STRUCTURE AND PHYSICAL PROPERTIES OF THE QUATERNARY PHASE "CAALSIFER" IN INDUSTRIAL Fe-Si ALLOYS

F. MARGARIDO[1], M. O. FIGUEIREDO[2]

1-Dep. Eng. Materiais, IST and Centro de Valorização de Recursos Minerais, INIC, Av. Rovisco Pais, 1096 Lisboa Codex.

2-Centro de Cristalografia e Mineralogia, Instituto de Investigação Cientifica Tropical,

Al. D. Afonso Henriques, 41, 4 E, 1000 Lisboa, Portugal.

ABSTRACT -From the structural study of Fe-Si alloys with 75 wt.% Si it was possible to detect, beyond the well recognized phases - Si, $FeSi_2$ (α and β), Ca-Si, Fe-Si-Al, Ca-Al-Si - a quaternary phase Fe-Al-Si-Ca isotypic with $\alpha\text{-}Fe_{1-x}Si_2$ (leboite) which we designate as "Caalsifer" from the chemical constitution.

By comparing the X-ray intensities diffracted by "$\alpha\text{-}Fe_{1-x}Si_2$" phases with the corresponding values calculated on the basis of various chemical-structural models, the composition $(Fe_{0.8}Al_{0.1}\square_{0.1})(Si_{0.8}Ca_{0.2})_2$ was assigned to that phase.

A mechanism for the structural transition $\alpha\rightarrow\beta$ "$FeSi_2$" is suggested based on crystalchemical data of these phases. We suggest an explanation for the hindering of such structural transformation in these alloys and for the properties of the quaternary phase Caalsifer.

1 - INTRODUCTION

Studies on the metallurgical structures of iron alloys, namely of ferro-silicon alloys, are not frequently available, a fact that may be due to the assumption that these alloys are produced to be remelted and, therefore, their physical metallurgy is of minor importance [1]. However, the phase composition of ferro-silicon alloys may significantly affect some properties, beyond playing an important role in the leaching treatment for silicon extraction.

Fe-Si alloys contain, besides iron and silicon, minor elements, like Al, Ca, Ti, Cr, V, Mn. The fundamental chemical components, likely to give rise to changes in the constitution of the main phases are Fe, Si, Ca and Al. The other elements found in minute percentages are dispersed in the dominant phases.

Structurally, these alloys are essentially a composite formed by silicon metal, iron dissilicide (an intermetallic phase with nominal composition $FeSi_2$) and some "spurious" phases (Ca-Si, Fe-Si-Al, Ca-Al-Si) which contain other impurities [2].

Gibbs phase's rule (P+F=C+2) does not hold, since alloy solidification takes place outside the equilibrium conditions. The number of observed phases is then higher than expected for an essentially quaternary system (Si, Fe, Al, Ca). The presence of trace elements and the large span of percentages of main elements (Fe+Si versus Al+Ca) give sporadically rise to the appearance and local concentration of phases with minute dimensions.

The growing demand of high grade silicon metal together with the high level of energy-consumption associated to the electrometallurgical process of refining, have led to the development of an alternative hydrometallurgical treatment for ferro-silicon alloys with 75 wt. % Si.

The leaching efficiency depends critically on the access of the leaching agent to those intermetallic phases. The corrosive attack by this acid solute must give rise to an early disintegration of the alloy and dissolve the impurities (Fe, Ca and Al) to the desired level, leaving the less contaminated and chemically stable silicon grains unaltered [3]. Conse-

quently, the ferro-silicon microstructure, its fracture, intra and inter-phase residual stresses will be important factors to take into account when the hydrometallurgical process is optimized.

2 - CRYSTALCHEMISTRY AND PHYSICAL PROPERTIES OF "FeSi$_2$" PHASES

In the silicon rich region of Fe-Si phase diagram, two structural forms of the intermetallic compound "$FeSi_2$" exist beyond silicon: the α phase, usually called "leboite", stable at high temperature, and the low temperature β phase.

The high temperature α phase, exhibits a non-stoichiometric composition "$Fe_{1-x}Si_2$" and has a tetragonal crystal symmetry with parameters $\mathbf{a} = 2.68$ Å and $\mathbf{c} = 5.134$ Å, space group P4/mmm, with iron in the equivalent position 1(a) (0,0,0), silicon in 2(h) $\pm (\frac{1}{2}, \frac{1}{2}, z)$ and a positional parameter $z = 0.27$ [4].

