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STUDIES OF (La,Gd)-Sr-Cu-O SYSTEM

by

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ABSTRACT

The increase of Gd concentration induces a structural phase transition in the $(\text{La}_{1-x}\text{Gd}_x)_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ system, going through the T, T* and T'-phases, for which Cu has octahedral, pyramidal and planar oxygen coordinations, respectively. Samples with $x = 0.0, 0.35, 0.45, 0.75$ and 1.0 , substituting 1 at % of Cu by ^{57}Fe , were studied at room temperature by Mössbauer spectroscopy and x-ray diffraction measurements. Five different quadrupole doublets were needed to fit the Mössbauer spectra for all the samples of the system. The isomer shifts (IS) values corresponds to Fe^{3+} ions, except for two contributions of the $x = 1.0$ sample (T'-phase), showing a sharp reduction. The systematics of all the results for the system as a whole allows an interpretation of the different contributions to the Mössbauer spectra in terms of local oxygen surroundings.

Key-words: Mössbauer spectroscopy; Layered cuprates; Local oxygen configurations.

1. Introduction

The structural studies of superconducting oxides have revealed a variety of novel features and have contributed substantially to the understanding of these new materials. The role of the local geometry around the copper ions in the Cu-O₂ plane, which exists in all cuprate superconductors, were considered to be important factors for controlling the superconducting behavior; however, it is unclear why many cuprates containing the Cu-O₂ plane are not superconducting at all. Therefore, the study of such oxides is of particular interest, because it may offer relevant information in connection with their superconducting counterparts.

One of the effective means to study the cuprate superconductors is cation doping by different elements and fortunately Fe, a valious probe for Mössbauer measurements, is a good candidate for substituting the Cu ions in these compounds. Many Mössbauer studies have been reported for ⁵⁷Fe in H-T_c superconducting oxides, revealing a variety of local coordinations [1-7]. In most of the cases, it is difficult to decide whether they correspond to the original Cu ions neighborhoods or to new ones induced by the Fe capability for attracting extra oxygen atoms around the Cu sites. A series of compounds, in which the variation of the composition of the same constituents produces different Cu coordinations, seems to be a good system to study in a systematic way the structural features for Fe species.

The (La_{1-x}Gd_x)_{1.85}Sr_{0.15}CuO₄ series of compounds, which are

formed from the substitution of La by Gd in the LSCO superconductor, is a suitable system for the study of local geometries, since by increasing the Gd content one can pass from the T-phase (octahedral coordination for Cu ions) to the T^{*}-phase (five-fold pyramid) and finally to the T'-phase (planar square) [8]. Figures 1(a) to 1(c) show the corresponding unit cells. The Cu-O₂ plane remains along the series, while the conducting character changes from a superconductor to an insulator. The three stable phases of the (La_{1-x}Gd_x)_{1.85}Sr_{0.15}CuO₄ system have tetragonal structure at room temperature (RT) and exist as pure phases in the following composition ranges: 0 ≤ x ≤ 0.1 for the T-phase, 0.42 ≤ x ≤ 0.49 for the T^{*}-phase and 0.95 ≤ x ≤ 1.0 for the T'-phase; out of these ranges there is a mixture of two phases. Detailed studies about the crystal structure, magnetic and superconducting features have been already reported [8].

One additional interest is the fact that the T' cell is isomorphous with the n-type superconductors of the Nd_{2-x}Ce_xCuO₄ system, for which no reliable ⁵⁷Fe doping has been obtained [9]. In the present work we report on Mössbauer and x-ray diffraction studies performed at RT in ⁵⁷Fe: (La_{1-x}Gd_x)_{1.85}Sr_{0.15}CuO₄ samples for x = 0.0, 0.35, 0.45, 0.75 and 1.0, substituting 1 at. % of Cu by ⁵⁷Fe, which is expected to occupy the Cu site. Mössbauer Spectroscopy (MS) may contribute to obtain a various local information about the structural characteristics of these phases.

