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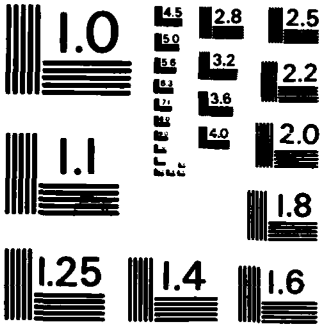

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STABILITY OF SEVERAL SUBSTITUTED FERRITES IN A REDUCING ATMOSPHERE

by

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ABSTRACT

The stability of α-Fe_2O_3 and a number of ferrites were studied in a reducing atmosphere of 85%Ar/15%H_2. The reduction processes were followed by both thermogravimetric and x-ray analyses. These results allowed for the unambiguous characterization of the reduction processes. A relationship between the nature of the products and the reduction process is proposed.

INTRODUCTION

Qian et al. (1) have recently shown that reduction of the spinel $MgFe_2O_4$ results in the initial formation of the solid solution $Mg_{1-x}Fe_xO$ and that this phase persists even after 80 hr of heating at 450°C in a pure hydrogen atmosphere. This is in contrast to the reduction of Fe_2O_3 under similar conditions. At the end of 12 hr they observed the presence of only iron peaks in x-ray diffraction patterns of the products. Thus, it appeared that the formation of an intermediate solid solution $Mg_{1-x}Fe_xO$ inhibits the reduction of the spinel to Fe and MgO.

Trivalent iron is present in a number of ferrites crystallizing with the spinel structure. In addition, a divalent ion is present either on tetrahedral or octahedral sites. The stability of Fe^{3+} in the structure should depend to a large degree on the reducibility of the divalent ion as well as on the stability of any intermediate products formed by heating the spinel in a hydrogen atmosphere. The present study deals with the stability relative to Fe_3O_4 of the spinels MFe_2O_4 where $M = Cu^{2+}$, Cd^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+}, as compared to the stability of Fe_3O_4.

EXPERIMENTAL

Preparation of samples. Copper diiron(III) oxide and cadmium diiron(III) oxide were prepared by grinding together the appropriate oxides and heating them to 800°C in porcelain crucibles (2). The other ferrites MFe_2O_4 (M=Co,Ni,Zn,Mg) were prepared according to the method of D.G. Wickham (3) by the addition of an oxalic acid solution to a solution containing appropriate quantities of the desired ions. The metal-oxalate solid solution is precipitated, and if decomposed in the presence of air, yields MFe_2O_4 according to the following equation:

$$MFe_2(C_2O_4)_3 \cdot 6H_2O + 2O_2 \longrightarrow MFe_2O_4 + 6H_2O + 6CO_2$$

X-ray diffraction studies. Powder diffraction patterns of the samples were obtained with a Philips diffractometer using monochromated high-intensity CuKα_1 radiation (λ=1.5405Å). For qualitative identification of the phases present, the patterns were taken from $30° \leq 2\theta \leq 80°$ with a scan rate of 1° 2θ/min and a chart speed of 30 in/hr.

Thermogravimetric analysis. A thermogravimetric analysis was performed on each of the ferrites, using a Cahn electrobalance (Model RG). An atmosphere of either pure hydrogen (99% Linde) or 85%/15% Ar/H_2 was used in these studies. Both gases were predried through a P_2O_5 column before passing over the sample.

The TGA patterns obtained by reduction with pure hydrogen were used to determine the temperature for each step in the reduction process. Those obtained with Ar/H_2 as the reducing atmosphere were important in ascertaining quantitatively the phase relationships of the intermediate products formed during the reduction process.

Typical TGA experiments required 50 mg of the ferrite. The gases were passed over the sample at a flow rate of 50 cc/min and a maximum temperature of 700°C was reached at a heating rate of 30°C/hr.

RESULTS AND DISCUSSION

The reduction of $\alpha\text{-}Fe_2O_3$ and a number of iron spinels was carried out under the conditions given in Table I. A reducing atmosphere of 85%/15% Ar/H_2 was chosen because the use of this gas mixture allowed for clear identification of the intermediate step in the reduction process for several of the ferrites. With pure hydrogen gas, the reduction proceeded too rapidly and careful analysis of the reduction process could not be performed.

The reduction mechanism of $\alpha\text{-}Fe_2O_3$ has been reported (4) as a two-step process and can be represented by the following equations:

A. $1.5\ Fe_2O_3 + 0.5\ H_2 \longrightarrow Fe_3O_4 + 0.5\ H_2O$

B. $Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$

In this study, the reduction process was carried out in an 85%/15% Ar/H_2 atmosphere, and the TGA pattern is shown in Fig. 1a. It is evident that under such conditions the reduction process begins at 270°C and all of the $\alpha\text{-}Fe_2O_3$ is converted to Fe_3O_4 at 305°C. The reduction of the Fe_3O_4 to metallic iron is essentially complete at 470°C. Differences in the reported temperatures for the reduction of α-Fe_2O_3 are caused by different rates of heating as well as by the composition of the reducing atmosphere. In these studies when pure hydrogen was used the Fe_3O_4 began to be reduced to metallic iron before all of the α-Fe_2O_3 was completely converted to Fe_3O_4. In addition, the observed reduction temperatures were much lower than those reported for reductions carried out in an 85%/15% Ar/H_2 atmosphere.

It can be seen from Fig. 1 that the ratio of the weight loss for Step B to the loss for Step A is 7.97:1. The ratio of the calculated weight loss for the reduction of α-Fe_2O_3 to Fe_3O_4 and finally to iron (8:1) can be obtained from the relative amounts of water formed as represented in the equations for Steps A and B. This ratio also represents the relative weight removal of oxygen from the iron oxides.