The Si-Si interatomic distance is 2.36 Å along the quaternary axis. Parallel to (001) there are quadrangular layers of Fe atoms with interatomic distances Fe-Fe = 2.68 Å, similar to those found in the metal [5,6]. Fe atoms are almost cubically surrounded by eight Si atoms at a distance of 2.35 Å, and by four Fe atoms in the (001) plane at z = 0 and at a distance of 2.68 Å. However, the actual situation is more complex because the Fe sublattice contains 13-23% vacancies,
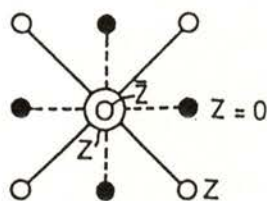
22

which means that there is no real equivalency of all the Fe atoms in the compound [7]. The nearest neighbours of silicon are four Fe atoms at a distance of 2.35 Å and six Si atoms at 2.36 Å (1), 2.68 Å (4), and 2.77 Å (1) [4].
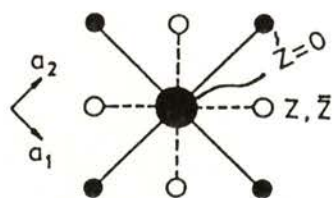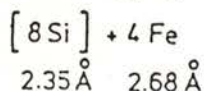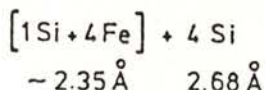
Fe and Si coordinations in the structure of α-$Fe_{1-x}Si_2$ phase are represented in Fig. 1. The structural characteristics of this phase determine, as a result of the above mentioned Fe layer, the bidimensional character of its physical properties.

Coordination of Fe(Z=0)

$$\begin{bmatrix} 8\,Si \end{bmatrix} + 4\,Fe$$
$$2.35\,\overset{o}{A} \quad 2.68\,\overset{o}{A}$$

Coordination of Si (Z)

$$\begin{bmatrix} 1\,Si + 4\,Fe \end{bmatrix} + 4\,Si$$
$$\sim 2.35\,\overset{o}{A} \quad 2.68\,\overset{o}{A}$$

● — Fe atoms   O — Si atoms

Fig. 1 -Coordination of Fe and Si atoms in α-$Fe_{1-x}\,Si_2$ structure.

The stoichiometric β phase has an orthorhombic crystal lattice with parameters **a** = 9.8795 ± 0.0005 Å; **b** = 7.7977 ± 0.0003 Å ; **c** = 7.8392 ± 0.0003 Å [8], Cmca space group symmetry, and contains 48 atoms per unit cell (16 Fe and 32 Si) [9]. This phase has an atomic arrangement corresponding to a severe distortion of fluorite (CaF_2) structure type, with two kinds of deformed [$FeSi_8$] cubes, with Fe atoms in their centers, identified by I and II but in crystallographically distinct equivalent positions (Fig. 2).

Si atoms occupy two crystallographically identical mono-variant equivalent points with distinct positional z parameters, (Si_I and Si_{II}). Si-Si interatomic distances are comparatively more homogeneous (2.51 - 2.59 Å) in [$Fe_{II}Si_8$] cubes, while in [Fe_ISi_8] cubes such distances give rise to long (3.56 Å) and short (2.45 Å) edges. Consequently, Fe_I atoms are geometrically surrounded by Si in a more regular way than Fe_{II} atoms, a feature clearly apparent in the Mössbauer spectrum of β phase [8].
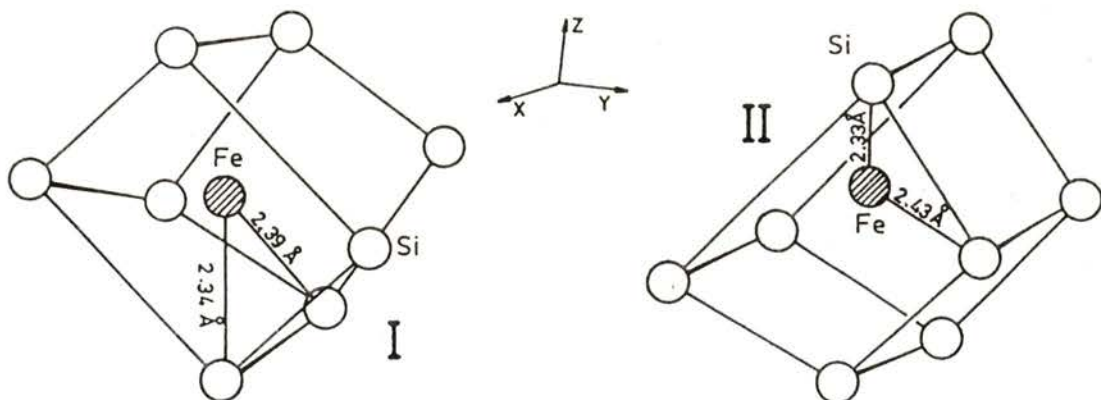
Fig. 2 - Fe coordination in β-$FeSi_2$ structure.

