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## VACANCY-CATION DISTRIBUTION IN NON STOICHIOMETRIC LAYERED IRON-TITANIUM CHALCOGENIDES

G.A. Fatséas<sup>+</sup>\*, J.L. Dormann<sup>+</sup> and M. Danot<sup>++</sup><sup>+</sup>Laboratoire de Magnétisme, C.N.R.S., 1, Place A. Briand, 92190 Meudon, France<sup>++</sup>Laboratoire de Chimie minérale A - Chimie des Solides, U.E.R. de Chimie, 2, rue de la Houssinière, 44072 Nantes Cedex, France

Résumé.- Sept chalcogénures lamellaires de fer et de titane, non stoechiométriques, ont été étudiés par spectroscopie Mössbauer, en relation avec des calculs de distribution statistique des cations et des lacunes. Les résultats obtenus, nous ont permis de déterminer la distribution des cations et des lacunes dans les différents plans, et d'identifier les différents sites de fer.

Abstract.-In an extension of a previous study of layered iron titanium chalcogenides /1/, we have studied Mössbauer spectra of seven non-stoichiometric compounds, in the vicinity of the  $\text{FeTi}_2\text{S}_4$  composition, in relation with statistical distribution calculations. The results, enabled us, mainly, to obtain informations on the cations-and-vacancy distribution, and to identify the different detected iron-sites.

1. Introduction.- In a previous paper /1/ we have reported X-ray and Mössbauer spectroscopy results on the crystallographic and magnetic ordering of stoichiometric ( $x = 0$ ) and non-stoichiometric ( $x \neq 0$ ) iron titanium layered chalcogenides  $\text{Fe}_{1+x}\text{Ti}_{2(1+x)}\text{S}_4$ . Although those results /1/ contributed to a better understanding of some structural and magnetic properties, they showed the necessity of further experimental work for the determination of the cations-and-vacancy distribution in the non-stoichiometric compounds.

This is due to the fact that the ternary non-stoichiometric compounds of general formula  $\text{M}_{3+x}\text{X}_4$  ( $-1 \leq x \leq 0.5$ , M : Fe + Ti, X : S, Se) show frequently, and according to previous known studies, different structural modifications, with formation of different types of superstructures, such as  $\text{M}_5\text{X}_8$ ,  $\text{M}_2\text{X}_3$ ,  $\text{M}_3\text{X}_4$  and  $\text{M}_7\text{X}_8$ . These superstructures are related to different situations of more or less ordered occupation of the octahedral positions and depend on the composition ( $x$ ) /2/ and on the thermal and mechanical treatments /2,3/.

The unambiguous determination of the cations-and-vacancy distribution in such compounds is, thus, a difficult problem and asks systematic experimental work on several compositions and types of non-stoichiometry with well defined preparation conditions. The present work is an attempt for a better understanding of this problem by obtaining Mössbauer spectroscopy results on seven non-stoichiometric compounds belonging to four different types of

non-stoichiometry in the vicinity of the  $\text{FeTi}_2\text{S}_4$  composition : namely,

N° 1	$\text{Fe}_{1-x}\text{Ti}_{2+x}\text{S}_4$	$x = 0.052$ , sample a $x = 0.104$ , sample b
N° 2	$\text{Fe}_{1+x}\text{Ti}_{2-x}\text{S}_4$	$x = 0.052$ , sample c
N° 3	$\text{Fe}_{1+x}\text{Ti}_{2(1+x)}\text{S}_4$	$x = 0.030$ , sample e $x = 0.052$ , sample f
N° 4	$\text{Fe}_{1+x}\text{Ti}_2\text{S}_4$	$x = 0.052$ , sample d $x = 0.400$ , sample g

These types of non-stoichiometry were chosen to cover different regions of interest in order to obtain a reasonably unambiguous approach to the problem of the cations-and-vacancy ordering. The regions of interest are : deficiency (N° 1) or excess (N° 2,3,4) in Fe atoms, relative to the stoichiometric composition  $\text{FeTi}_2\text{S}_4$ , and, also, perturbed (N° 3, 4) or not-perturbed (N° 1, 2)  $\text{M}_3\text{S}_4$  formula (M : Fe + Ti). It is, in fact, interesting to see what happens when the relative amounts of Fe and Ti atoms are changed with or without perturbation of the stoichiometric  $\text{M}_3\text{S}_4$  composition.