2. Experimental

Samples were prepared by using the conventional solid state reaction method. Appropriate amounts of high purity La_2O_3 , SrCO_3 , Gd_2O_3 , CuO and enriched $^{57}\text{Fe}_2\text{O}_3$ compounds were well mixed in stoichiometric amounts and pressed into pellets. Two pre-firing treatments were performed in air : at 900°C for 12 hours and at 980°C for 15 hours; the final heat treatment was performed at 1100°C in an oxygen flow for 15 hours. Intermediate grinding and pressing operations were performed before the treatments. In each stage the samples were cooled at a rate of 45°C/h .

The quality of the samples and the lattice parameters were determined by using Cu-K_α radiation from a x-ray powder diffractometer.

The Mössbauer spectra were obtained at RT in transmission geometry and in constant acceleration mode using a ^{57}Co source in Rh matrix. They were analysed by fitting the data with several symmetrical doublets.

The $^{57}\text{Fe}:(\text{La}_{1-x}\text{Gd}_x)_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ samples with $X = 0.0, 0.35, 0.45, 0.75$ and 1.0 will be abbreviated in the following as $\text{Gd}(0)$, $\text{Gd}(0.35)$, $\text{Gd}(0.45)$, $\text{Gd}(0.75)$ and $\text{Gd}(1.0)$, respectively.

3. Results and discussion

The x-ray diffraction patterns show that the samples have tetragonal structure in all the cases. The dependence of the lattice constants a and c as a function of Gd concentration are

shown in fig 2(a) and 2(b), respectively. The a parameter increases monotonically while the c -axis decreases in the sequence $T \rightarrow T^* \rightarrow T'$ -phases, in such a way that the c/a ratio also decreases in the same order. This behavior is related to a diminishing Jahn-Teller distortion, (strong for Cu^{2+} ions in octahedral coordination) as less oxygenated configurations appear. For the samples Gd(0.35) and Gd(0.75) there is a mixture of $T + T^*$ and $T^* + T'$ - phases, respectively, in agreement with data reported for samples without iron doping [8]. In fact, the substitution of only 1 at. % of Cu by Fe was not expected to induce any change in the crystal structure of these systems and the x-ray diffraction data were taken mainly to control the quality of sample preparation.

Figures 3(a) to 3(e) show the Mössbauer spectra for all the samples after the final heat treatment in flowing oxygen at 1100°C . There is a clear evidence of the change in the number of iron doublets as well as in their quadrupole splittings (QS) values. For the Gd(1.0) sample a species with negative isomer shift (IS) is formed, as we discuss below.

To analyse all the spectra, five species with different QS were considered, namely A, B, C, D and E; they are associated to the subspectra in fig. 3 and the corresponding hyperfine parameters for the different Gd concentrations are shown in Table I (IS values are given relative to $\alpha\text{-Fe}$). In the Gd(0.0) sample some small amount of iron is present in a minor phase, not included in Table I, (less than 5 % with $\text{QS} = 0.30 \text{ mm/s}$ and $\text{IS} = 0.33 \text{ mm/s}$) which disappears with further heat treatments).

The dependences on Gd composition of the isomer shift and the quadrupole splitting are shown in fig. 4(a) and 4(b), respectively. There is a smooth decrease of the QS values for species A, B and C up to $x = 0.75$, while the IS values are almost constant and correspond to Fe^{3+} in the high spin state. The decrease of the QS values is related to the regular variation of lattice parameters induced by Gd doping, a fact that is connected with the appearance of new oxygen neighborhoods that relax the lattice.

For the Gd(1.0) sample a remarkable change occurs. Two contributions (D,E) showing reduced IS values were detected, one of them been negative relative to $\alpha\text{-Fe}$ (-0.14 mm/s for doublet E). Figure 5 shows the relative area dependence of the different contributions with the Gd content.