Si atoms are in an approximately tetrahedral coordination, being surrounded by two Fe_I and two Fe_{II} atoms. This coordination geometry approaches that of Si atoms in silicon "metal" and is quite different from that found in α-$Fe_{1-x}Si_2$ phase, where each silicon atom is surrounded by four iron atoms and by another silicon atom at a short distance (2.36 Å) plus (1+4)Si atoms at larger distances (2.77 Å+2.68 Å).

The $\alpha \rightarrow \beta$ transition of $FeSi_2$ takes place during the cooling of the ferro-silicon alloy, at a temperature close to 1210K, changing from a metallic behaviour at higher temperature to a semiconductor behaviour at lower temperature [10]. The technical importance of $FeSi_2$ arises from the thermoelectric properties of β phase, and also from its electric properties that show at T_t a metal-nonmetal transition. According to an energy band model, this transition is related to the occurrence of vacancies in the Fe sublattice, and therefore it is not a true metal-nonmetal transition in the usual sense [11]. β-$FeSi_2$ is a semiconductor compound of **n** type when doped with cobalt and of **p** type if doped with aluminium impurities.

3 - CONTRIBUTION TO THE MECHANISM OF $\alpha \rightarrow \beta$ "$FeSi_2$" STRUCTURAL TRANSITION

The mechanism of the $\alpha \rightarrow \beta$ transformation was explained by some previous authors within a structural [12,13] or crystallographic [14] framework, but it may also be explained using crystalchemical data.

α-$Fe_{1-x}Si_2$ is grown from a liquid rich in silicon ; however, owing to the large amount of iron present, during the so-

lidification of this phase, Si atoms do not occur in a tetrahedral configuration characteristic of the "metal". A tetragonal Fe-Si phase is formed with two consecutive Si layers, alternating with one Fe layer, and as a result, each Si atom is linked to another Si atom at a short distance (2.36 Å) close to the Si-Si distance in the metal (2.352 Å). This phase can easily accommodate some chemical elements (impurities) which are present in the liquid phase, due to the variety of chemical bonding: quasi metallic for Fe atoms and intermetallic for Si atoms.

On the other hand, the structure of α-$Fe_{1-x}Si_2$ seems to have a "memory effect", causing an atomic rearrangement leading to the stoichiometric orthorhombic type (β-$Fe_{1-x}Si_2$), where Si layers alternate with half-filled Fe layers. In this new structure the Si atoms

are not bonded to each other, but tetrahedrally surrounded by Fe atoms, in an environment geometrically similar to that of Si "metal". The plane of Fe atoms in the α phase separates into two levels during the structural rearrangement, thus breaking the Si-Si double layer and giving rise to alternate [Si_2-Fe-Si_2-Fe] layers in β phase. Physical properties displayed by these two $FeSi_2$ phases agree with this mechanism, the α phase exhibiting metallic behaviour due to Fe quadrangular layers identical to those present in iron metal. Conversely, β phase exhibits semiconductor properties similar to those of metallic silicon.

(001) and (100) planes of α and β phases respectively, are represented in Fig. 3. By comparing lattice parameters it is clear that $a_\beta \approx 2c_\alpha$ and $b_\beta \approx c_\beta \approx 2\sqrt{2}a_\alpha$.
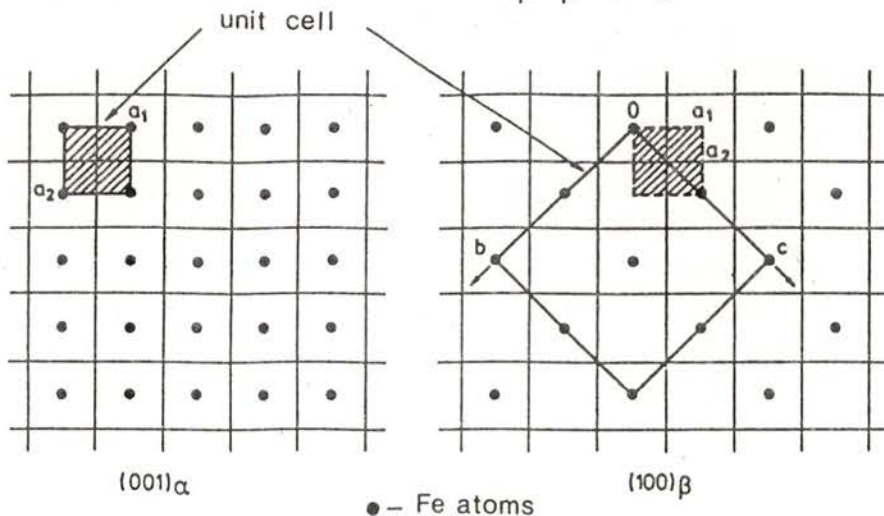