2. Experimental and samples preparation.- High statistics spectra were obtained with a  $^{57}\text{Fe}$  (Rh) source and a Mössbauer spectrometer, using a symmetrical saw-tooth vibrator and a high counting-rate system /4/.

All samples contain  $\approx 10$  mg natural iron per  $\text{cm}^2$ , corresponding to a "thin Mössbauer absorber". The least squares fitting-routine uses Lorentzian line shapes and equal Mössbauer absorption coefficients for all iron sites.

The Mössbauer samples are slowly cooled polycrystalline materials prepared from direct reaction of

\*New address : ++.

high purity iron, titanium and sulphur. The preparation and heat treatment were described in reference /1/.

3. Results and discussion.- The Mössbauer spectra were obtained at 4.2 K /5/ and are shown in figure 1 for the Fe-deficient compounds and in 2 and 3 for the Fe-excedent compounds.

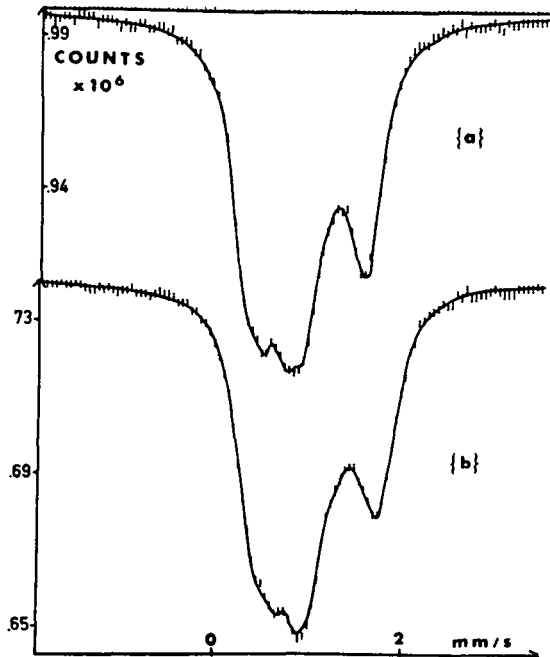


Fig. 1 : Computer-analysed spectra of the Fe-deficient compounds  $\text{Fe}_{1-x}\text{Ti}_{2+x}\text{S}_4$  at 4.2K.

(a) :  $x = 0.052$  (b) :  $x = 0.104$

The zero velocity is the centre of gravity of a metallic iron spectrum at 300K.

The distinction of two different groups can be justified by the observation of the specific feature (already reported in our previous study /1/) of presence of a strong-field Fe-site in all the Fe-excedent compositions (figures 2,3), this field being absent in the Fe-deficient ones (figure 1), (see additional peaks outside the central part of the spectra in figures 2 and 3). The spectra were computer-analysed to several overlapped patterns (Fe-sites) of Zeeman (6-line pattern) and combined electric and magnetic (8-line pattern) hyperfine interactions.

The table I summarizes the detected Fe-sites, their relative intensities and the hyperfine parameters; field (H), quadrupole splitting ( $\epsilon$ ) and isomer shift ( $\delta$ ).

The identification of the different Fe-sites was obtained by comparing the experimental relative intensities with the theoretical ones, calculated

with some assumptions of preferential or random distribution of the excedent Fe or (and) Ti atoms in the cations-and-vacancy positions.

