Phase Relations and Ageing Effects in $Fe_{1-x}Co_xS$ System

E. BARTHELEMY AND C. CARCALY

Laboratoire de Chimie Minérale Structurale, associé au CNRS UA n° 200, Faculté de Pharmacie Paris V 4, Avenue de l'Observatoire 75270 Paris Cedex 06, France

The phase relations of the $Fe_{1-x}Co_xS$ system have been established by the X-ray powder diffraction method and lead to the characterization of two regions on both sides of the composition $x = 0.17$ when samples are quenched from 700°C to room temperature. Ageing effects and thermal treatments through the transition T_α are discussed with respect to the phase diagram in order to explain the mechanisms of the phase transformations. © 1987 Academic Press, Inc.

I. Introduction

At $T_\alpha = 425 \pm 2$ K, stoichiometric FeS exhibits by heating a first order phase transition $2C \rightarrow 1C$. The high temperature 1C-phase crystallizes in the NiAs (B_8) structure. The low temperature 2C-phase is a slightly distorted model of the NiAs structure, in which the elementary cell can be described as a superstructure ($a\sqrt{3}$, $2c$) of the 1C-phase (1, 2). More recently, King and Previtt have described another high temperature 1C-phase which exhibits a diffuse superstructure ($2a$, c), close to the NiAs structure (3). The transition $2C \rightarrow 1C$ is endothermic and is associated with a drastic volume contraction. Another change in physical properties like resistivity and magnetic susceptibility is also found at the transition stage and has been reported by several authors (4–7).

In the $Fe_{1-x}Co_xS$ system, a continuous solid solution (NiAs type) between FeS and CoS can be obtained by quenching from high temperature ($\simeq 700$°C) to room temper-
ature. This solid solution has been partially described by several authors for $x \leq 0.15$ and some of its properties have been reported (8–11). In this system, a first order phase transition can be observed as in FeS.

Here we report the results of our investigations on the full range of compositions and also present some new characteristics of the T_α transition. We show that the transition is sensitive to

—Co contents,
—ageing effects,
—thermal treatments.

II. Experimental Procedures

(1) Synthesis

(a) The Starting Materials

FeS and CoS were prepared by reaction between pure elements. Fe and Co were previously heated in a current of hydrogen, at 900°C for 1 day, to prevent any oxidation of the starting metal. Immediately after, the metal was mixed in an appropriate ratio with

pure sulfur. This mixture was heated gradually from room temperature to 700°C in an evacuated silica-glass tube for 2 weeks and quenched in cool water. Then the material was reduced to powder, heated once more at 700°C for a week, and quenched in cool water. In fact, it is impossible to obtain exactly stoichiometric CoS, but rather a mixture of $Co_{1-x}S$ with a small amount of Co_9S_8, as it has been established by Rau (12). Therefore, this mixture can be used to prepare the solid solution and any trace of Co_9S_8 can be detected in the $Fe_{1-x}Co_xS$ solid solution.

(b) The Solid Solution

The solid solution was prepared by mixing the required quantities of CoS and FeS. The mixture was put in a evacuated silica tube, heated at 700°C for a week, quenched in cool water, reground in a mortar to obtain a good homogeneity, and annealed once more at 700°C before being quenched at room temperature.

In these experimental processes, two points have to be taken into account: the stoichiometry of the phases and the thermodynamic equilibrium of the materials at the temperature of quenching.

Special care was taken to ensure that the samples, prepared by the above method, did not present an important deviation from the stoichiometry of the metal/sulfur ratio. It would be actually more convenient to write the general formula of the solid solution: $[Fe_{1-x}Co_x]_{1-\delta}S$, in which δ indicates the metallic vacancies. Nevertheless, δ is estimated to be near zero and cannot be determined by microprobe analysis. It is well known that the amplitude of the T_α transition of $Fe_{1-\delta}S$ is strongly reduced with respect to iron vacancies. By increasing δ, the T_α transition disappears completely while a ferrimagnetic behavior is observed at room temperature for $\delta \simeq 0.10$, near the composition Fe_7S_8.

Therefore, we have prepared, under the same experimental conditions, the nonstoichiometric phases for $\delta = 0.02$ and $\delta = 0.05$.

For a given value of the metallic ratio Co/Fe + Co, and by increasing δ, we note an important decrease of the amplitude of the T_α transition and the hysteresis in the magnetic and thermal properties at the transition which are broadened very strongly. Nevertheless, in no case, is a ferrimagnetic behavior at room temperature observed, corresponding to a (Fe, Co)$_7S_8$ composition. With these supporting remarks, we assume that the phase composition is close to the stoichiometry. $Fe_{1-x}Co_xS$ will be used henceforth to represent the formula $[Fe_{1-x}Co_x]_{1-\delta}S$.

Concerning the thermodynamic equilibrium of the material at the temperature of quenching, the samples are annealed, after a first synthesis, for 2 weeks at 700°C. We have noted that the duration of annealing at this temperature was sufficient.

Various annealings have been carried out on a same composition. Results are as follows:

—No changes have been observed (1) on samples annealed at 700°C either for 2 weeks or 3 months, (2) by repeating the same sample an annealing at 700°C for three times for 2 weeks.

—Some samples also have been pelletized in order to be sintered either at 700°C or at higher temperature in vitreous carbon crucibles, without changes in the behavior of the samples.

—Annealings at lower temperature (indeed, above the temperature of the T_α transition) do not indicate little change either in the composition of the sample or in the temperature T_α of the unaged specimen.