First of all, it must be pointed out why in the Gd undoped compound there are two doublets, meaning two different contributions. One iron species (B) in this Gd(0) sample is related to the existence of oxygen defects near the Cu sites that are intrinsic to the La_2CuO_4 . These defects can be either vacancies or trapped interstitial atoms [10]. Doublet A, with a QS higher than the one for B, corresponds to lattice positions that are not affected by close structural defects. The octahedral configuration of site A is highly distorted by the Jahn-Teller effect of Cu^{2+} ions in that type of coordination, which relax when the mentioned oxygen defects appear inducing a microtwinning structure [11]. Since iron ions are able to catch additional

oxygen atoms locally, contributions from the more oxygenated coordinations are still present even for samples for which, according to the Gd concentration, they were to be absent. This explains why doublet B can persist up to $x = 0.75$. Since these configurations are disordered in the lattice, they do not reflect themselves in the x-ray measurements. For example, species B is present in the Gd(0.45) sample, although its x-ray diffraction pattern corresponds to a pure T^* -phase, which has only pyramidal sites in an ideal perfect lattice. However, the contribution of the more oxygenated configurations (A,B) systematically diminishes in the $T \rightarrow T^* \rightarrow T'$ direction (fig. 5).

Species C appears in the Gd(0.35) sample, just when some quantity of the T^* -phase is formed, has a maximum in its contribution to the whole area of the spectra (fig. 5) and it is still present in the Gd(1.0) spectrum. We attribute the C doublet to iron with a pyramidal oxygen coordination. Its presence in the Gd(1.0) sample which, in principle, would have only square coordinations for the Cu sites, should be due to the mentioned tendency of iron to add extra oxygen atoms. This is also the reason that explains why the maximum of its intensity is near $x = 0.75$ and not exactly at the expected $x = 0.45$ value (pure T^* -phase).

For the Gd(1.0) sample, in the T' -phase, the two mentioned above doublets with reduced values of the IS, (D,E), sharply appear and contribute with the 80 % of the total area. The -0.14 mm/s value of the IS for species E is very similar to that

obtained for one of the Fe species located at the chains of YBaCuO samples [6], while species D shows a jump in the QS value. Both contributions can not be attributed to the normal Fe^{3+} ion, and probably corresponds to a higher valence and/or to a low or intermediate spin state. By considering as a whole the regular variation of the parameters describing the system under study, one conclude that D and E species may be sensing specific oxygen surroundings characterizing the T'-phase. It is possible that the different sizes of the Gd^{3+} and Sr^{2+} ions would promote a short range accommodation order inducing different local environments. As a matter of fact, Müther et al. [12] have recently reported from ^{155}Gd -Mössbauer studies that Gd ions in $\text{Gd}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ are mainly located in two inequivalent sites, one with no Sr^{2+} on the nearest sites and the other one with strong local distortions, caused by two Sr^{2+} neighbors probably associated with an oxygen defect. So, D and E contributions to the iron Mössbauer spectra might be intrinsic to the T'-phase. In our case, however, a definitive assignment identifying which of the two components corresponds to the square planar coordination can not be made yet. In order to obtain further information in this sense, more samples of the T'-phase were prepared by changing the Gd concentration (within the narrow range for which the T'-phase exists), sintering temperature and partial oxygen pressure, and significative variations of the relative population of D and E species were detected. A systematic study is in course.

4. Conclusions

The results concerning the Fe occupation of Cu sites in the $^{57}\text{Fe}:(\text{La}_{1-x}\text{Gd}_x)_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ series of compounds can be summarized as follows:

a) Five different types of doublets are needed to describe the Mössbauer spectra when the $T \rightarrow T^* \rightarrow T'$ - phase transition is followed. The fact that Fe ions are able to trap extra oxygen atoms at the Cu sites surroundings impedes sharp changes of the spectra when going from one structure to another, since it promotes the coexistence of different oxygen configurations. In spite of this, the systematics of all the results presented here for the system as a whole allows a first approach interpretation of the different contributions to the Mössbauer spectra.

b) The contribution of the sites of the parent Gd-undoped compound (A,B) systematically decreases with doping, as well as the corresponding QS splitting values. Species B persists up to $x = 0.75$.

c) Doublet C was assigned to pyramidal sites.

d) Iron in the A, B and C species has IS values typical of Fe^{3+} , while for D and E contributions, characterizing the T' -phase, has reduced values. For the E doublet $\text{IS} = -0.14$ mm/s relative to $\alpha\text{-Fe}$, a result that matches well with the value reported for one species located at the chains of the YBaCuO compound.

e) The relative intensity of doublets D and E depends in a significative degree on the details of sample preparation, including different partial oxygen pressures. This implies that Fe

is sensing a second configuration (probably with a defect of oxygen atoms) in addition to the square planar one; however, inhomogeneous electronics states through the lattice can not be discarded.