The TGA plot for the reduction of the ferrite $CuFe_2O_4$ with 85%/15% Ar/H_2 and the x-ray analysis of the reduction products which were formed for the two-step process are shown in Fig. 2a and 2b. These results indicate that the initial reduction step is complete at 270°C and at this temperature the Cu^{2+} was reduced to metallic copper; in addition, the tetragonal $CuFe_2O_4$ was transformed to a cubic spinel containing all of the iron. Further reduction resulted in the appearance of metallic iron in the product and, finally, the reduction end product consisted of iron and copper. The reduction was complete at 440°C.

If the product formed at the end of the first stage of the reduction process had been pure Fe_3O_4, then the following equations would indicate how the reduction proceeded:

A. $1.5\ CuFe_2O_4 + 2H_2 \longrightarrow 1.5\ Cu + Fe_3O_4 + 2H_2O$

B. $Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$

The calculated ratio of the weight loss for Step A to Step B is 1:2. From the TGA results plotted in Fig. 2, it can be seen that the ratio is acutally 1:2.15. This discrepancy in the ratio of the observed weight loss to the calculated value is consistent with the reduction of copper ferrite to an intermediate phase which still contains copper. Accordingly, the reduction process can be represented by the following equations:

A. $0.5(3-x)CuFe_2O_4 + 2(1-x)H_2 \longrightarrow 1.5(1-x)Cu + (Cu_xFe_{1-x})Fe_2O_4 + 2(1-x)H_2O$

B. $(Cu_xFe_{1-x})Fe_2O_4 + 4H_2 \longrightarrow xCu + (3-x)Fe + 4H_2O$

From the above equations, it can be seen that the weight loss which occurs in the reduction process is directly related to the amount of water formed. Hence, for the reduction products prepared at 270°C, the ratio of the weight loss in Step A to that in Step B is $2(1-x):4$. From Fig. 2a, the ratio was determined to be 1:2.15, and therefore the value of $x = 0.07$.

The TGA plot for the reduction of the ferrite $ZnFe_2O_4$ with 85%/15% Ar/H_2 and the x-ray analysis of the reduction products are given in Fig. 3a and 3b. The reduction process of $ZnFe_2O_4$ takes place in two steps. The initial products formed at 495°C were identified as Fe and ZnO. The reduction process continued with the gradual loss in weight due to the formation of zinc and its volatilization at higher temperatures. The final reduction product at 690°C was identified as iron by x-ray diffraction analysis.

The reduction process for $CdFe_2O_4$ begins at 365°C and is complete at 465°C. As the temperature is increased to 380°C there is a continual separation and volatilization of metallic cadmium as well as the formation of magnetite and metallic iron. At 465°C the reduction process was complete and only iron remained. The cadmium was completely volatilized at this temperature. The results of x-ray diffraction analyses are shown in Fig. 4.

The TGA data for $CoFe_2O_4$ indicate that the reduction in 85%/15% Ar/H_2 is continuous and begins at 355°C and is complete at 485°C. The x-ray diffraction pattern for the product indicates the presence of an alloy which crystallizes with the α-Fe structure and contains both α-Fe and cobalt.

The reduction of $NiFe_2O_4$ begins at 360°C and is complete at 490°C. The x-ray diffraction data are shown in Fig. 5. It can be seen that metallic iron and an alloy of iron and nickel crystallizing with the γ-(Ni,Fe) structure are formed at 400°C. At 500°C, only the γ-(Ni,Fe) alloy can be identified in x-ray diffraction patterns of the product.

CONCLUSIONS

The stability of iron(III) oxide and five ferrite spinels, where the divalent ion was Cu,Zn,Cd,Co,Ni, was studied under an 85%/15% Ar/H_2 atmosphere. The thermogravimetric studies indicated that for Fe_2O_3, $CuFe_2O_4$, and $ZnFe_2O_4$, the loss of oxygen occurred in two distinct stages. Fe_3O_4 was formed as the intermediate product in the reduction of Fe_2O_3 to Fe. Reduction of $CuFe_2O_4$ gave initially a mixture of metallic copper and an iron-rich copper ferrite with the stoichiometry $Cu_{0.07}Fe_{0.93}Fe_2O_4$. The final reduction product was a mixture of copper and iron. The reduction of $ZnFe_2O_4$ first gave iron and ZnO. However, by 690°C the ZnO was reduced to metallic zinc, which was volatilized. On reduction, the spinel $CdFe_2O_4$

first forms volatile cadmium as well as magnetite and iron. The final end product of the process was metallic iron since all of the cadmium volatilized at 465°C.

The inverse spinels $CoFe_2O_4$ and $NiFe_2O_4$ showed a continuous loss of oxygen on reduction and the final products were α-(Fe,Co) and γ-(Ni,Fe) alloys, respectively.

Thus it can be seen that for each of the compounds studied, the reduction proceeds by a different mechanism depending on the nature of the reduction products.

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TABLE I

Reduction Mechanisms of Some Ferrites in Ar/H_2 Compared with α-Fe_2O_3

Compound	Reduction Temperature A	B	Intermediate Phase	Final Phase
α-Fe_2O_3	270	470	Fe_3O_4	α-Fe
$CuFe_2O_4$	215	440	$Cu_xFe_{1-x})Fe_2O_4$	α-Fe, Cu
$CdFe_2O_4$	365	465	Fe_3O_4	α-Fe
$ZnFe_2O_4$	370	690	ZnO	α-Fe
$CoFe_2O_4$	355	485	-	α-(Fe,Co)
$NiFe_2O_4$	360	490	α-Fe+γ-(Ni,Fe)	γ-(Ni,Fe)

A. Reduction of compound starts

B. Final reduced phase

FIGURE CAPTIONS

Figure 1 - (a) Relative weight versus temperature for Fe_2O_3 reduced in 85%/15% Ar/H_2.