(2) Experiments

Several kinds of measurements have been carried out on these samples.

Crystallographic determinations have been performed by X-ray powder diffraction methods, with a Guinier-Lenné camera using Si as standard.
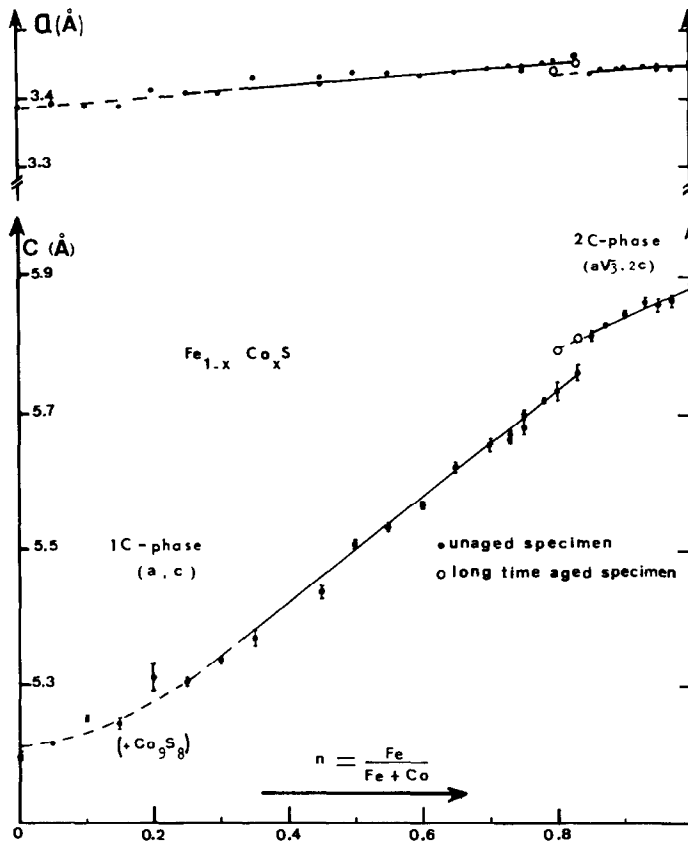
FIG. 1. Lattice parameters measured at room temperature of Fe$_{1-x}$Co$_x$S quenched from 700°C, versus composition (n is calculated from the nominal composition).

The T_α transition has been studied either by DTA or magnetic measurements (Faraday method), in the temperature range 77–500 K.

Ageing effects and thermal treatments have been mainly performed by DTA. Entropy and enthalpy changes at T_α have been calculated after calibration of the DTA apparatus. For determination of transitions near room temperature, Ga has been used as standard.

III. Results

(1) Crystallographic Data

Lattice spacing parameters of Fe$_{1-x}$Co$_x$S

have been measured for samples quenched from 700°C to room temperature (Fig. 1).

The phase diagram exhibits two distinct regions: one, for $0 \leq x < 0.17$, the other, for $0.17 < x \leq 1$.

—For $0 \leq x < 0.17$, a superstructure $a\sqrt{3}$, $2c$ of the NiAs type is observed (2C-phase).

—For $0.17 < x \leq 1$, the phase exhibits a pure NiAs form (1C-phase). Weak diffuse X-ray lines of the superstructure ($2a$, c) are sometimes observed around the composition $x = 0.20$ and indicate a short range order.

—Usually, for $x = 0.17$, 2C- and 1C-phases are mixed for this composition.
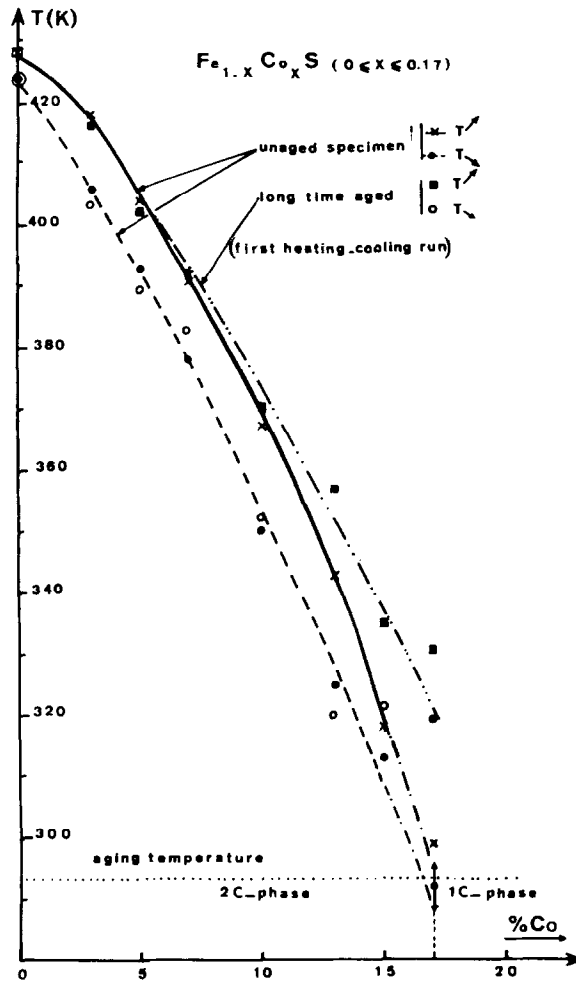
—For $x > 0.60$, compositions are not

FIG. 2. Transition temperature of $Fe_{1-x}Co_xS$ versus composition, in the 2C-phase. Measurements have been performed either just after quenching, or after a sufficiently long time.

well established because a mixture of the 1C-phase and Co_9S_8 is generally precipitated.