ACKNOWLEDGEMENTS

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Figure captions

Figure 1

Crystallographic structures of (a) the T-phase: $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, (b) the T^* -phase: $(\text{La}_{0.55}\text{Gd}_{0.45})_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, and (c) the T' -phase: $\text{Gd}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, after Xiao et al. [8].

Figure 2

Unit cell lengths dependence on Gd concentration x in the tetragonal $^{57}\text{Fe}:(\text{La}_{1-x}\text{Gd}_x)_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ system. (a) parameter a and (b) parameter c .

Figure 3

Mössbauer spectra for samples of the $^{57}\text{Fe}:(\text{La}_{1-x}\text{Gd}_x)_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ system sintered in an oxygen flow at 1100°C . (a) $x = 0.0$, (b) $x = 0.35$, (c) $x = 0.45$, (d) $x = 0.75$, and (e) $x = 1.0$. The different spectra associated to specific oxygen surroundings are indicated (see text for identification).

Figure 4

Dependence on Gd content x of the (a) isomer shift IS and (b) the quadrupole splitting QS of the different contributions to the Mössbauer spectra for samples of the $^{57}\text{Fe}:(\text{La}_{1-x}\text{Gd}_x)_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ system (see text for identification).

Figure 5

Relative area dependence of the different subspectra with the Gd content x for samples of the $^{57}\text{Fe}:(\text{La}_{1-x}\text{Gd}_x)_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ system.