(b) X-ray patterns of initial, intermediate, and final materials.

Figure 2 - (a) Relative weight versus temperature for $CuFe_2O_4$ reduced in 85%/15% Ar/H_2.

(b) X-ray patterns of initial, intermediate, and final materials.

Figure 3 - (a) Relative weight versus temperature for $ZnFe_2O_4$ reduced in 85%/15% Ar/H_2.

(b) X-ray patterns of initial, intermediate, and final materials.

Figure 4 - X-ray patterns of initial, intermediate, and final materials formed in the reduction of $CdFe_2O_4$ in 85%/15% Ar/H_2.

Figure 5 - X-ray patterns of initial, intermediate, and final materials formed in the reduction of $NiFe_2O_4$ in 85%/15% Ar/H_2.

Fig. 1a

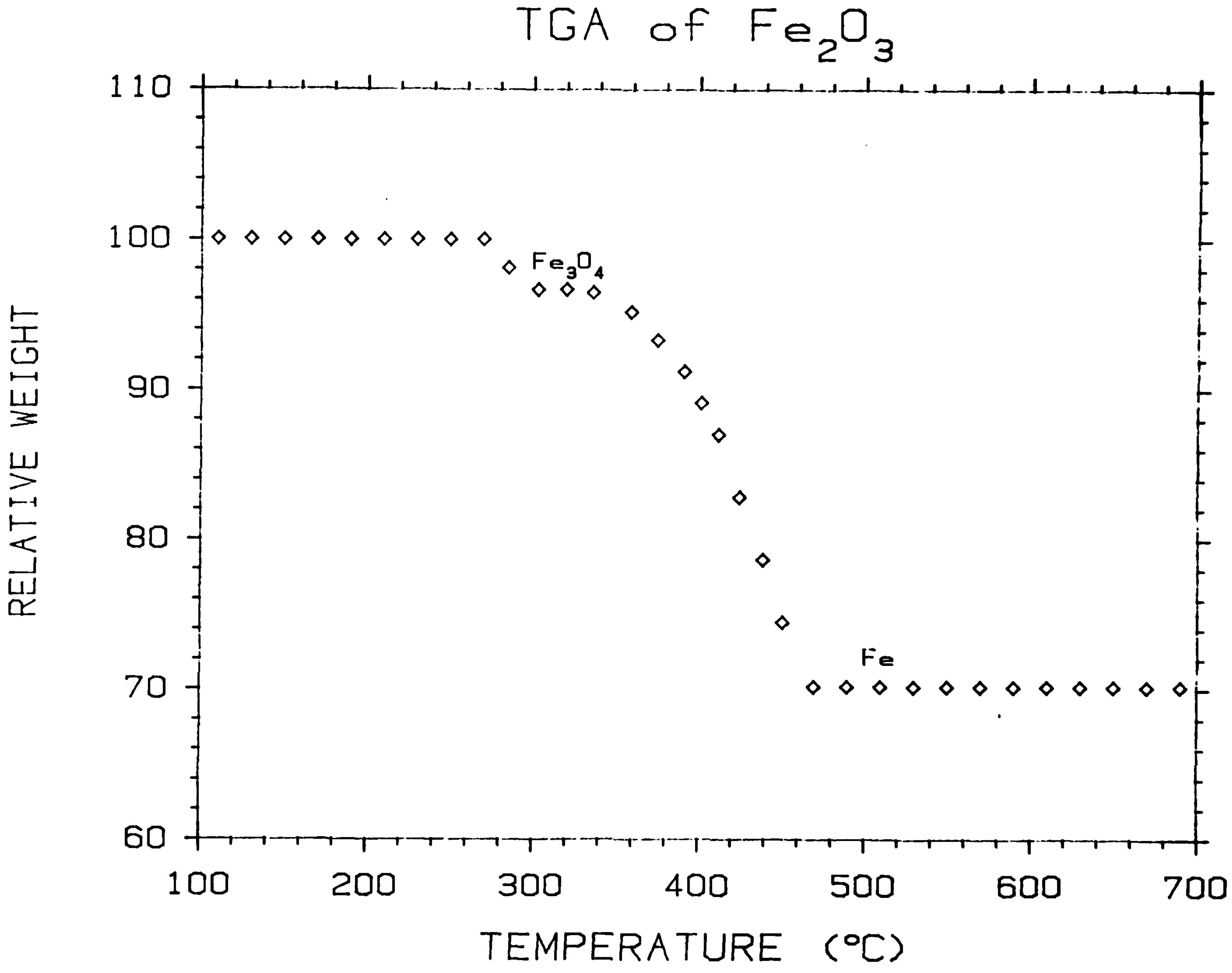

TGA of Fe_2O_3
RELATIVE WEIGHT
110
100
90
80
70
60
Fe_3O_4
Fe
100
200
300
400
500
600
700
TEMPERATURE (°C)