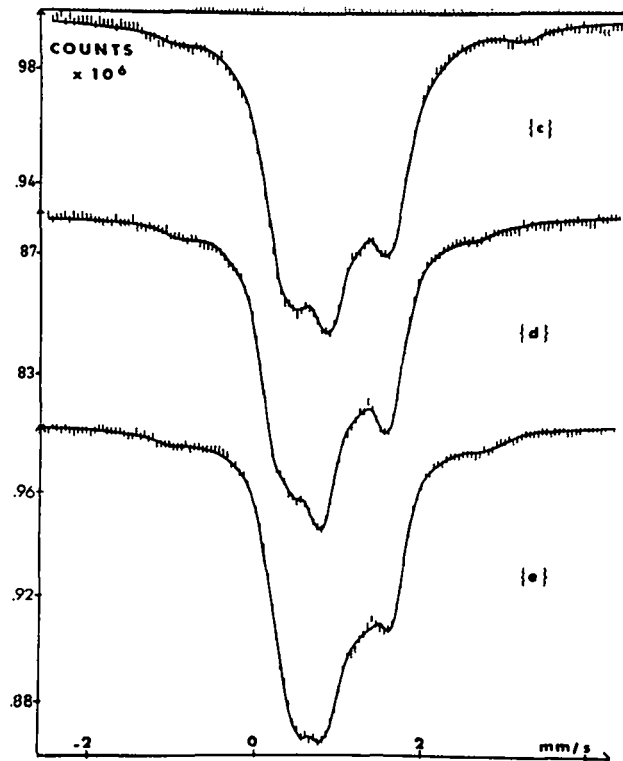


Fig. 2 : Computer analysed spectra of the Fe-excedent compounds (c), (d) and (e) at 4.2K.

(c) :  $\text{Fe}_{1+x}\text{Ti}_{2-x}\text{S}_4$  ( $x = 0.052$ )

(d) :  $\text{Fe}_{1+x}\text{Ti}_2\text{S}_4$  ( $x = 0.052$ )

(e) :  $\text{Fe}_{1+x}\text{Ti}_2(1+x)\text{S}_4$  ( $x = 0.030$ )

This was done as follows :

We used, as starting point of our reasoning, the stoichiometric  $\text{FeTi}_2\text{S}_4$  compound, in which full Ti-layers alternate with layers containing ordered Fe atoms and vacancies  $\square$ , that is,  $(\text{Fe} + \square)\text{Ti}_2\text{S}_4$  <sup>(1)</sup> /1/. In this structure, of  $\text{Cr}_3\text{S}_4$ -type (space group  $I 2/m$ ), the Fe atom is surrounded by 2 Fe and 4  $\square$  within the  $(\text{Fe} + \square)$  layer /1/. The question is, now, to determine the populations of these six neighbours-positions and also the populations of the Ti-layers, in the non-stoichiometric compounds, by testing different possible cations-and-vacancy distributions compatible with the experimental intensities.

To do this, we distinguish, as above, the Fe-deficient and the Fe-excedent compounds.

3.1. Fe-deficient compounds (a and b).-Both compounds, (a) and (b), have, for any x, the  $\text{M}_3\text{X}_4$  formula and, thus, a constant number of vacancies

<sup>(1)</sup> Throughout this article the terms Ti-layer and  $(\text{Fe} + \square)$ -layer refer to these two distinct layers even if they contain different additional atoms and vacancies.

(1 vacancy per formula).

Fe - sites surrounded by :		H kOe	$\epsilon$ mm/s	INTENSITIES (error, $\pm 0.02$ )						
				Compounds						
				a	b	c	d	e	f	g
Fe - site and neighbours situated on the (Fe + $\square$ )-layer	5 $\square$ + 1 Fe	12 $\pm$ 4	0. $\pm$ 0.10	0.07 (0.08)	0.12 (0.15)	-	-	-		
	4 $\square$ + 2 Fe (FeTi <sub>2</sub> S <sub>4</sub> )	25 $\pm$ 4	0.36 $\pm$ 0.05	0.76 (0.75)	0.50 (0.54)	0.62 (0.62)	0.55 (0.56)	0.66 (0.67)	0.22 (0.25)	0.16 (0.13)
	3 $\square$ + 2 Fe+1Ti	32 $\pm$ 3.	0.05 $\pm$ 0.05	0.17 (0.18)	0.22 (0.26)	0.33 (0.29)	0.40 (0.33)	0.29 (0.25)	0.175 (0.24)	
	2 $\square$ + 2 Fe+2Ti	46 $\pm$ 6	0.03 $\pm$ 0.05	- (0.01)	0.16 (0.05)	- (0.04)	- (0.06)	- (0.03)	0.22 (0.15)	0.09 (0.10)
	1 or zero $\square$ + 2 Fe + 3 Ti	75 $\pm$ 5	0.07 $\pm$ 0.04	-	-	-	-	-	0.07 (0.06)	0.10 (0.12)
Fe - site on both (Fe + $\square$ )-and- Ti-layers	1 Fe near neighbour along the c-axis	125 $\pm$ 15	0. $\pm$ 0.10	-	-	0.05 (0.05)	0.05 (0.05)	0.05 (0.05)	0.315 (0.30)	0.65 (0.65)
linewidth $\longrightarrow$				2.20	1.80	2.52	2.44	2.25	2.90	3.00