—For $x > 0.17$, it is necessary to quench the 1C-phase. If this is not the case, the composition is segregated into 1C-, 2C-phases and Co_9S_8.

(2) The Phase Transition

The transition is very sensitive to several parameters such as: Co contents, ageing effects, and thermal treatments. So, measure-ments have been performed either on un-aged specimens, just after quenching, or on specimens aged for a sufficiently long time at room temperature.

(a) Influence of Co Contents

—Results on unaged specimens are as follows: in the forward direction (i.e., heating rate for $x > 0.17$; cooling rate for $x < 0.17$):

—T_α decreases with increasing x. Figures 2 and 3 show the variations of T_α versus

composition respectively in the 2C- and 1C-phases. Magnetic susceptibility as a function of temperature for various compositions of the 2C-phase is plotted in Fig. 4.

—The transition is endothermic by heating, exothermic in the reverse direction.

—The amplitude of the transition is strongly reduced with increase in Co content. The entropy change at T_α for $x = 0$ has been estimated $\Delta S_{2C \to 1C} \approx 5$ J K^{-1} mole^{-1}, for the transformation 1C → 2C, in the 1C-phase, we have calculated an entropy change $\Delta S_{1C \to 2C} \approx 2.5$ J K^{-1} mole^{-1} for $x = 0.22$.

For $x > 0.30$, the transition is not detected.

—The width of thermal hysteresis is within several degrees and seems to increase for $x > 0.17$ (1C-phase).

(b) Ageing Effects

When specimens are aged at room temperature, a typical behavior is observed in each region of the solid solution. Measurements as a function of time have been carried out on various specimens of fixed composition either in the first heating–cooling run ($x < 0.17$) or in the first cooling–heating run ($x \geq 0.17$).

Results are as follows:

(i). The 2C-phase. For $x < 0.17$, ageing temperature is below the transition temperature of the 2C → 1C transformation.

—For a given value of x, in the forward direction (first heating run), T_α gradually increases with the lapse of time and reaches its final value about 3 weeks later. The reverse transition (i.e., first cooling run) is not so sensitive to ageing effects and we observe an increase of the thermal hysteresis by ageing. Figure 5 shows these variations for the $Fe_{0.85}Co_{0.15}S$ composition.

—Small fluctuations in entropy and enthalpy changes at T_α are observed during the ageing process and indicate that the 2C-phase is stabilized by ageing. Determinations of ΔS and ΔH at the transition point
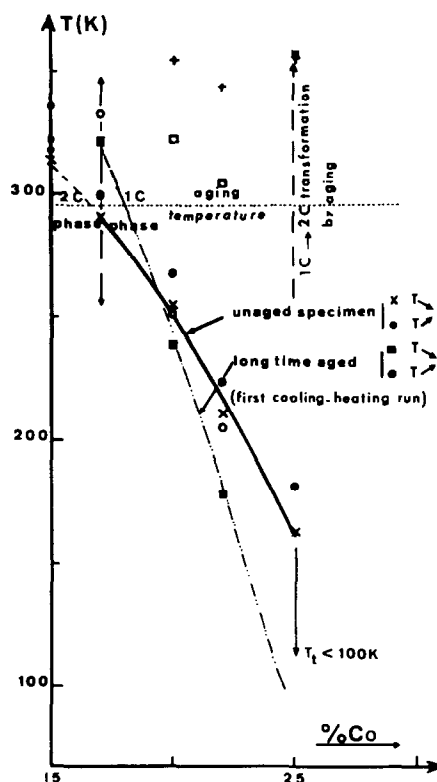

FIG. 3. Transition temperatures of $Fe_{1-x}Co_xS$ versus composition in the 1C-phase, on unaged and aged specimens.

are reported in Fig. 6 for the $Fe_{0.85}Co_{0.15}S$ composition.

—For a given composition, no crystallographical differences are found in X-ray diagrams, between unaged and aged specimens.

—An increase in T_α depends on composition: about 20 K for $x = 0.15$, while no ageing effects are detected for $x \leq 0.05$ (Fig. 2).

(ii). The 1C-phase. Over this range of compositions, the temperature of the transition 1C → 2C is below the ageing temperature. The transition 1C → 2C is exothermic, hence it can be expected that the annealing at room temperature of the 1C-phase produces some transformations in the 1C-phase.
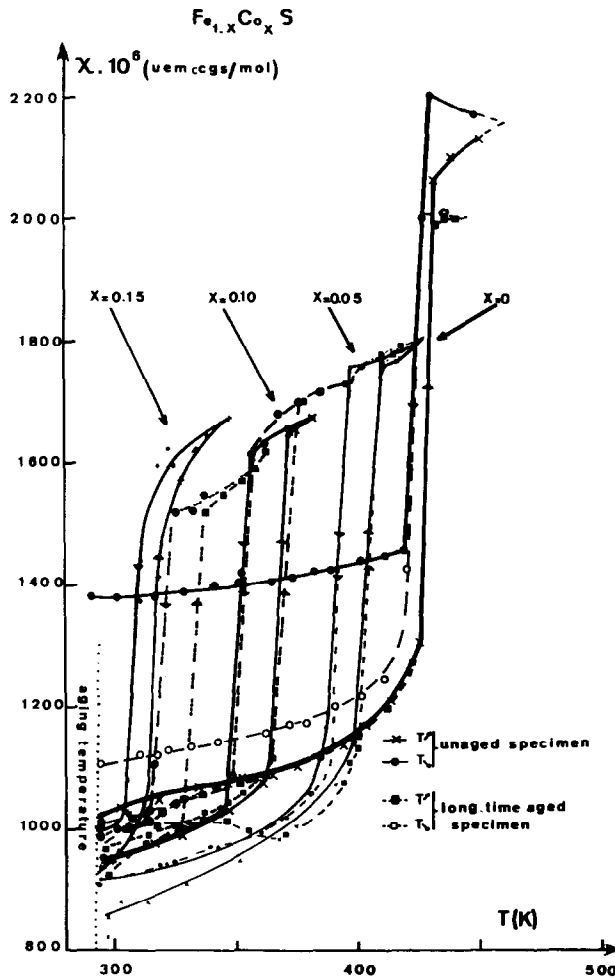
FIG. 4. Magnetic susceptibility as a function of temperature for various compositions of the 2C-phase on unaged specimens just after quenching and aged specimens.