Fig 1b

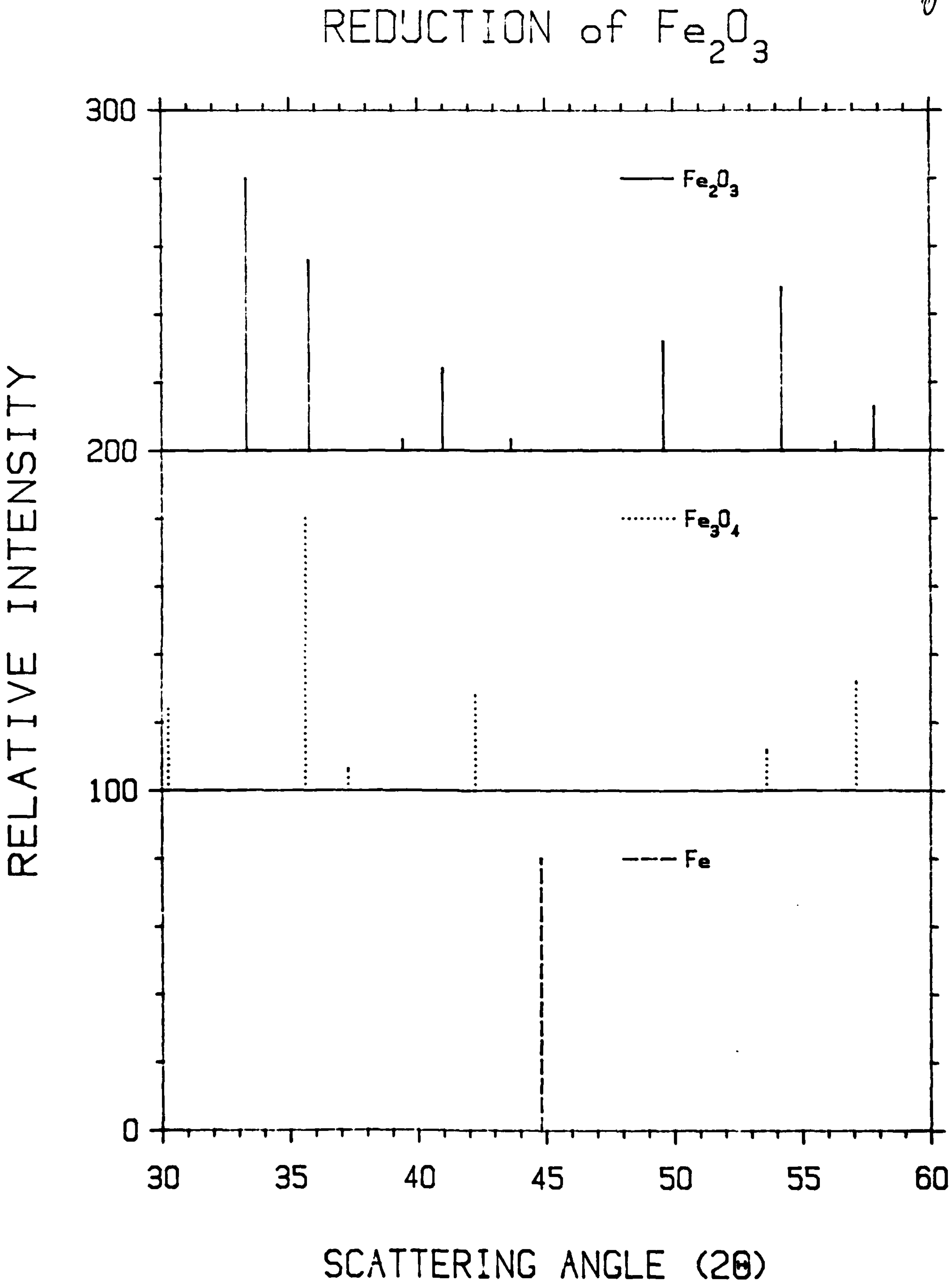
