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MAGNETIC PHASE PRESENT IN $YBa_2(Cu_{1-x}Fe_x)_3O_{6+\delta}$ OXIDES*

by

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The Mössbauer study of ^{57}Fe: $YBa_2Cu_3O_{6+\delta}$ oxides was very important to establish the preferential occupation of Cu(1) site by Fe at very low concentrations. Recent determination of antiferromagnetic ordering for Cu moments in Cu(2) sites ($T \sim 450K$) and our early observation of a small proportion of a magnetic phase at room temperature for Fe:$YBa_2Cu_3O_6$ lead us to perform systematic studies of $YBa_2(Cu_{1-x}Fe_x)_3O_6$ with $x = 0.005$, 0.03, 0.05, 0.10 and 0.15 in order to obtain information about the iron occupation of Cu(2) sites.

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

1. INTRODUCTION

The superconductor oxide $YBa_2Cu_3O_7$, with orthorhombic structure reveals a transition to a tetragonal semiconductor phase when the oxygen content goes below 6.3. The ^{57}Fe Mössbauer studies in both phases allowed the determination of preferential occupation of Cu(1) site in the low concentration limit[1]. This result has been confirmed by neutron and electron diffraction experiments[2,3]. Moreover the iron species characteristic of tetragonal phase (IS = 0.06mm/s, QS=2.0mm/s) may be present in the orthorhombic $YBa_2Cu_3O_7$ which has not the proper oxygen content, and this fact led several authors to attribute its Mössbauer parameters to iron in Cu(2) site.

The preferential occupation of Cu(1) sites by iron may be modified at higher concentrations mainly if we consider that the Cu(2) site is twice more abundant than the Cu(1) site. The iron species corresponding to the Cu(2) sites should have an electronic configuration resulting in different hyperfine parameters compared with the Cu(1) site, and consenquently produce new absorption lines in the Mössbauer spectra. However, the Mössbauer studies for higher iron concentration in the $YBa_2(Cu_{1-x}Fe_x)_3O_7$, x=0.10 and 0.15 do not indicate the presence of new absorption lines which could be attributed to the occupation of Cu(2) sites[4].

The aim of this work is to obtain additional information about the occupation of the Cu(2) site by iron by studying the magnetic phase observed at room temperature for some oxygen deficient samples. Here we report the Mössbauer studies of $YBa_2(Cu_{1-x}Fe_x)_3O_{6+\delta}$ samples with x=0.005, 0.03, 0.05, 0.10 and 0.15.

The formation of linear clusters of iron at Cu(1) sites was determined from the electron diffraction experiments[2], and this result may be relevant to understand the magnetic phase observed at room temperature in the $YBa_2(Cu_{1-x}Fe_x)_3O_{6+\delta}$ samples.

2. EXPERIMENTAL

The samples were prepared by reducing the oxygen content of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ by heating in Ar atmosphere at 600C for 3h. The relative intensity of the magnetic phase depends on the preparation conditions: the results for the same iron concentration may be different for samples from independent batches and varies with the annealing temperature used to remove the oxygen.

The Mössbauer spectra at room temperature and 4.2K were obtained with absorber and source at equal temperatures. The measurements at higher temperatures were performed "in situ" using and Elscint oven for Mössbauer spectroscopy with a ceramic sample holder; in this case the ^{57}Co source was kept at room temperature.

3. RESULTS AND DISCUSSION

The Mössbauer spectra obtained at room temperature (RT) for the oxygen deficient phase $YBa_2(Cu_{1-x}Fe_x)_3O_{6+\delta}$ samples for some iron concentrations can be seen in Fig.1. For the samples with low iron concentration there is a predominance of the the species with QS=2.0mm/s (A) which is assumed to be characteristic of this phase. For higher x values another iron species with QS =0.70mm/s (B) appears together with a magnetic spectrum which is better resolved for $x \geq 0.10$, indicating the presence of a magnetic phase (MP) at RT. The two quadrupole doublets (A and B) may be attributed to Fe on Cu(1) site with two different oxygen coordination in the $YBa_2(Cu_{1-x}Fe_x)O_{6+\delta}$ samples, since they have very similar isomer shift (IS_A=0.04mm/s, IS_B=-0.05mm/s).