Fig. 3 –Sketch of (001) and (100) planes of α and β phase, respectively, at the level of Fe layer.

4 - EXPERIMENTAL RESULTS

A structural characterization by X-ray diffraction (XRD) and microstructural observations by scanning electron microscopy (SEM-EDS) were performed on four alloys with 75 wt. % Si and other chemical elements.

X-ray diffraction patterns (XRPD) were recorded in a non-automated Phillips powder diffractometer under optimized instrumental conditions, namely a curved graphite crystal monochromator, small aperture slits and a scanning speed of $(1/4)^\circ$ $2\theta.min^{-1}$. The following phases were found: α-Fe$_{1-x}$Si$_2$ (tetrag.), β-Fe$_{1-x}$Si$_2$ (orthorh.), CaAl$_2$Si$_{1.5}$, CaSi$_2$ and Al-Fe-Si.

A distinct asymmetry in the "α-Fe$_{1-x}$Si$_2$" X-ray reflections was detected which was tentatively ascribed to the presence of calcium and aluminium impurities in solid solution. This would imply the coexistence of the major α-Fe$_{1-x}$Si$_2$ phase (practically free from Ca and Al) with domains containing a minor Al-Si-Ca phase plus a quaternary Fe-Si-Ca-Al phase isostructural with α-leboite.

The crystalchemical model could explain the presence of such quaternary Fe-Si-Ca-Al phase, in view of the structural similarity with the binary phase α-Fe$_{1-x}$Si$_2$ [15]. In fact, the domains with quaternary composition, observed by SEM-EDS and which do not correspond to an explicit phase in the XRPD pattern, can be related to the asymmetry effect just mentioned.

The equidistances (d,Å) of hkl reflections of FeSi$_2$ phases were calibrated against coexisting silicon as an internal standard. 28 reflections observed for "α-Fe$_{1-x}$Si$_2$" phases (binary and quaternary) were recorded at least three times each, and the mean value of the areas under the peaks were used as a weighing of the intensities of the X-ray spectra.

The two FeSi$_2$ "phases" with tetragonal structure and slightly different lattice parameters turned out to be very important. The presence of this quaternary phase has implications on the hydrometallurgical treatment of industrial Fe-Si alloys, which will be more liable to chemical attack due to internal stresses. Its presence could, therefore, benefit the hydrometallurgical processing of ferro-silicon alloys for silicon production.

5 - STRUCTURE AND COMPOSITION OF THE QUATERNARY PHASE Fe-Al-Si-Ca

Four different structural models were considered for the structural analysis of the quaternary phase and calculation of the structure factors. These models differ due to the nature and distribution of substitutional impurities (Ca and Al) and other structural defects (vacancies):

model I - stoichiometric $FeSi_2$; model II - non-stoichiometric, with 20% vacant iron sites ($Fe_{0.8}Si_2$); model III - still defective, with some aluminium replacing iron and some calcium substituting for silicon, with the formula $(Fe_{0.8}Al_{0.1}\square_{0.1})(Si_{0.8}Ca_{0.2})_2$; model IV -stoichiometric, with calcium partially replacing silicon, with the formula $Fe(Si_{0.8}Ca_{0.2})_2$.

For each model three hypothetical values of the positional z parameter of the equivalent position 2(h) occupied by Si atoms were deduced. This parameter influences directly the Si-Si interatomic distance in α-leboite crystal structure, being therefore sensitive to any extensive replacement of silicon in the ideal structural models.