Ageing effects are as follows. For a determined composition, in the forward direction (first cooling run), we observe:

(α) THE STABILIZATION OF THE 1C-PHASE. At first, T_α decreases and seems stabilized by ageing (Fig. 7).

• The stabilization of the 1C-phase is accompanied by some variations of the entropy and enthalpy changes at T_α, during the ageing process (Fig. 8).

• No change in lattice parameters are noticed during this ageing time.

(β) THE DECOMPOSITION OF THE 1C-PHASE. Several months later, we observe the broadening of X-ray lines, consecutive to a slight distortion of the unit cell (c is increasing and a is decreasing), and the vanishing of the transition.

• For specimens which have been aged for a very long time, the transition disappears completely at low temperature and a 1C → 2C transformation can be observed. Magnetic measurements for the composition $Fe_{0.80}Co_{0.20}S$ illustrate the phase trans-
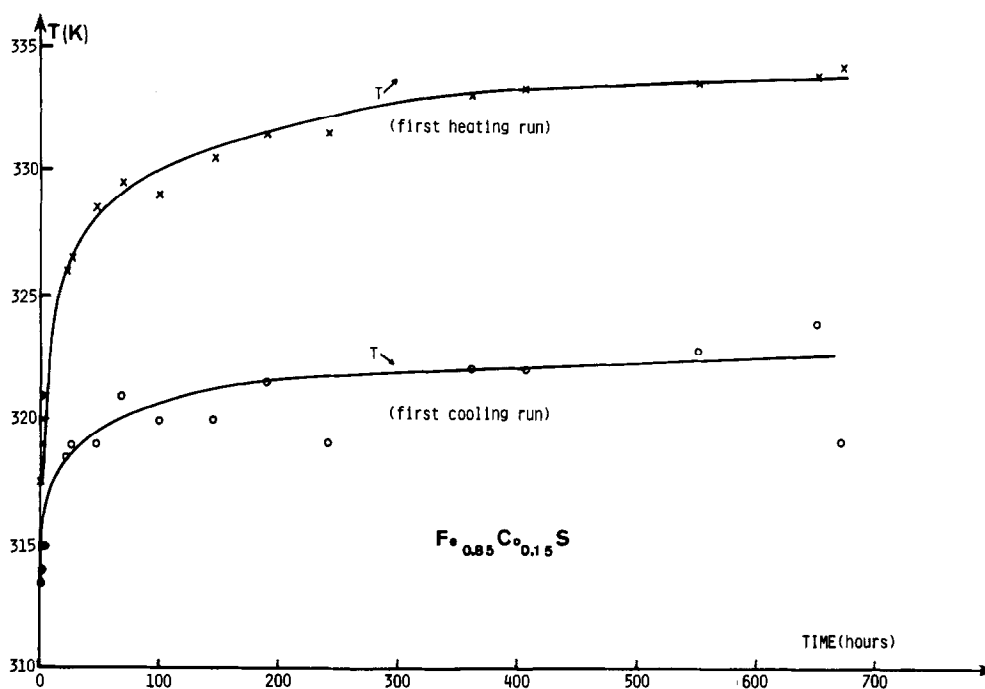
FIG. 5. Transition temperatures as a function of ageing time for $Fe_{0.85}Co_{0.15}S$. Ageing temperature is room temperature. Measurements have been carried out on various specimens of the same composition in the first heating–cooling run.
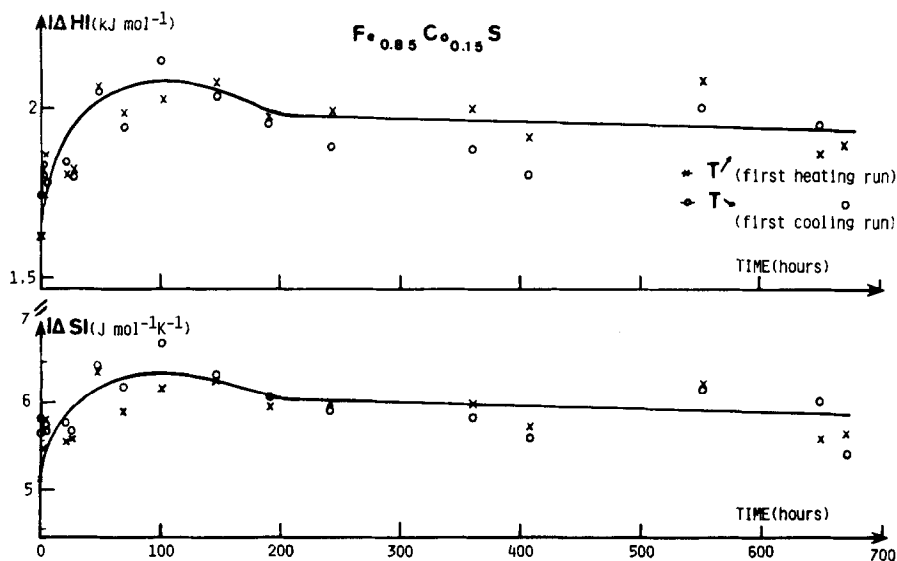