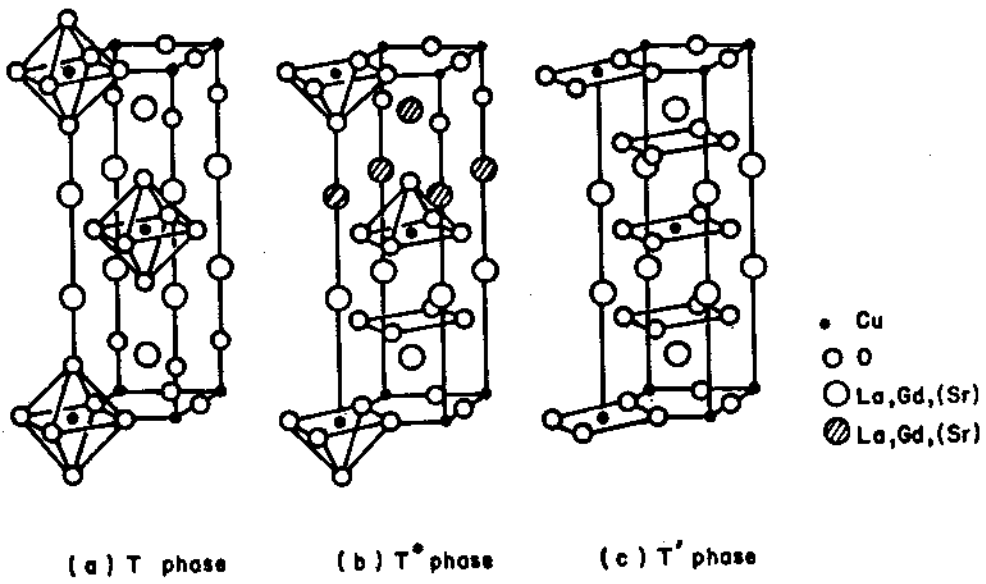


FIG. 1

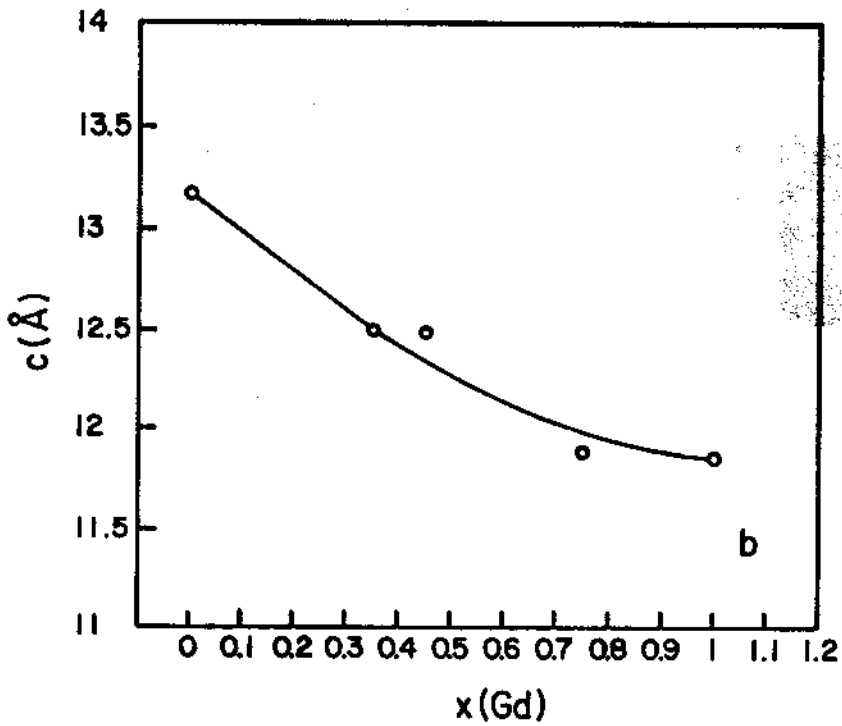
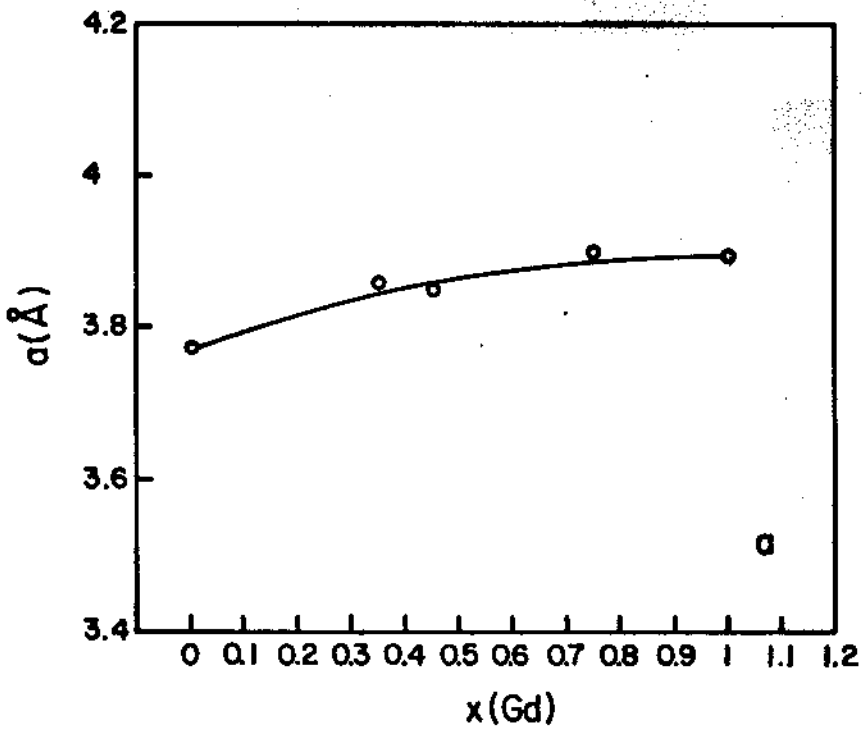


