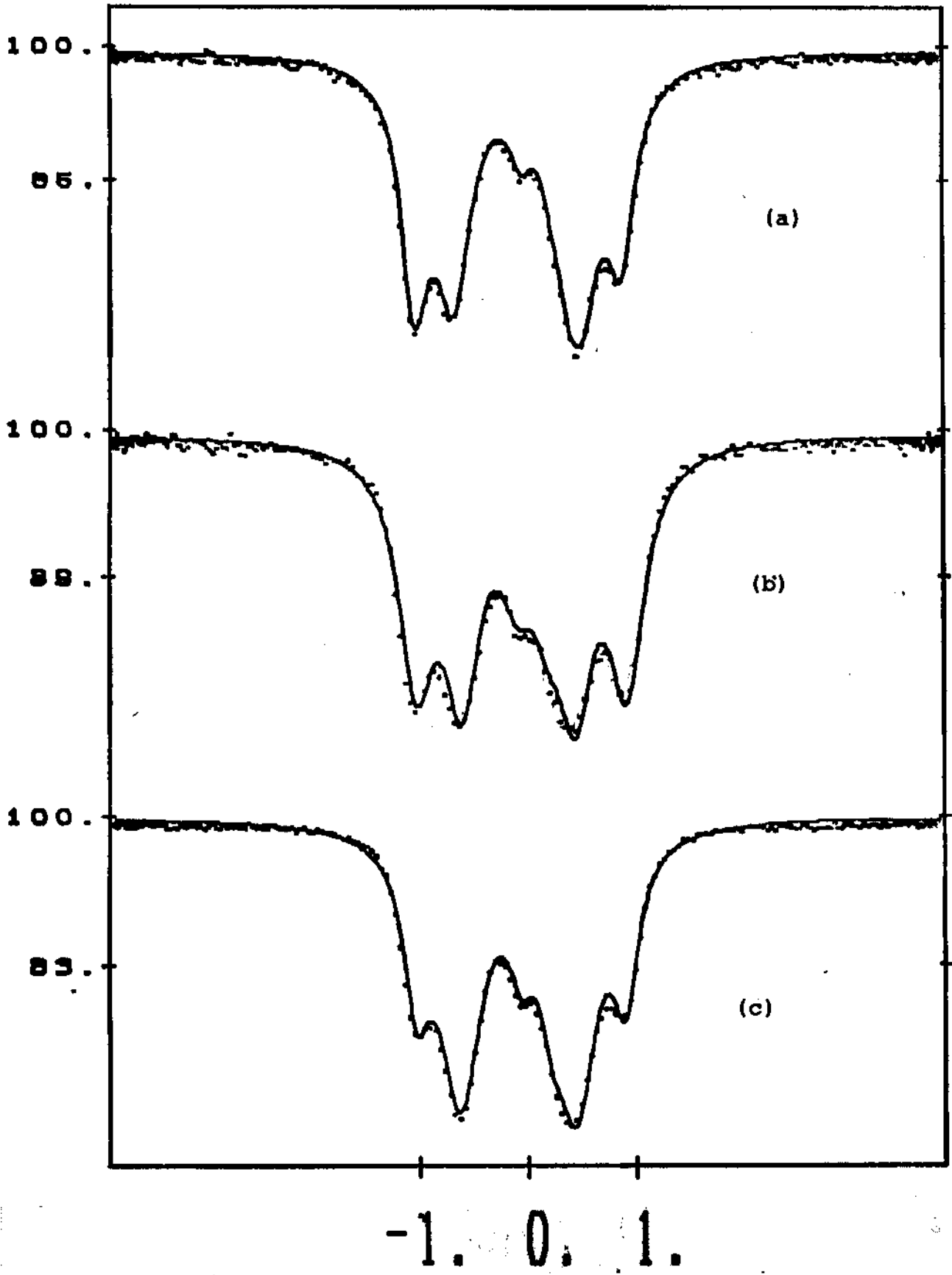


Fig. 4

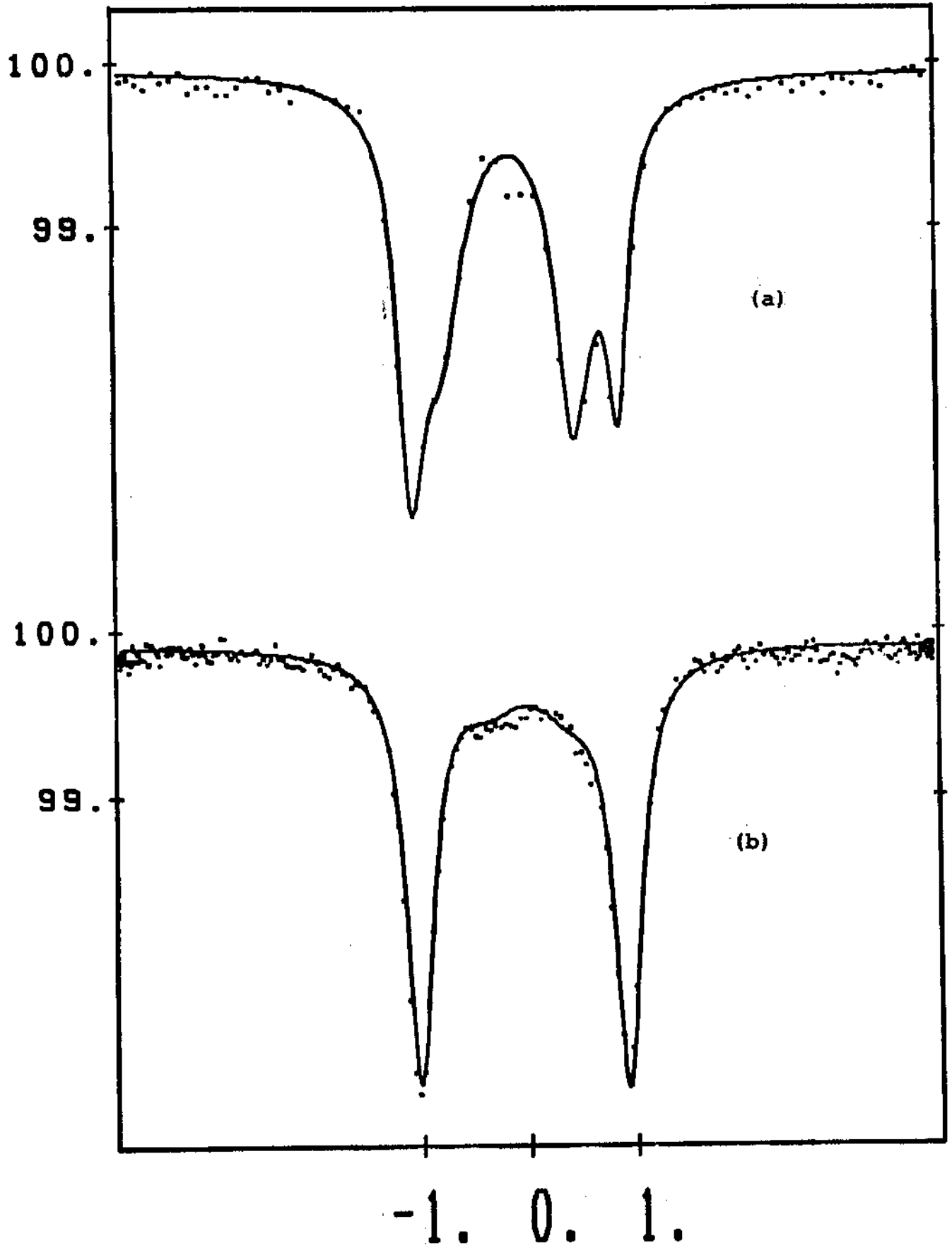


Fig. 5

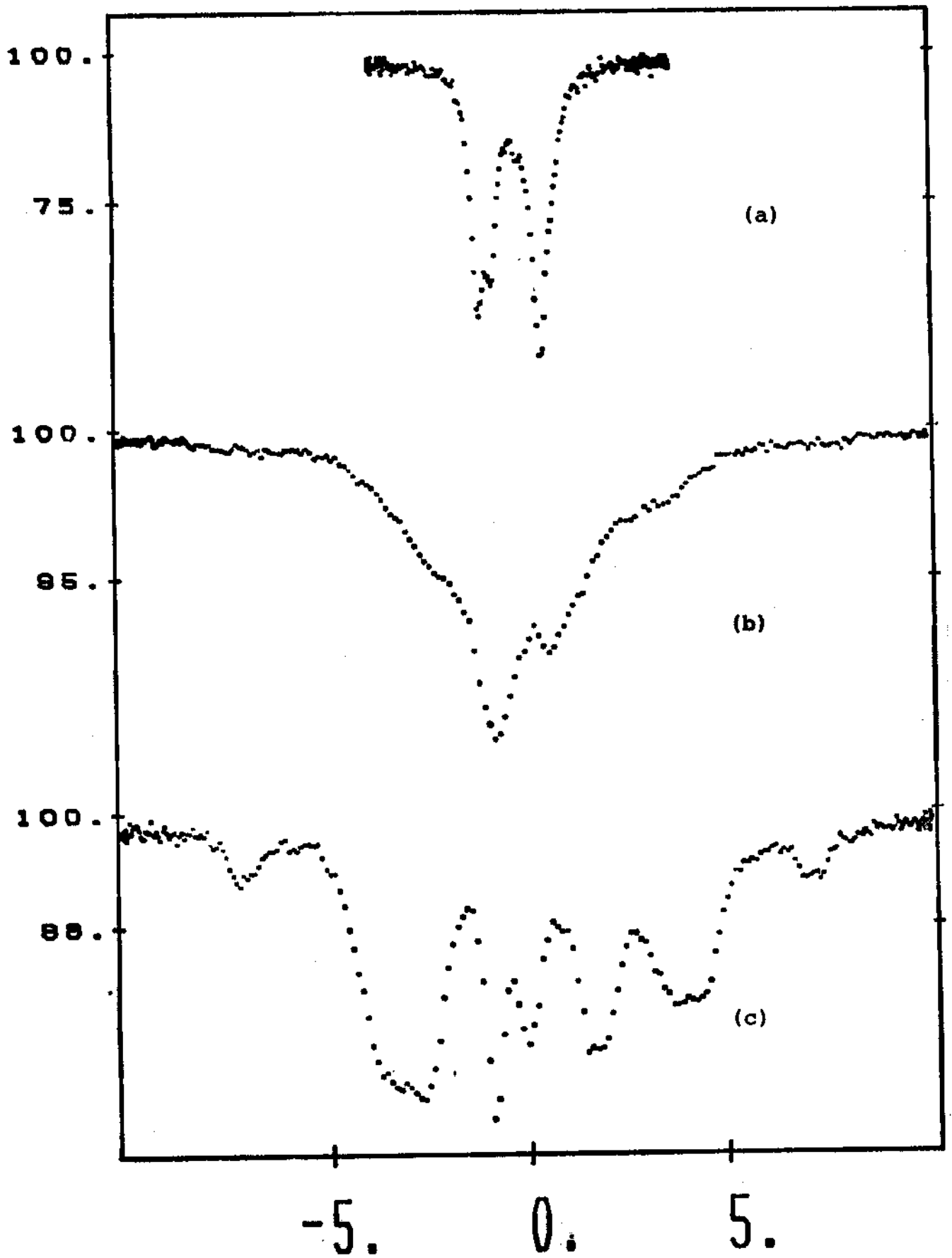


Fig. 6

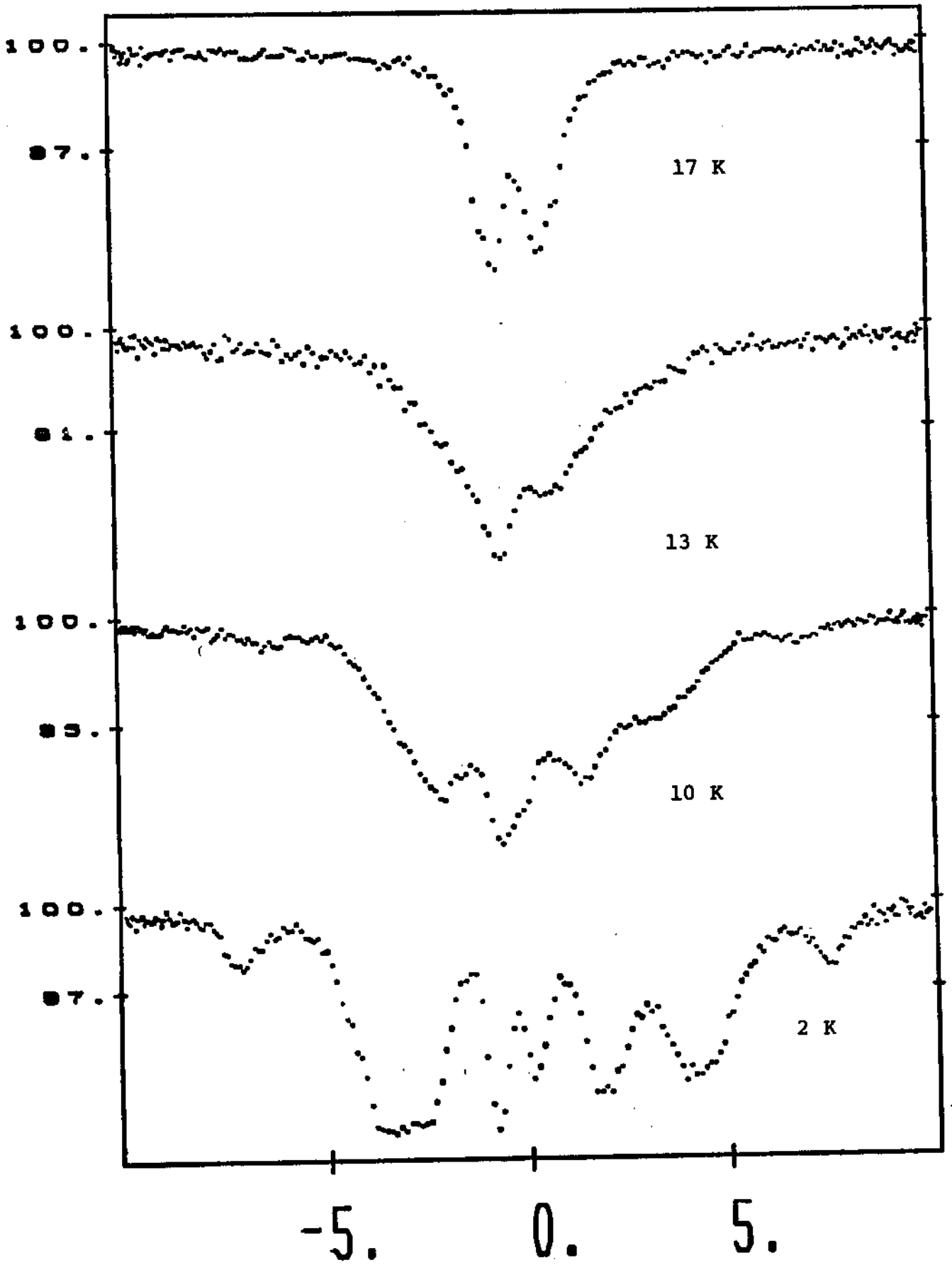


Fig. 7

TABLE I  
 $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_y$

| C(x)   | D <sub>1</sub> |      |         | D <sub>2</sub> |      |         | D <sub>3</sub> |      |         | D <sub>4</sub> |      |         | D <sub>5</sub> |      |         |
|--------|----------------|------|---------|----------------|------|---------|----------------|------|---------|----------------|------|---------|----------------|------|---------|