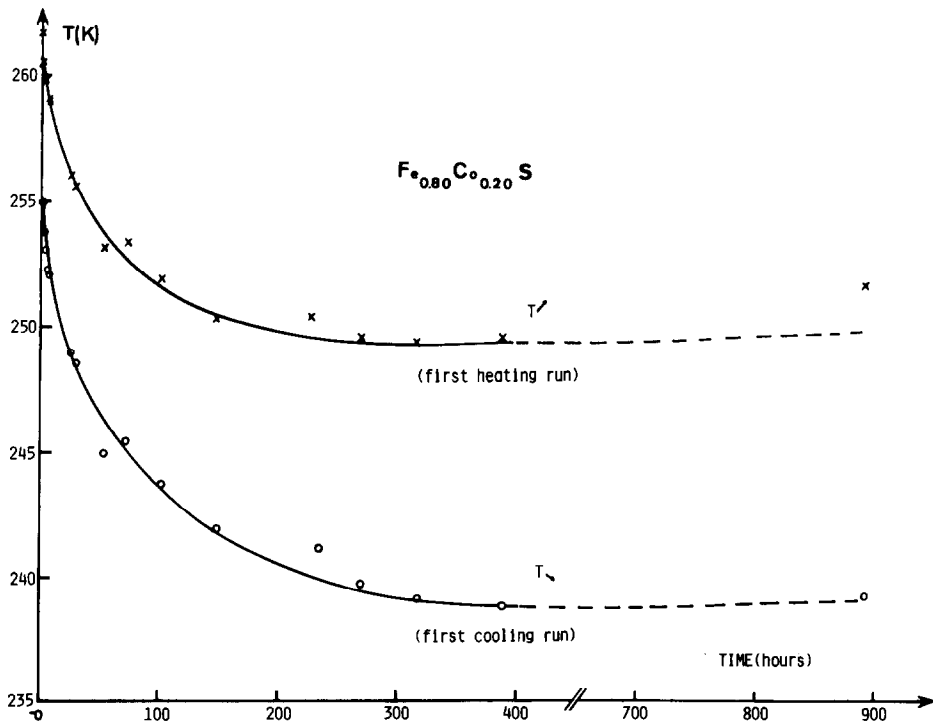FIG. 6. Entropy and enthalpy changes as a function of ageing time for $Fe_{0.85}Co_{0.15}S$.

FIG. 7. Transition temperatures as a function of ageing time for $Fe_{0.80}Co_{0.20}S$ determined on the first cooling–heating run of various specimens of the same composition.
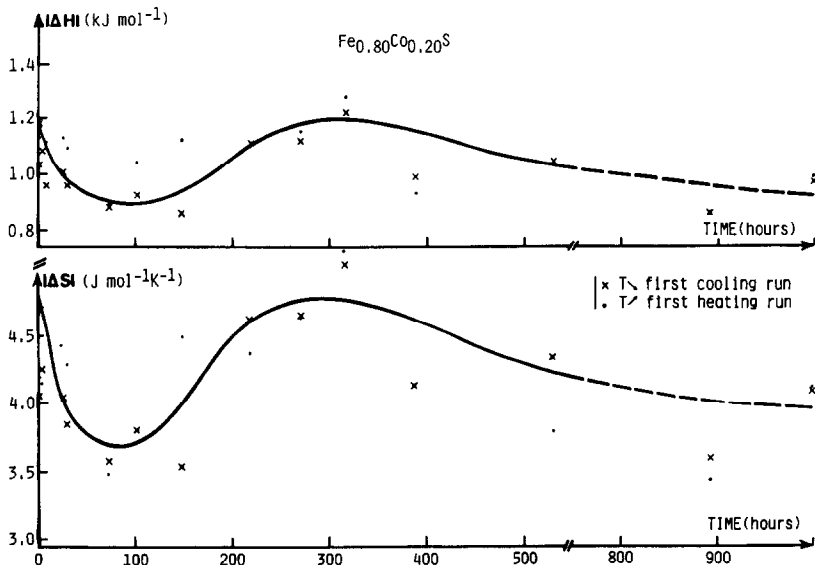