Table I : Detected Fe-sites (and their neighbours in Fe, Ti and vacancies), hyperfine field (H), quadrupole splitting ( $\epsilon$ ), linewidth and experimental and theoretical intensities (...) for the different compounds. The quadrupole splitting  $\epsilon$  is equal to  $1/4 e^2qQ$  for both the 8-line and the 6-line patterns (supposing for the second-one,  $\Theta$  and  $\eta$  equal to zero,  $\eta$ , asymmetry parameter,  $\Theta$  the known polar angle).

For reasons of limited space, only the mean H-value is given for each site. For ex. H = 25  $\pm$  4 kOe means that this site was detected, in all the compounds, with values lying between 21 and 29 kOe. ( $\pm 4$  is not, thus, the error !). Same remark for the  $\epsilon$ -values.

When the theoretical intensity (...) is given alone, without experimental value, it means that this site was not detected in the spectrum. Only the Fe-site with (4 $\square$  + 2 Fe) configuration is an 8-line pattern ( $\eta = 0.3 \pm 0.1$ ,  $\Theta = 30^\circ \pm 5$ ,  $\phi = 0$ ). The other sites are 6-line patterns because of the very small quadrupole splitting.

The linewidths are given in the form of a coefficient. With the same coefficient the experimental linewidth of a thin natural metallic iron absorber at 4.2K is equal to 1.80.

The isomer shift ( $\delta$ ) is equal to 0.94  $\pm$  0.02 mm/s at 4.2K for all sites and all compounds (relative to the metallic iron at 300K) and equal to 0.78  $\pm$  0.02 at 300K.

The most simple situation is to suppose, that the Ti-layers remain unchanged and that the excedent Ti atoms, either replace the deficient Fe or are randomly distributed in the vacancy-positions (both the original vacancies of the (Fe +  $\square$ ) Ti<sub>2</sub>S<sub>4</sub> compound and the vacancies coming from the iron deficiency as well).

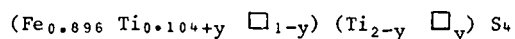
The situation of random distribution has given /6/ the best result (best goodness of fit) for both compounds (a) and (b) but it is particularly suitable for (a), as can be seen from the agreement between the fitted experimental intensities (numbers without parenthesis) and the theoretical ones (numbers in parenthesis). This leads to the following cations-and-vacancy distribution formula :

(Fe<sub>0.948</sub> Ti<sub>0.052</sub>  $\square_1$ ) (Ti<sub>2</sub>) S<sub>4</sub> for (a)  
where the first parenthesis represents the (Fe+ $\square$ )  
-layer and the second-one the Ti-layer.

In the more Fe-deficient compound (b), the agreement is less good, particularly for the (2  $\square$  + 2 Fe + 2 Ti) configuration, in which the experimental intensity (0.16) is much larger than the theoretical (0.05). Things are happening as if the increase of the amount of the Ti atoms in (b) relative to (a), brings out the pure statistical distribution, (existing in (a)), by favouring the formation of the Fe-site surrounded by Ti-pairs, at the expense of the three other sites.

The full statistical calculation and the comparison with the experimental intensities show, that the

best result corresponds to a distribution where the Ti-layers are slightly perturbed by the presence of a small amount of vacancies, according to the formula :