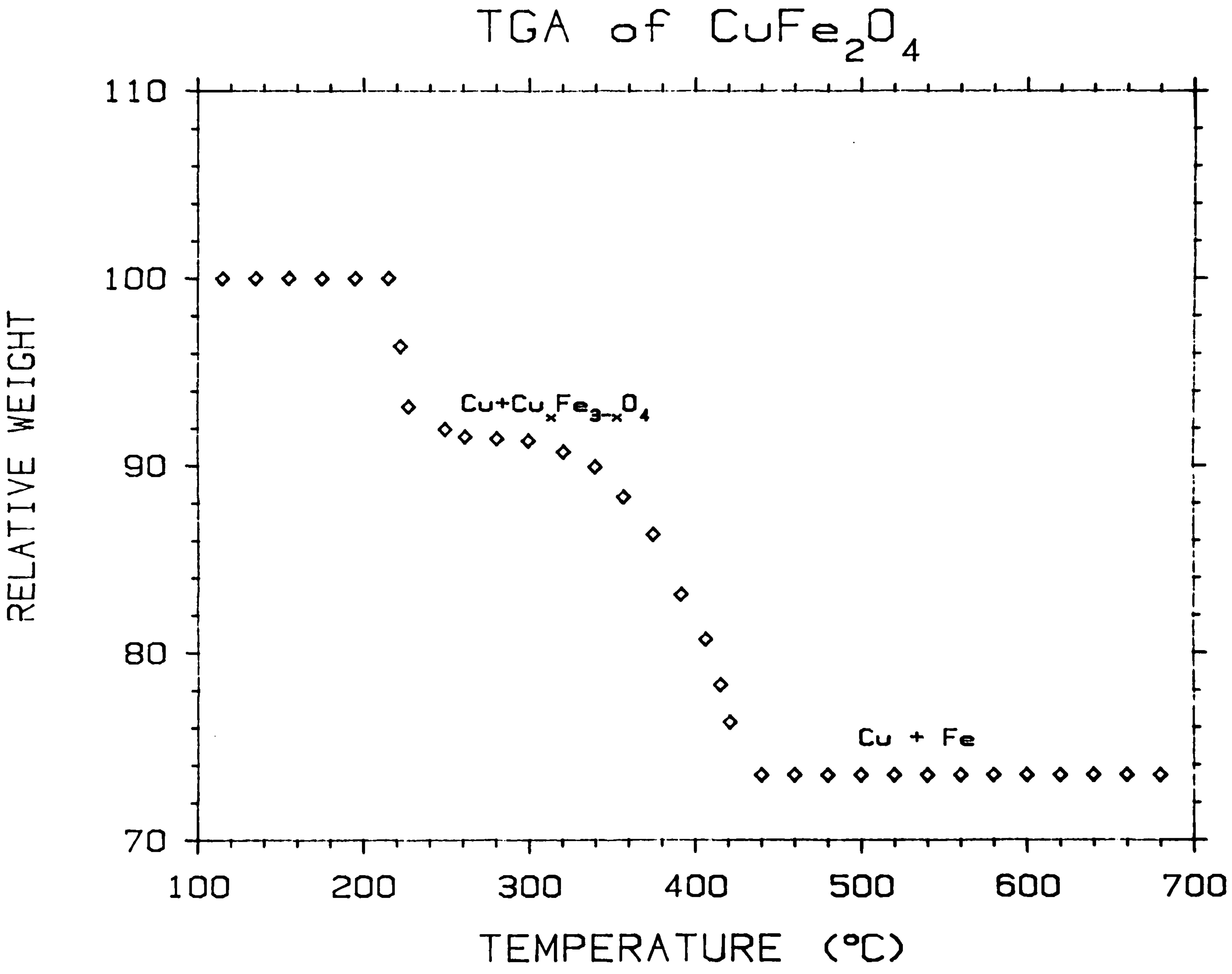
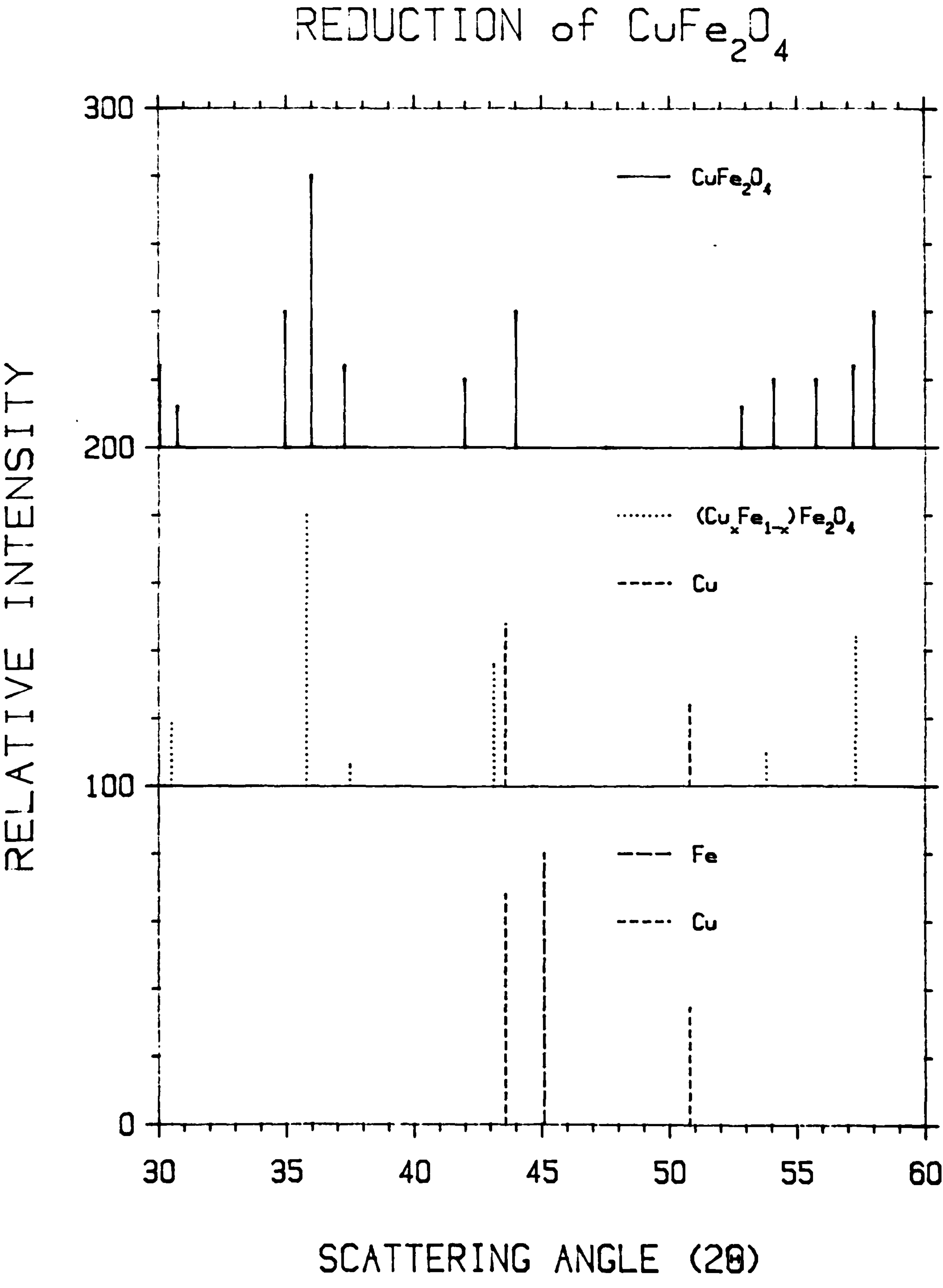