FIG. 8. Entropy and enthalpy changes during the ageing process for the $Fe_{0.80}Co_{0.20}S$ composition.
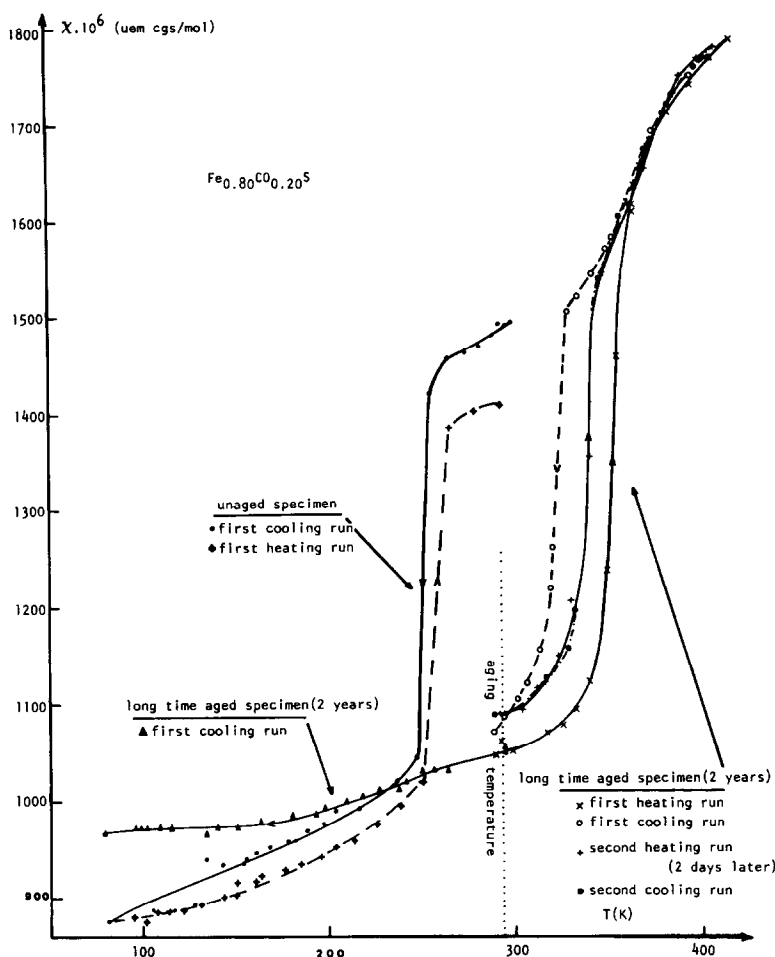
FIG. 9. Magnetic susceptibility as a function of temperature for $Fe_{0.80}Co_{0.20}S$, showing the decomposition of the 1C-phase by ageing.

formation of the 1C-phase by ageing (Fig. 9).

• Ageing effects in the 1C-phase depend on composition and increase with x (Fig. 3).

(c) Thermal Treatments

Thermal treatments through the transition have been performed by subsequent heating–cooling runs on the same sample, either just after quenching, or aged at room temperature. Results are quite different in the 2C- and 1C-phases.

(i) The 2C-phase. Figure 10 shows the

typical behavior of the transition for $Fe_{0.85}$ $Co_{0.15}S$, aged for a sufficiently long time at room temperature. By subsequent heating–cooling runs on the same sample, through the transition, T_α decreases gradually and returns to the initial value observed for the unaged specimen. Relatively extended effects as a function of ageing time in the entropy change are noticed at the transition in the forward direction (first heating run) of the thermal treatment. Figure 11 shows the entropy changes at the transition, in the first heating run, as a function of elapsed
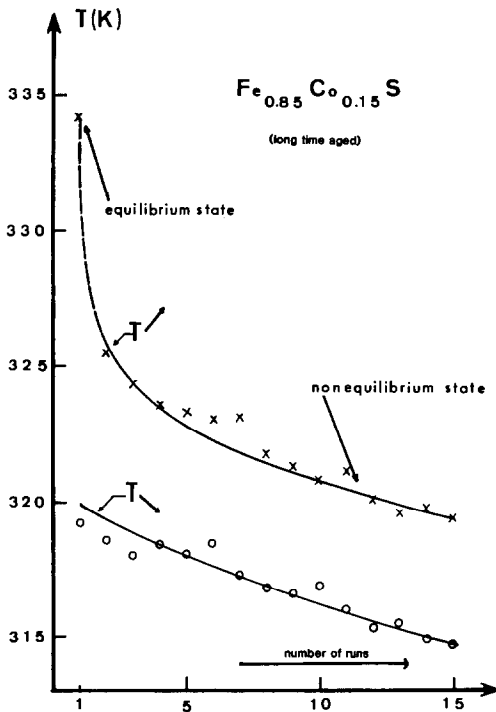
FIG. 10. Thermal treatments on $Fe_{0.85}Co_{0.15}S$ by subsequent heating–cooling runs on a sufficiently long time aged specimen.

time, on the same sample of composition $Fe_{0.85}Co_{0.15}S$. On the other hand, we notice that unaged specimens are not very sensitive to thermal treatments.

(ii) *The 1C-phase.* Thermal treatments through the transition have been performed on the composition $Fe_{0.80}Co_{0.20}S$, either on unaged specimens, or a sufficiently aged one. Figure 12 shows that 1C-phase is never affected by thermal treatments. This result suggests that the mechanical properties of the 1C-phase and the 2C-phase are quite different. We assume that the 1C-phase can be deformed plastically at the transition, while the specimens of the 2C-phase are brittle when they pass by heating through the transition.