FIG. 2

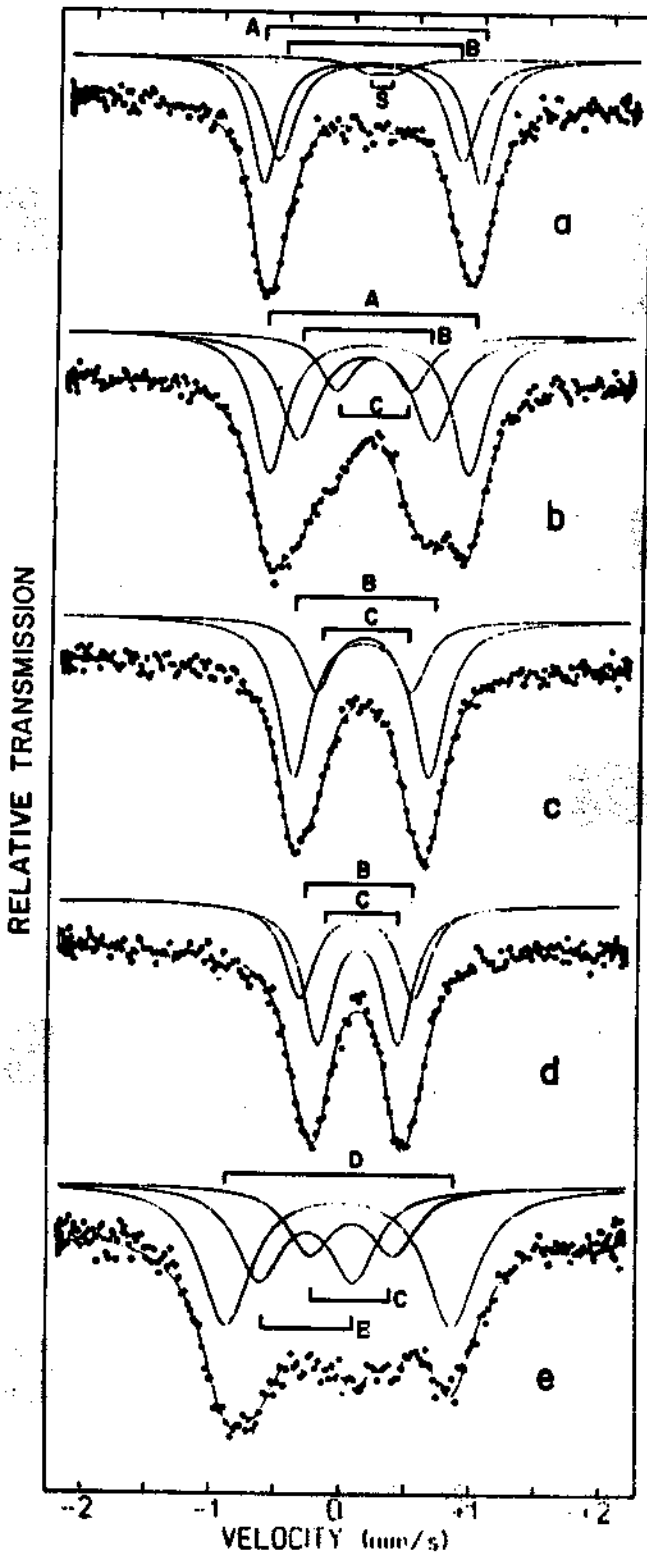


FIG. 3

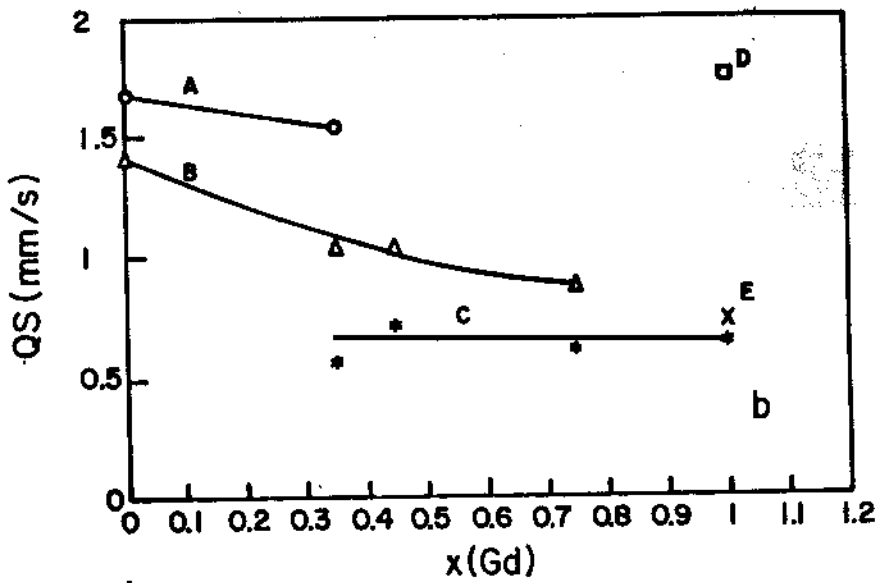
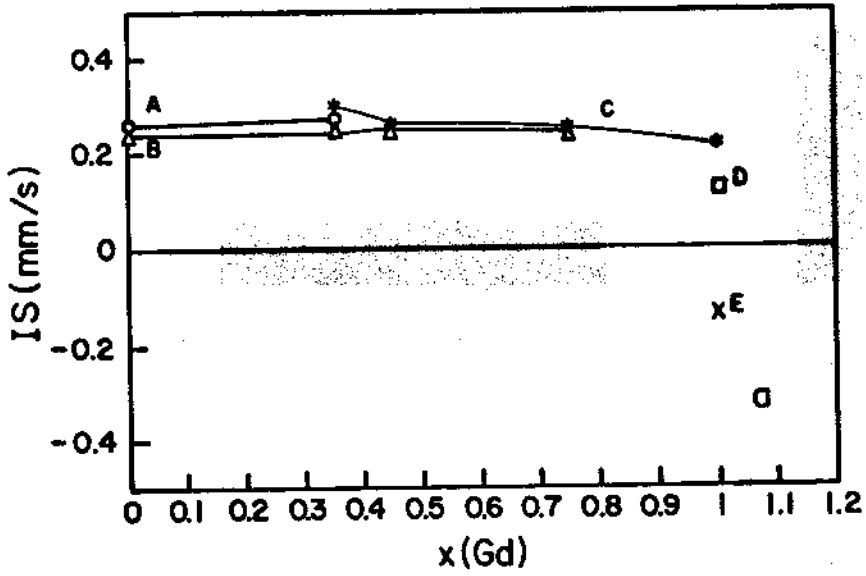