|        | δ              | ΔE   | Γ A     | δ              | ΔE   | Γ A     | δ              | ΔE   | Γ A     | δ              | ΔE   | Γ A     | δ              | ΔE   | Γ A     |
| 0.1    | -0.176         | 1.55 | 0.30 61 | —              | —    | —       | —              | —    | —       | —              | —    | —       | —              | —    | —       |
| 0.5    | -0.186         | 1.55 | 0.23 30 | —              | —    | —       | —              | —    | —       | —              | —    | —       | —              | —    | —       |
| 1.0    | -0.156         | 1.59 | 0.27 44 | 0.174          | 1.62 | 0.24 13 | —              | —    | —       | —              | —    | —       | —              | —    | —       |
| 3.0    | -0.196         | 1.38 | 0.24 7  | —              | —    | —       | 0.204          | 0.31 | 0.25 9  | 0.024          | 1.95 | 0.30 29 | 0.024          | 1.19 | 0.42 55 |
| 10     | —              | —    | —       | —              | —    | —       | 0.194          | 0.26 | 0.29 10 | 0.054          | 2.00 | 0.33 32 | 0.034          | 1.07 | 0.52 58 |
| 0.1*   | -0.185         | 1.50 | 0.22 31 | 0.224          | 1.61 | 0.20 9  | —              | —    | —       | —              | —    | —       | —              | —    | —       |
| 0.5**  | —              | —    | —       | —              | —    | —       | 0.174          | 0.50 | 0.55 13 | 0.074          | 1.97 | 0.32 73 | 0.084          | 1.13 | 0.50 14 |
| 0.5*** | —              | —    | —       | —              | —    | —       | 0.134          | 0.74 | 0.67 18 | 0.064          | 1.96 | 0.31 82 | —              | —    | —       |

\* - sample annealed under argon atmosphere at 450 C.

\*\* - sample annealed under argon atmosphere at 700 C.

\*\*\* - sample quenched from 1000 C to liquid nitrogen temperature.

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