The discrepancy factor (R %) of each model was obtained by comparing the intensities diffracted by α-$Fe_{1-x}Si_2$ phases to those calculated from the proposed model. The best (minimum) discrepancy factor is attained for model III - $(Fe_{0.8}Al_{0.1}\square_{0.1})$ $(Si_{0.8}Ca_{0.2})_2$ and z close to 0.28 (R = 18%). Consequently the quaternary phase detected in this study will have a tetragonal crystal structure similar to α-leboite, with unit cell parameters **a** = 2.69 (0) Å, **c** = 5.1 (9) Å. We called this phase "Caalsifer" [16] in order to stress its quaternary constitution.

A high R' value relating observed and calculated intensities for model III is ac-

ceptable in view of the reduced number of reflections used for the structural analysis (necessarily performed over the industrial composite) and given the low concentration of iron dissilicide in these alloys. The structure model of the Caalsifer phase is shown in Fig.4.
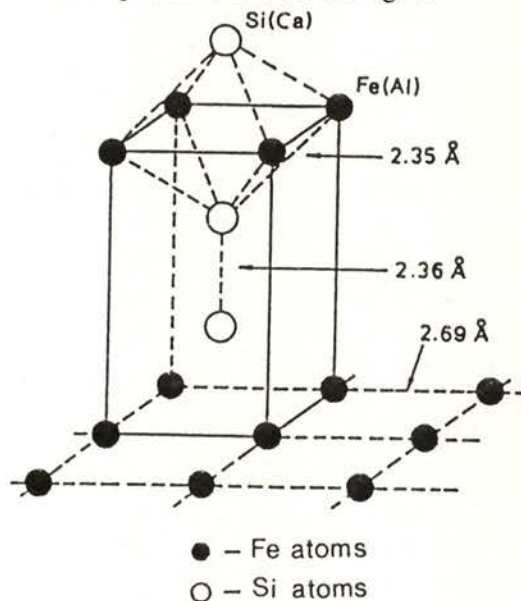

Fig. 4 –Structural model of Caalsifer phase.

6 - HINDERING MECHANISM OF $\alpha \rightarrow \beta$"FeSi$_2$" STRUCTURAL TRANSITION.

The structural study of Fe-Si alloys with 75 wt. % Si shows that the formation, during cooling, of the stable phase at room temperature β-$FeSi_2$ (orthorh.), is intrinsically associated to the precipitation of binary phases Ca-Si and ternary Ca-Al-Si and Al-Si-Fe phases. Even in alloys with similar content of

impurities (Ca and Al), the amounts of these spurious phases are clearly lower when the high temperature phase $\alpha\text{-Fe}_{1-x}\text{Si}_2$ (tetrag.) remains metastable at room temperature, e.g., when domains of the binary phase $\alpha\text{-Fe}_{1-x}\text{Si}_2$ coexist with the quaternary phase, $(\text{Fe}_{0.8}\text{Al}_{0.1}\square_{0.1})\,(\text{Si}_{0.8}\text{Ca}_{0.2})_2$.

It was checked that the $\alpha\rightarrow\beta$ transformation was effectively hindered by the formation of the quaternary phase [17]. The presence of useful impurities in the right amounts allows the stabilization of the quaternary phase and prevents the formation of the stoichiometric compound $\beta\text{-FeSi}_2$ (Fig. 5) which is stable at low temperature.
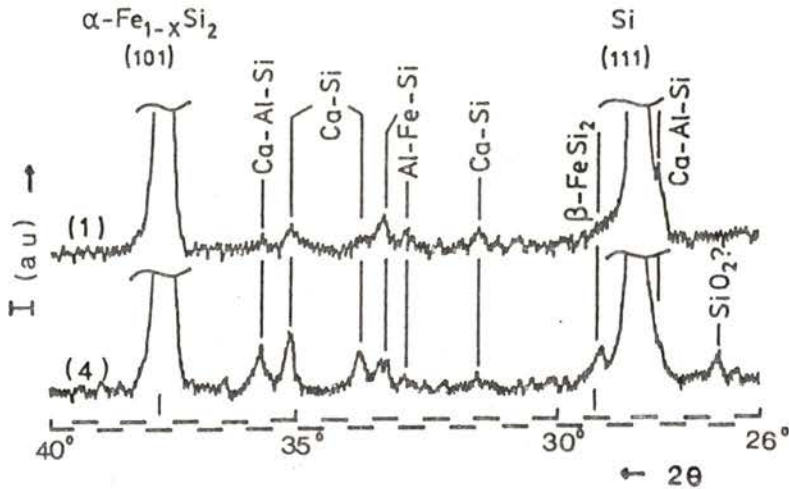

Fig. 5 – XRPD patterns (Cu Kα radiation) and phase identification.