REDUCTION of Fe_2O_3
RELATIVE INTENSITY
300
200
100
0
— Fe_2O_3
······ Fe_3O_4
– – – Fe
30
35
40
45
50
55
60
SCATTERING ANGLE (2Θ)

Fig 2a



TGA of $CuFe_2O_4$
RELATIVE WEIGHT
110
100
90
80
70
$Cu+Cu_xFe_{3-x}O_4$
Cu + Fe
100
200
300
400
500
600
700
TEMPERATURE (°C)

Fig 2D



REDUCTION of $CuFe_2O_4$
RELATIVE INTENSITY
300
200
100
0
$CuFe_2O_4$
$(Cu_xFe_{1-x})Fe_2O_4$
Cu
Fe
Cu
30
35
40
45
50
55
60
SCATTERING ANGLE (2θ)

Fig 3a

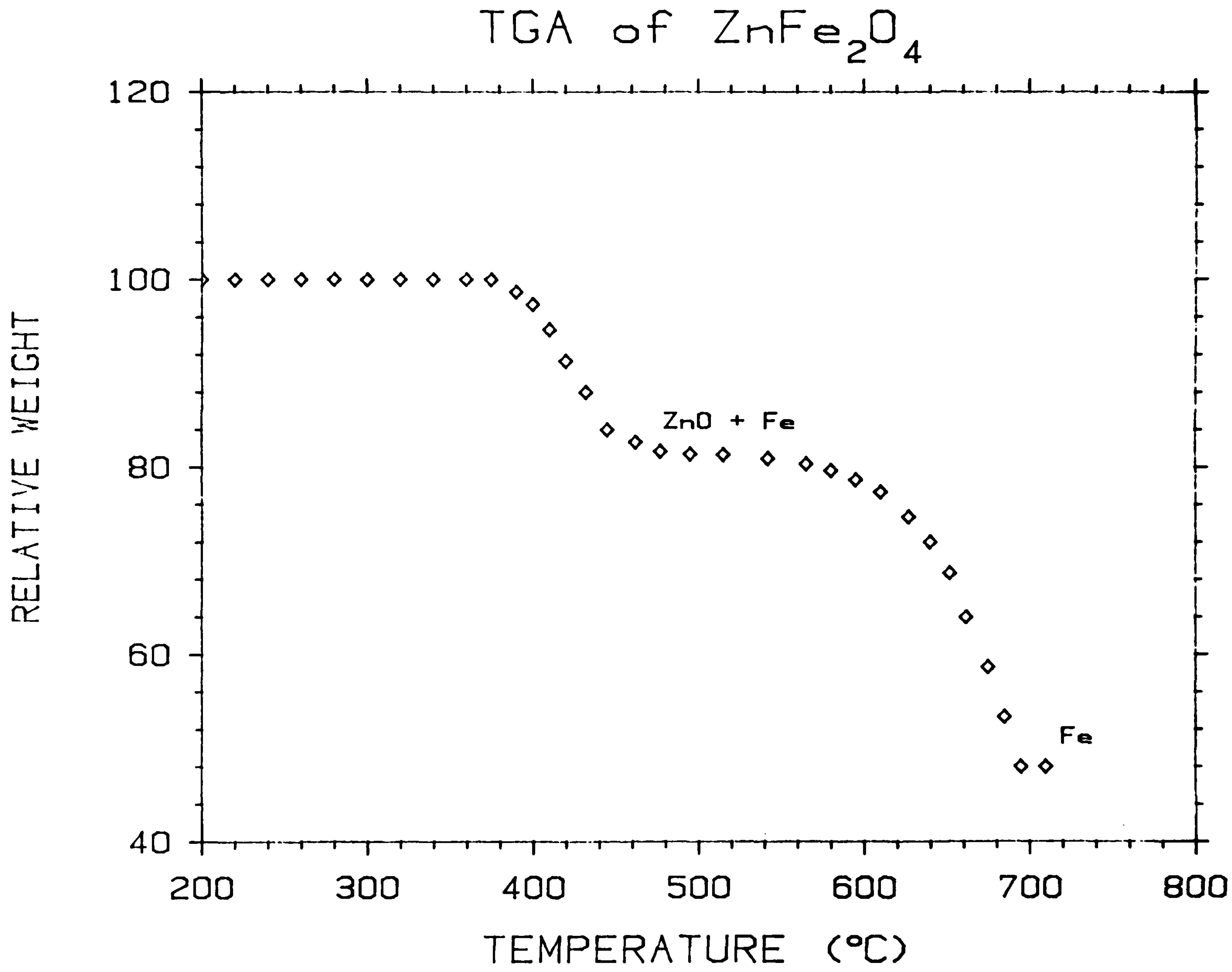

TGA of $ZnFe_2O_4$
RELATIVE WEIGHT
120
100
80
60
40
200
300
400
500
600
700
800
TEMPERATURE (°C)
ZnO + Fe
Fe

Fig 3b

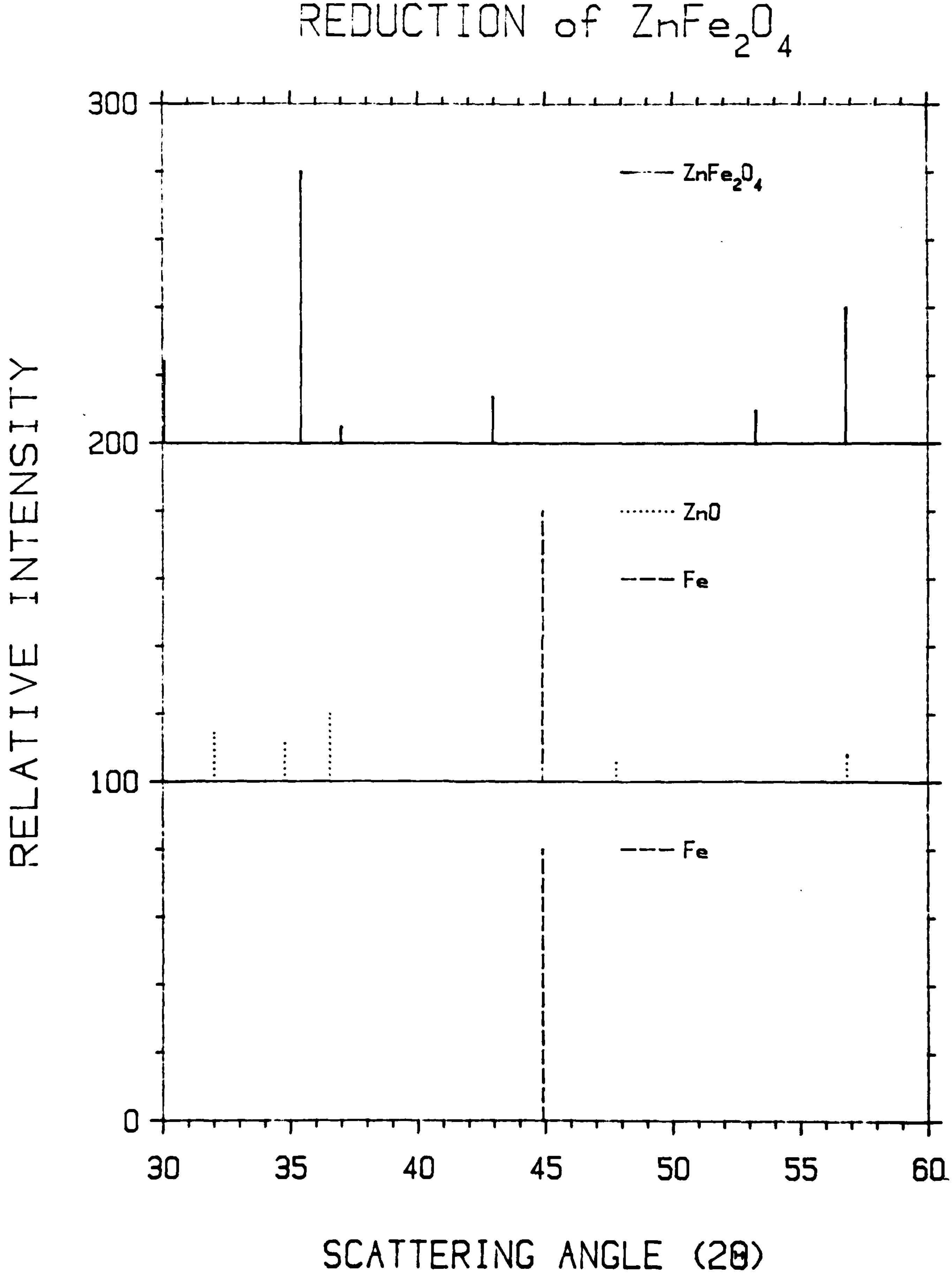

REDUCTION of $ZnFe_2O_4$
$ZnFe_2O_4$
ZnO
Fe
Fe
300
200
100
0
30
35
40
45
50
55
60
RELATIVE INTENSITY
SCATTERING ANGLE (2Θ)