IV. Discussion

(1) The Solid Solution

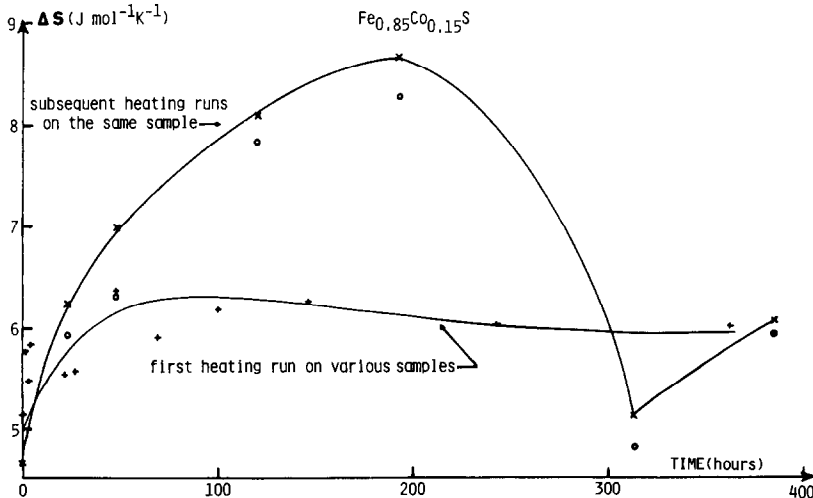By quenching from 700°C to room temperature, the $Fe_{1-x}Co_xS$ system exhibits two distinct regions of solid solution, on

FIG. 11. Entropy changes at the transition by thermal treatments on $Fe_{0.85}Co_{0.15}S$, as a function of time, compared to entropy changes by ageing on various specimens of the same composition. For each value of ageing time, thermal treatments, on the same sample have been performed by making a succession of ten subsequent heating–cooling runs in order to return every time to the initial temperature of transition observed for the unaged specimen. Values of ΔS which are reported here correspond to the first heating run of the thermal treatment.
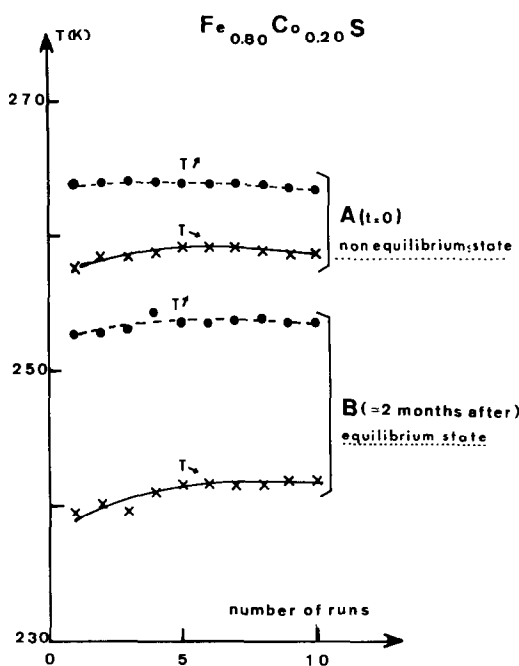
FIG. 12. Thermal treatments on unaged and aged $Fe_{0.80}Co_{0.20}S$ by subsequent cooling–heating runs on the same specimen.

both sides of the composition $Fe_{0.83}Co_{0.17}S$, while a mixture is observed for $x = 0.17$.

A fall in temperature of the T_α transition is observed by increasing x and the transition lies near room temperature for $x = 0.17$.

This result can be considered a common feature in the NiAs phases. Indeed, we have previously reported such a conclusion in the $Ni_{1-x}Fe_xS$ system, quenched from 550°C to room temperature (13, 14). In this system we have found one phase for $0 \le x \le 0.07$, another one for $0.12 \le x \le 0.25$, the c parameter of the second phase being greater than that of the first one, and a mixture of the two phases for $0.08 \le x \le 0.1$ in which the transition temperature lies near room temperature. Although no superstructures have been found for $x > 0.12$, this phase has to be compared on all points to the 2C-phase of the $Fe_{1-x}Co_xS$ system.

(2) Ageing Effects

Two typical behaviors have been observed in the 2C- and 1C-phases of the $Fe_{1-x}Co_xS$ system. In both cases, the T_α transition is stabilized by ageing, indicating that the phase, initially in nonequilibrium, passes gradually into equilibrium. Similar data have been reported by Ohtani et al. in the $Ni_{1-x}Fe_xS$ system (15). These authors have studied various compositions of this system which exhibit the crystallographic transition above the ageing temperature. Consequently, their results can be compared, in the present case, to those observed for specimens of the 2C-phase. According to their resistivity measurements at room temperature, they conclude that ageing effects correspond to a relaxation phenomenon, between a thermally nonequilibrium state to equilibrium state, in which the strain energy resulting of the volume change at the transition is stored in the low temperature phase and relieved by ageing.

We have checked that ageing effects can be reproduced. Indeed, a specimen, aged for a very long time, supposedly in equilibrium at room temperature, exhibits the same ageing effects after annealing at 700°C as before quenching.

Let us now consider the phase diagram of the $Fe_{1-x}Co_xS$ system.

Samples were prepared at 700°C and quenched from this temperature to room temperature.

At 700°C, we assume that the system exhibits a continuous solid solution of the 1C-type, the 1C → 2C transformation occurring below this temperature on the whole range of compositions.

With a fall in temperature, the disordered high temperature 1C-phase becomes metastable and can be changed into the ordered 2C-phase if the crystallographic transformation occurs above room temperature and if the phase cannot be quenched whatever the rapidity of quenching. This is the case

for $x < 0.17$. For $x > 0.17$, T_α lies below room temperature and consequently these compositions do not pass immediately by quenching through the transition and can be obtained at room temperature.

The transition 1C → 2C is associated with a drastic volume expansion. If the material is not sufficiently soft or quenched in extreme conditions, the sample cracks through the transition, and dislocations can be produced, while strain energy is stored in the material.