Since the copper ions in Cu(2) sites in $YBa_2Cu_3O_6$ present an antiferromagnetic order with $T_N \simeq 450K$[5,6], one may be induced to assume that the MP is due to iron in this site. However, the Mossbauer spectra for samples with different x values taken at a high velocity scale (Fig. 2), indicate that the magnetic hyperfine field B_{hf}, at room temperature, depends on iron concentration. The saturation value of B_{hf} at 4.2K (Fig.3) is almost independent of x

(see the position of the most external lines). Consequently the different values obtained for B_{hf} at room temperature are due to a dependence of the ordering temperature (T_o) of the MP on iron concentration.

In order to confirm this result the Mössbauer spectra have been taken at fixed temperatures in an interval from 295 to 458K. The analysis of the Mössbauer spectra obtained for x=0.15, 0.10, 0.05 indicates an upper limit of $T_o \sim$ 420, 370 and 350K respectively. These values are plotted against iron concentration in Fig. 4, together with the values reported by Coey at al[7] for a sample of $YBa_2(Cu_{0.98}Fe_{0.2})_3O_{6.2}$, whose oxygen content was determined with Thermopiezic Analyser. The fact that the ordering temperature for copper moments at Cu(2) site depend on the oxygen content of $YBa_2Cu_3O_{6+\delta}$ could be used to explain the variation of T_o. However the determination of δ may underestimate the real oxygen content in the linear clusters which tends to be higher than the values for the undoped compounds[2]. Consequently T_o should decrease with iron concentration in disagreement with the experimental observation displayed in Fig.4.

The measurements performed in some samples at 458K, above the magnetic ordering temperature of the MP (Fig.5) reveal that the doublet related to the MP has an IS=0.33mm/s and a QS=0.58mm/s. Its relative intensity, corresponding to the central part of the spectra, increases with iron concentration. Similar iron species are present in the room temperature MS for Fe: $YBa_2Cu_3O_{6+\delta}$, when prepared by vacuum annealing at high temperatures[7,8] or in some as prepared samples[7].

An alternative origin for the formation of the MP may be the interaction between magnetic moments of iron ions which form the linear clusters in Cu(1) plane[2]. In the $YBa_2(Cu_{1-x}Fe_x)_3O_7$ phase this interaction induces an antiferromagnetic or spin-glass-like arrangement[9] with an ordering temperature increasing with iron concentration (for x=0.10, $T_o \simeq$ 13K). The loss of oxygen in the Cu(1) plane to form the $YBa_2(Cu_{1-x}Fe_x)_3O_{6+\delta}$ phase can modify the interaction between the iron moments increasing dramatically T_o (for x=0.10, $T_o \simeq$ 370K), but still maintaining the dependence on iron concentration.

This ensemble of results indicate that one should be very carefull in attributing the MP to Fe in Cu(2) sites. A determination of Mössbauer parameters due to Fe in the Cu(2) site has to be done in order to correlate the relative intensities of this species in Fe: $YBa_2Cu_3O_7$ with the one corresponding to the MP observed in Fe: $YBa_2Cu_3O_{6+\delta}$. So far this kind of results were not achieved.

In conclusion, the magnetic phase observed at room temperature for $YBa_2(Fe_xCu_{1-x})_3O_{6+\delta}$ ($x \geq 0.05$) may be due to the occupation of Cu(2) sites or to the appearance of a different magnetic order in the linear iron clusters at the Cu(1) plane which is induced by the decrease of oxygen content. More experimental evidences are necessary to decide between the two possibilities.

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FIGURE CAPTIONS

Fig.1 - Mossbauer spectra at RT with different iron concentrations

Fig.2 - Mossbauer spectra at RT with different iron concentrations

Fig. 3 - Mossbauer spectra at 4.2K.

Fig.4 - Ordering temperature (T_o) of the magnetic phase as a function of iron concentration (x). Data points are results of this work (o) and Ref.7 (Δ).

Fig.5 - Mossbauer spectra at 185^{o}C as a function of iron concentration.