Actually, when β phase precipitation is observed, the content of impurities in the remanent phase is reduced and several extra compounds are formed - binary Ca-Si and ternary Ca-Al-Si and Al-Fe-Si; on the other hand, for alloys where the α phase is abundant at room temperature, the precipitation of β phase is not significant and the content of extra phases is attenuated.

It was inferred that the joint incorporation of two elements with different structural functions - Ca and Al - in α-leboite structure, improves the stability of this phase, preventing the $\alpha\rightarrow\beta+\text{Si}$ eutectoid transformation to take place.

7 - CONCLUSIONS

In spite of the low concentration of quaternary phase Caalsifer in ferro-silicon alloys, and of the reduced number of measurable reflections in the X-ray diffraction pattern, the discrepancy factor obtained in the present structural study suggests that, beyond the normal α-$Fe_{1-x}Si_2$ phase, domains of defect concentration are present containing a Fe-Si-Ca-Al phase, isostructural with α-leboite, with approximate formula $(Fe_{0.8}Al_{0.1}\square_{0.1})(Si_{0.8}Ca_{0.2})_2$. A relevant conclusion is that Al replaces Fe, whose sublattice still keeps vacancies while Ca replaces preferably Si.

The positional z parameter of Si/Ca atoms will be close to 0.28 (0.27 for α-leboite). Taken together with the increase in lattice parameter **c** it implies that both interatomic distances Fe-Si(Ca) and Si(Ca)-Si(Ca) will increase .

On the other hand, the fact that the lattice parameter **a** does not change, implies that the Fe(Al)-Fe(Al) distances are kept approximately constants. This is in agreement with the close atomic dimensions of the two metals, Fe and Al.

It is then confirmed that in industrial Fe-Si alloys where a high amount of impurities and a proper Ca/Al ratio occur, a quaternary phase isotypic with α-leboite ($FeSi_2$ tetrag.) will be present.

The importance of the quaternary phase, whose structural study was done under particularly unfavourable conditions, makes it necessary that laboratory synthesis of alloys with this phase clearly dominant should be made, in order to achieve the desirable crystal structure refinement.

REFERENCES

[1] Dehuff, J. A., Coppolechia, V. D. and Lesnewich, A., The Electric Furnace Proceedings, AIME, **27** 167/74 (1969).

[2] Margarido, F., Figueiredo, M. O. and Bastos, M. H. . 2º Encontro Sociedade Portuguesa de Materiais, Porto, Actas, Tema **I**, 16 pp (1985).

[3] Aas, H. , The Silgrain Process: Silicon Metal From 90% FerroSilicon, AIME STP **A71-47**, 653, (1971).

[4] Aronsson, B., Acta Chem. Scand., **14**, 1414/18, (1960).

[5] Sidorenko, F. A., Ryzhenko, B. V., El'ner, V. Ya and Gel'd, P. V., Sov. Phys. JETP, **43**, **3**, 518/21, (1976).

[6] Schubert, K., Zeit. Kristall., **179**, 192/3, (1987).

[7] Sidorenko, F. A., El'ner, V. Ya., Ryzhenko, B. V. and Gel'd, P. V., Sov. Phys. Solid State, **21, 4**, 705/6, (1979).

[8] Wandji, R., Le Corre, C., Genin. J. M. and Roques, B., Phys. Stat. Sol. (b), **45**, K123/7, (1971).

[9] Wäppling, R., Häggström and Rundqvist, S., Chemical Phys. Letters, **2, 3**, 160/1, (1968).

[10] Nishida, I., Phys. Rev. B, **7, 6**, 2710/3, (1973).

[11] Blauw, C., Woude, F. and Sawatzky, G. A., J. Phys. C. Solid State Phys., **6, 14**, 2371/81, (1973).

[12] Kojima, T., Masumoto, K. and Nishida, I., J. Japan. Inst. Metals, **48, 8**, 843/7, (1984).

[13] Boomgaard, J., J. Iron Steel Inst. **210**, 276/9, (1972).

[14] Le Corre, C. and Genin, J. M., Phys. Stat. Sol. (b), **51**, K85/8, (1972).

[15] Figueiredo, M.O. and Margarido, F., II Simpósio Ibérico de Física da Matéria Condensada, Sevilha (communication), (1986).

[16] Margarido, F. and Figueiredo, M.O., Materials Science and Engineering, **A104**, 249/54, (1988).

[17] Margarido, F., Figueiredo, M.O. and Bastos, M. H., 5ª Conferência da Sociedade Portuguesa de Física, Braga (communication), (1986).