On the other hand, when a first order phase transition occurs, two phases are simultaneously present during the transition. If the sample is cooled rapidly, it is possible to quench a nonequilibrium state in which the 1C-phase is not completely transformed into the 2C-phase. This seems not be the case here because no extra lines of the 1C-phase have been observed in the X-ray charts of the unaged 2C-phases.

Ageing effects in the 2C-phase depend on composition and increase with x. This result suggests that the stabilization of the 2C-phase can also be considered as the order–disorder process between Fe and Co atoms. Unfortunately, it is not possible to detect by X-ray powder diffraction any enhancement of the intensity of the superstructure X-ray lines.

Nevertheless, we assume that dislocations are the main factor controlling the ageing process in the 2C-phase. This result is supported by the effects of the thermal treatments through the transition. However, further experiments have to be carried out to understand clearly these phenomena. The 1C-phase is quite different, it is at first stabilized by ageing with a fall in the temperature of transition. Thermal treatments through the transition suggest that this phase is relatively soft and can be plastically deformed.

In X-ray charts of unaged specimens of compositions $0.20 \le x < 0.30$ we have observed some very diffuse extra lines which can be attributed to the superstructure ($2a$,

c) of the elementary cell, and which are probably due to a local order.

If we assume that the plasticity of the 1C-phase is sufficient at room temperature, these weak correlations can be enhanced by ageing and consequently contribute to the stabilization of the 1C-phase. This hypothesis is supported by the fact that, by ageing, we observe a distortion of the unit cell in which parameters a and c vary inversely as to direction, the decrease of the parameter a indicating that correlations are probably established in the hexagonal basal plane. On the other hand, the shape of DTA peaks at the transition is characteristic. Somewhat broadened in the forward direction (by cooling) the peaks are always well defined in the reverse direction (heating rate). This observation suggests a displacive mechanism for the transition 1C → 2C.

So ageing effects in the 1C-phase are accompanied:

(1) by an energy loss which contributes to the stabilization of the 1C-phase and the disappearance of the 1C → 2C transformation;

(2) by the distortion of the cell that leads to the crystallographic transformation 1C → 2C by ageing when the free energies of the 1C and 2C phases are the same.

In fact, the mechanism of the crystallographic transformation 1C → 2C seems to be more complicated. We have observed that the transition temperature T_α of the specimens aged for a very long time is not very sensitive to the nominal composition of the starting material and always lies above room temperature (340 K $< T_\alpha <$ 350 K) (Fig. 3).

This suggests that the last step of the transformation by ageing of the 1C-phase is rather a decomposition into a nonstoichiometric $(Fe_{1-x}Co_x)_{1-\delta}S$ 2C-phase and Co_9S_8. This assertion is supported by two observations:

(1) the segregation of the unaged 1C-phase if the composition is cooled slowly from 700°C to room temperature;

(2) the difficulty to obtain without some amounts of Co_9S_8, the composition of the 1C-phase for $x > 0.60$.

However again, we suppose that the 2C-phase which is formed by ageing is a ternary composition. If it was not the case, the T_α transition of the very old specimens would correspond to a nonstoichiometric $Fe_{1-\delta}S$ with $\delta \simeq 0.05$ (5). For such a composition, the amplitude of the transition is strongly reduced with respect to iron vacancies. This is not in agreement with the sharp increase of susceptibility observed at the transition for the very old composition $Fe_{0.80}Co_{0.20}S$ (Fig. 9).

In conclusion, we have tried to explain the typical behavior of the 2C- and 1C-phases, with respect to the phase diagram. Further work has to be done dealing with the mechanism of these phase transformations.

References

1. E. F. BERTAUT, Bull. Soc. Fr. Mineral. Cristallogr. 79, 293 (1956).
2. H. T. EVANS, Science 167, 621 (1970).
3. H. E. KING, JR. AND C. T. PREVITT, Acta Crystallogr., Sect. B 38, 1877 (1982).
4. W. MOLDENHAUER AND W. BRUCKNER, Phys. Status Solidi 34, 565 (1976).
5. J. L. HORWOOD, M. G. TOWNSEND, AND A. H. WEBSTER, J. Solid State Chem. 17, 35 (1976).
6. J. M. D. COEY, H. ROUX-BUISSON, AND R. BRUSSETTI, J. Phys. 37, C4, 1 (1976).
7. M. G. TOWNSEND, J. R. GOSSELIN, R. J. TREMBLAY, AND A. H. WEBSTER, J. Phys. 37, C4, 11 (1976).
8. E. I. TERUKOV, S. ROTH, G. KRABBLES, AND H. OPPERMANN, Phys. Status Solidi A 68, 233 (1981).
9. G. KRABBES, E. I. TERUKOV, AND H. OPPERMANN, Phys. Status Solidi A 71, K 143 (1982).
10. E. WIESER, G. KRABBES, AND E. I. TERUKOV, Phys. Status Solidi A 72, 695 (1982).
11. C. A. MCCAMMON AND D. C. PRICE, J. Phys. Chem. Solids 43, 431 (1982).
12. H. RAU, J. Phys. Chem. Solids 37, 931 (1976).
13. E. BARTHELEMY AND C. COLLIN, in "Proceedings, VI Int. Conf. on Solid Compounds of Transition Elements, Stuttgart (1979).
14. E. BARTHELEMY, Coll. Int. du CNRS, Chimie et Physique des sulfures, seleniures et tellurures à l'état solide, Paris (1981).
15. T. OHTANI, K. KOSUGE, AND S. KACHI, Bull. Chem. Soc. Jpn. 54, 568 (1981).