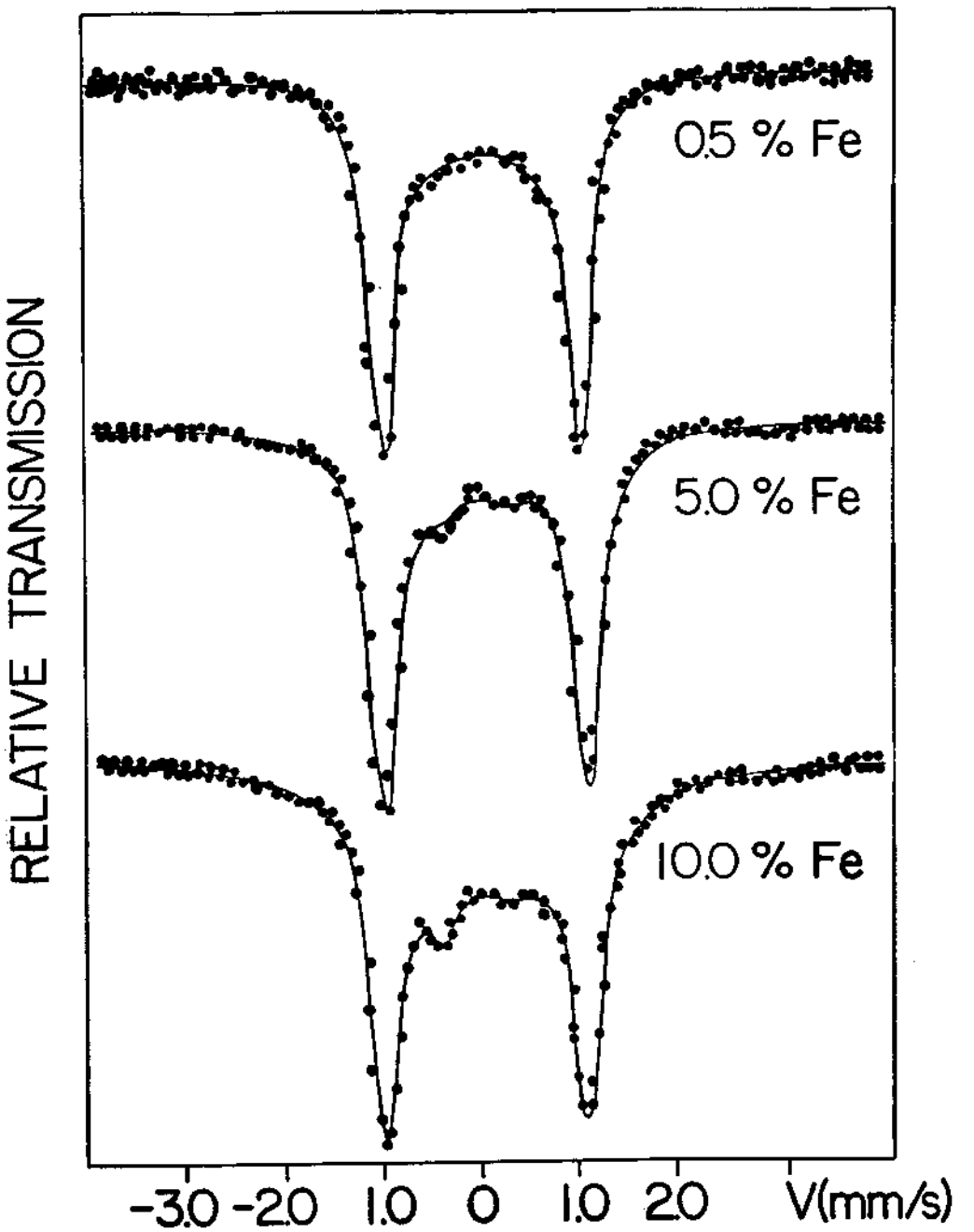

Fig. 1

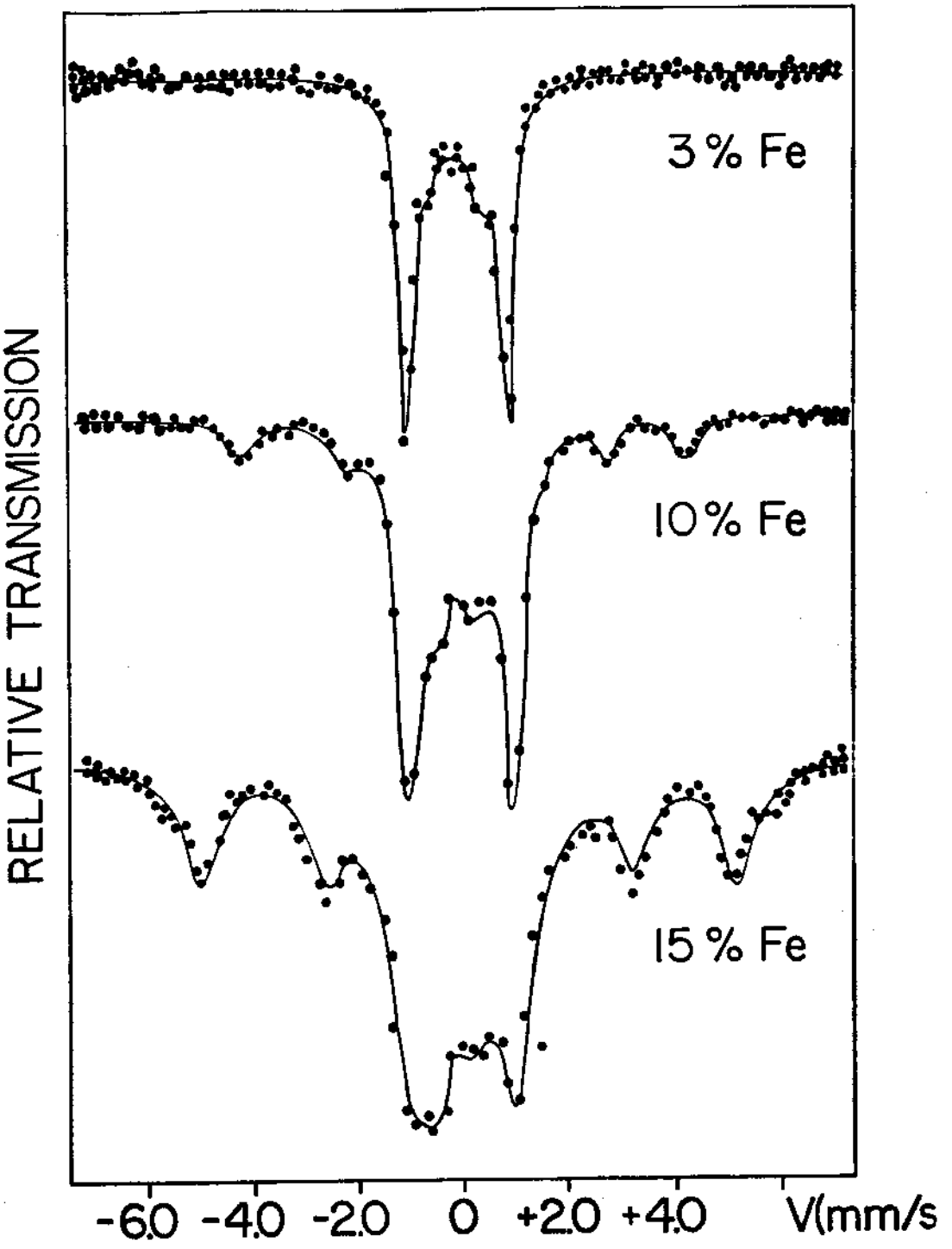