FIG. 4

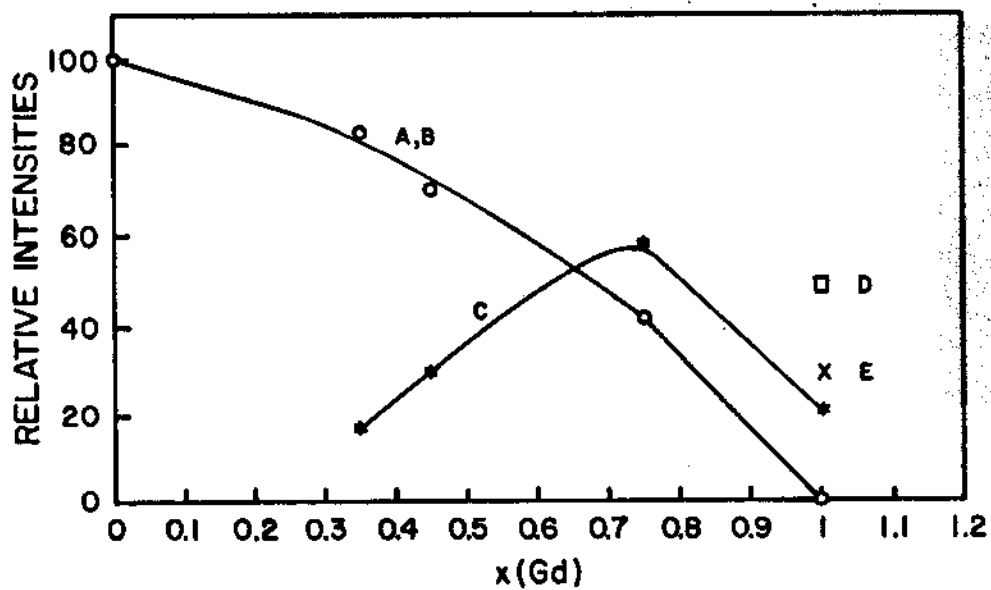


FIG. 5

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