Fig 4

REDUCTION of $CdFe_2O_4$

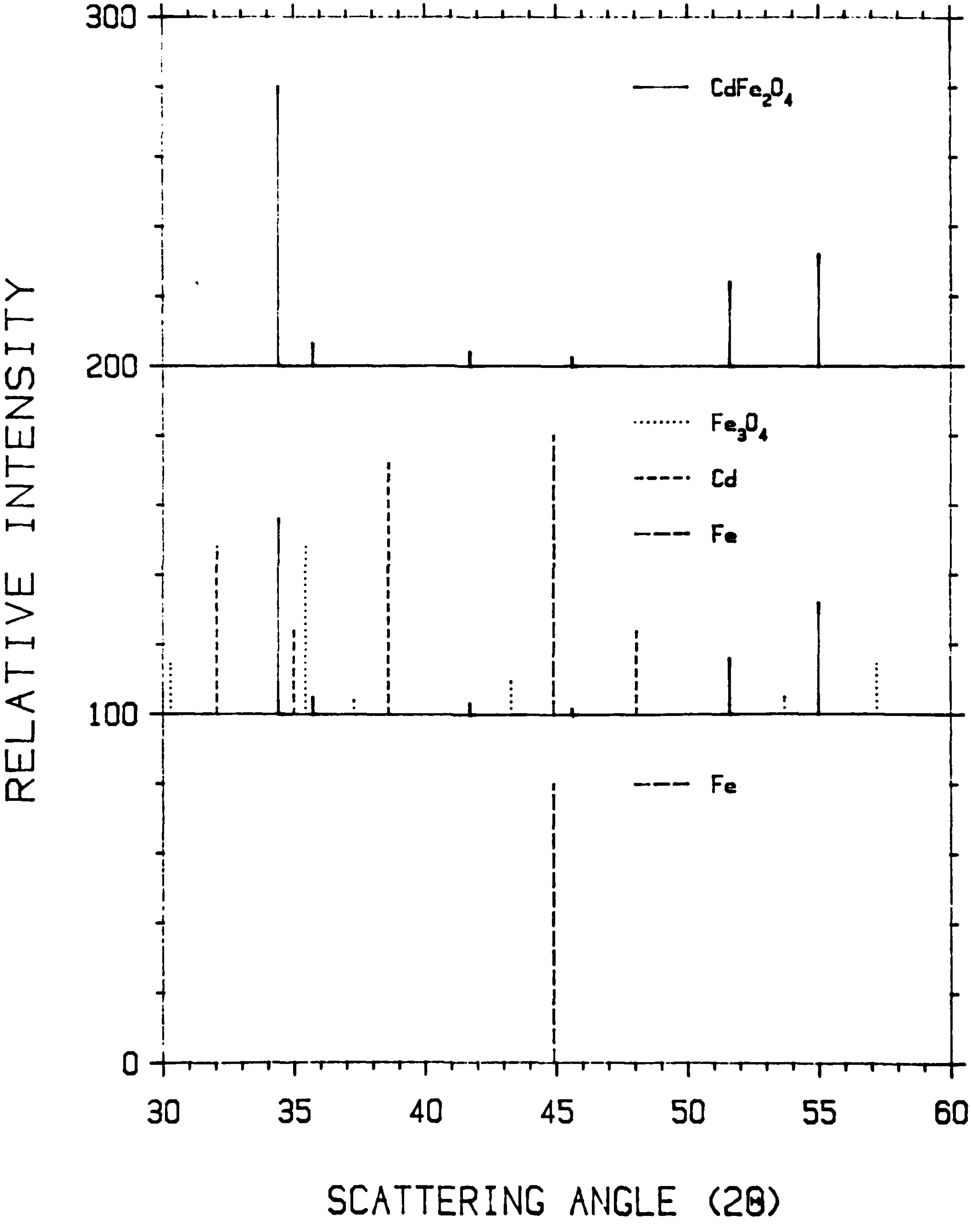
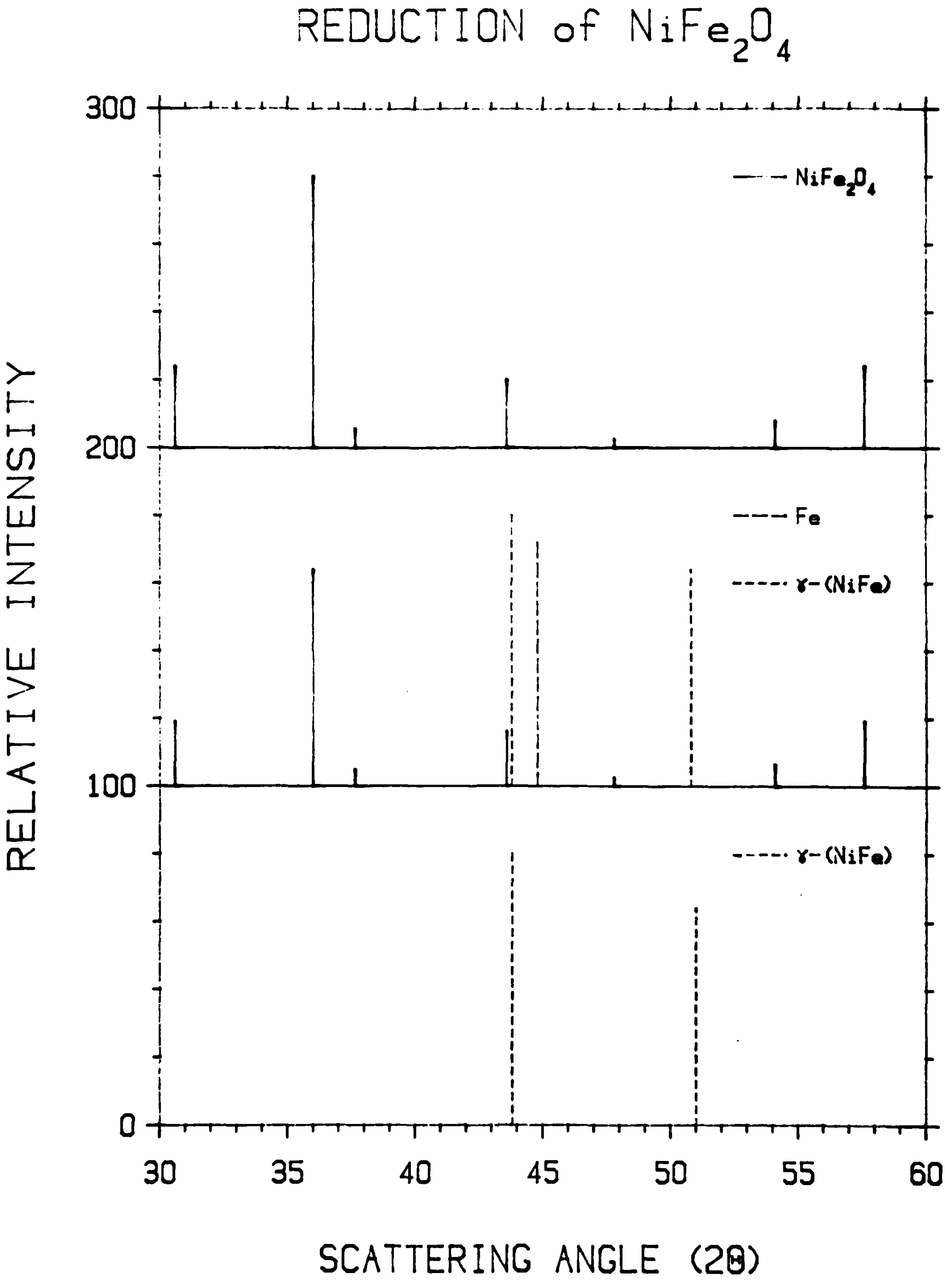


Fig 5



REDUCTION of $NiFe_2O_4$
300
200
100
0
RELATIVE INTENSITY
30
35
40
45
50
55
60
SCATTERING ANGLE (2Θ)
$NiFe_2O_4$
Fe
γ-(NiFe)
γ-(NiFe)