Fig. 2

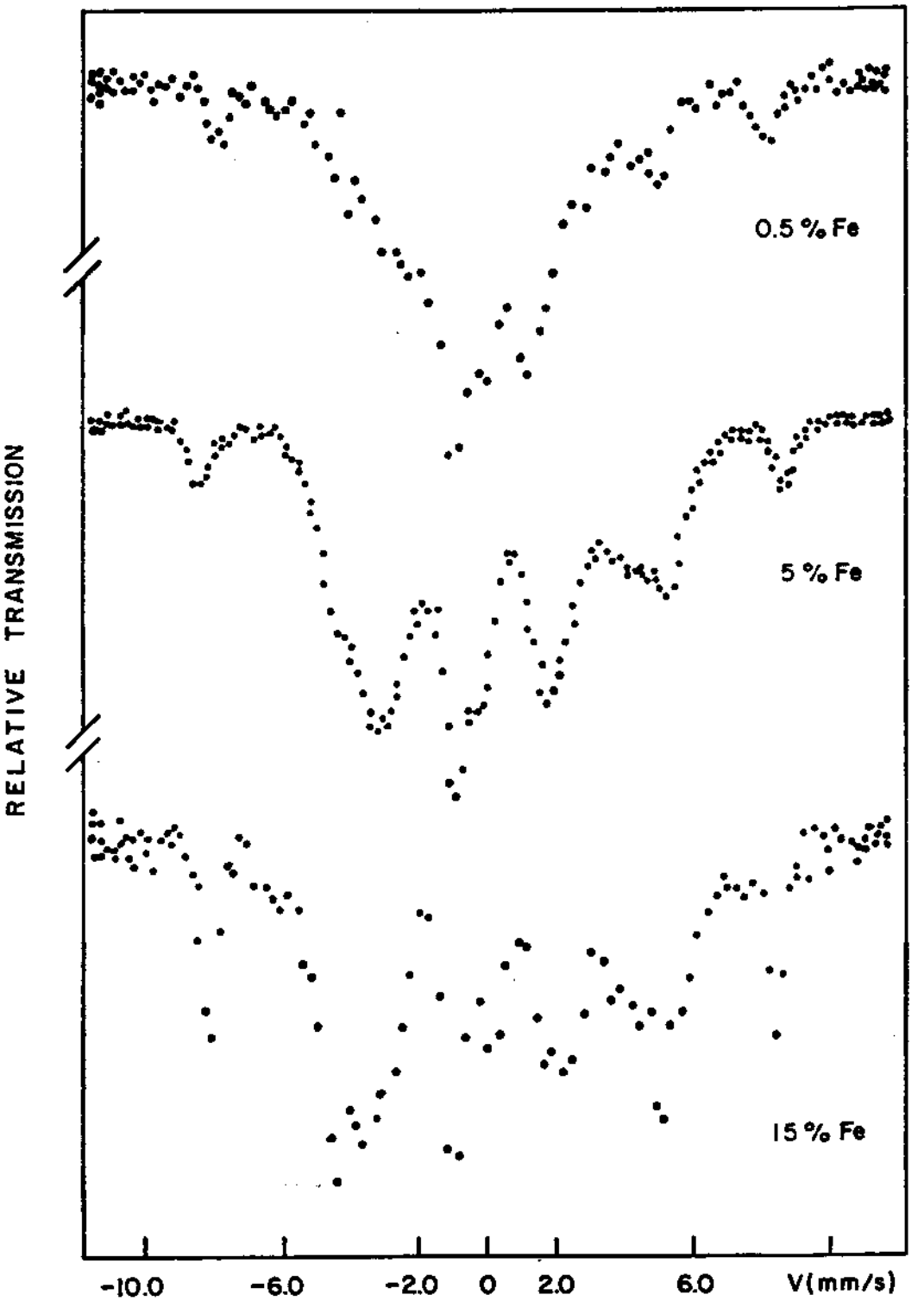

Fig. 3