with  $y = 0.03 \pm 0.01$

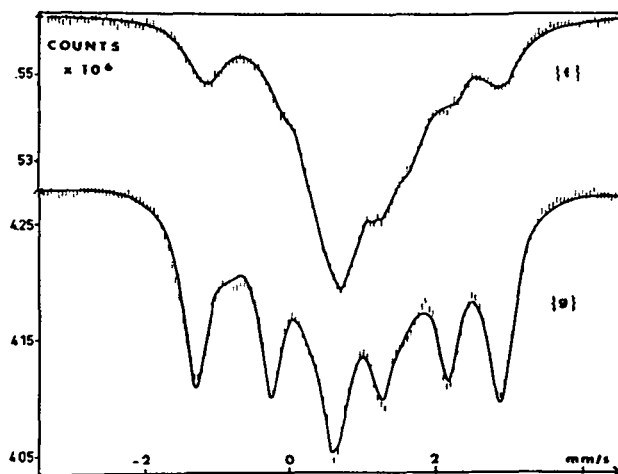


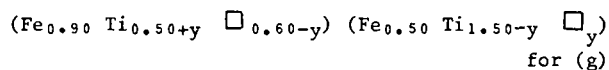
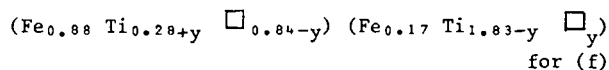
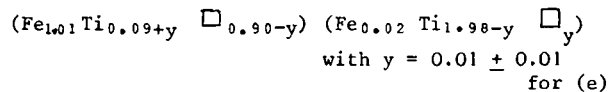
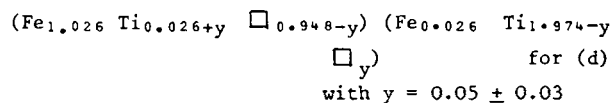
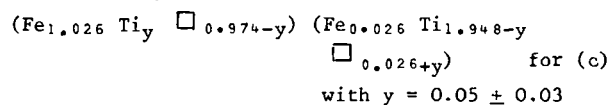
Fig. 3 : Same caption as figure 2, for the compounds (f) and (g).

(f) :  $\text{Fe}_{1+x}\text{Ti}_2(1+x)\text{S}_4$  ( $x = 0.052$ )

(g) :  $\text{Fe}_{1+x}\text{Ti}_2\text{S}_4$  ( $x = 0.4$ )

3.2. Fe-excedent compounds (c, d, e, f, g).- Here again we have tried to fit the spectra with theoretical intensities corresponding to different possible cations-and-vacancy distribution models. The spectra of these compounds (figures 2, 3) show additional peaks, outside the central part of the spectrum, corresponding to a strong-field Fe-site, not existing in the Fe-deficient compounds. The origin of this site remained a puzzle in our previous work /1/, particularly the fact that 5 % additional Fe atoms in the (f) compound (relative to the Fe atoms in the stoichiometric  $\text{FeTi}_2\text{S}_4$ ) could give a new site of  $\approx 34$  % intensity. Similarly to the Fe-deficient compounds and according, also, to the discussion of our previous study /1/, we started from the most simple situation, which is to suppose that the Ti-layers remain unchanged, the additional Fe-atoms ( $x$ -value) going, statistically, to the vacancy positions of the  $(\text{Fe} + \square)$  layers. This model has given results (not included in table I) in complete disagreement with the experimental intensities and led to the conclusion that the strong-field does not belong to Fe atoms having only Ti neighbours in the Ti-layers, and that it is necessary to consider distributions in which Fe atoms are also present in the Ti-layers. The full statis-

tical calculation on this distribution and the comparison with the experimental intensities led to the following distribution-formulae for the Fe-excedent compounds :



with  $y \approx 0$  and error  $\pm 0.04$

for all numbers of both (f) and (g)

The corresponding, to the above distribution; Fe-sites, intensities, and hyperfine parameters, are given in the table I.

These results can be commented as follows :

- Both layers contain Fe, Ti and vacancies, the excedent Fe being distributed half and half in the two layers for (c) and (d) (see formula above) and more than half in the Ti-layers for (e), (f) and (g).
- Small disagreements between experimental and theoretical intensities, reflect slight deviations from the ideal binomial law (see table I). This is the case of the compound (f) in which the disagreement between the experimental intensity (0.22) and the theoretical (0.15), reflects a preferential formation of Fe-sites surrounded by Ti-pairs.
- Identical low-field Fe-sites with, nearly, equal hyperfine parameters, were found for both the Fe-deficient and Fe-excedent compounds. This "coherence" was a reasonable requirement in the analysis of the different compounds and was used, sometimes, as a criterium for the choice between different inequivalent solutions.
- The existence of the  $(5\square + 1 \text{Fe})$ -configuration depends, not on the total number of vacancies, but on the number of iron-vacancies on the  $(\text{Fe} + \square)$ -layer. More than one Fe in the  $(\text{Fe} + \square)$ -layer, decreases the number of vacancies in this layer and the probability of this configuration becomes negligibly small (case of