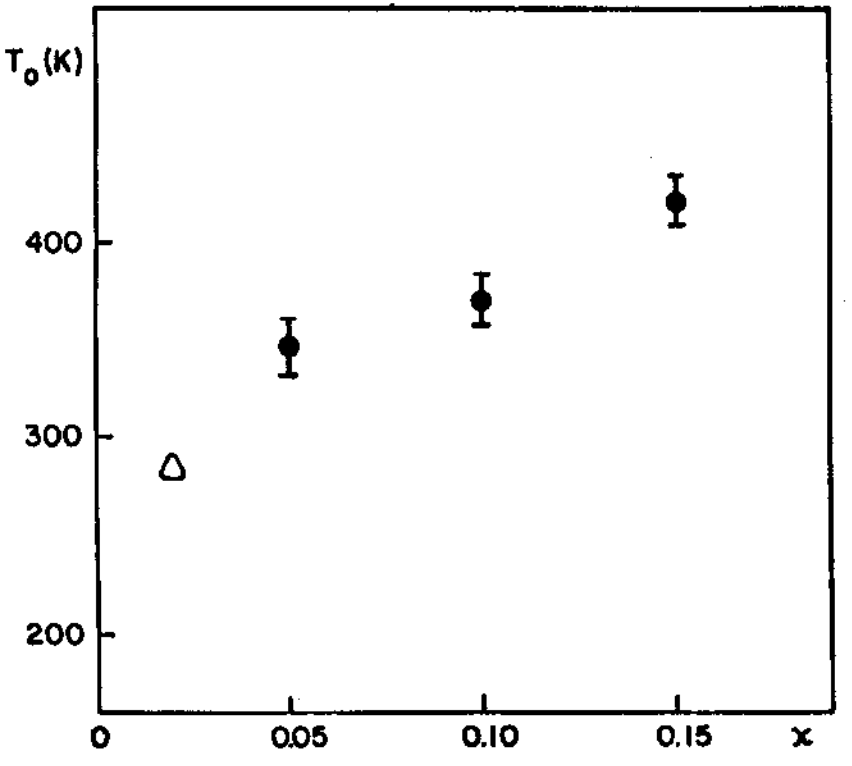

Fig. 4

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