- (c), (d) and (e)). This probability is no longer negligible if the number of Fe in the (Fe + □)-layer is smaller than one (case of (f) and (g)).
- The simulation of two or three sites in only one site in (f) (of 0.22 intensity) and (g) (of 0.16 intensity), respectively, is due to the large intensity of the strong-field Fe-site coming from the large excess in Fe and Ti atoms in these two compounds. This fact decreases the intensities of the low-field sites, and, some of them, become so small that they can be fitted with many different combinations of intensities, being for this reason undistinguishable. The spectra were, thus, fitted with a reduce number of sites. This is reflected in an increase of the linewidth (table I).
  - The strong-field Fe-site in all the Fe-excedent compounds, is a specific property of these compounds (see also reference /1/) and concerns Fe atoms having a near neighbour Fe atom along the c-axis. This configuration becomes possible with the presence of Fe atoms in the Ti-layers, and exists in  $\text{Fe}_3\text{Se}_4$  of similar structure /8/.
- Although this site is observed only in the compounds with excedent Fe, its intensity does not depend on the amount of the excedent-Fe, but on the total number of vacancies in the two layers. It seems, that more the number of vacancies deviates from one vacancy per formula (the number of the stoichiometric  $\text{FeTi}_2\text{S}_4$ ), higher is the intensity of the site. This is the reason why this site has a 31 % intensity in (f), and 5 % in (d), while (f) and (d) have the same amount of excedent iron. This explains also the large intensity of this site in (g).
- An intermediate-field Fe-site was detected in (f) and (g) compounds. This site is due to the large amounts of Fe and Ti in the (Fe + □)-layer (see distribution formula) which gives a "measurable" value to the probability of the (1 □ + 2 Fe + 3 Ti) configuration in this layer. The table I shows, that this site seems belong to the group of the low-field sites from both configuration and H-value point of vue. One can see, in fact, that all the low-fields, from 12 kOe to 75 kOe, lie in a straight line; H value versus number of vacancies, with a slope equal to  $\approx 12$  kOe per vacancy (figure 4). This result is very similar to the 11.5 kOe per vacancy observed, in a previous work /9/ for the octahedral sites ( $\text{Fe}_1$ -sites) of  $\text{Fe}_{2-x}\text{Ge}$ , of related structure ( $\text{B8}_2$ ) (see reference /9/).

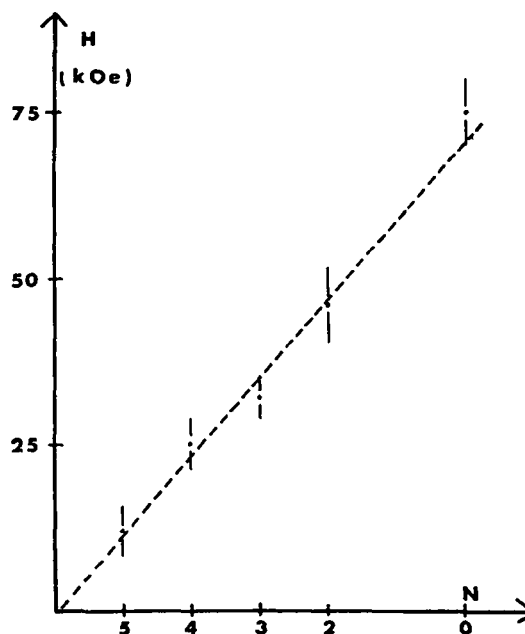


Fig. 4 : Hyperfine field-values versus the number (N) of vacancies surrounding the iron sites in the (Fe + □)

4. Conclusion.- In conclusion, from computer-analysis of Mössbauer spectra and statistical distribution calculations on seven non-stoichiometric iron-titanium layered chalcogenides, we have obtained the following results :

- We have proposed formulae giving the cations-and-vacancy distributions in both the (Fe + □)-and-Ti-layers,
- We have detected a preferential formation of the (2 □ + 2 Fe + 2 Ti)-configuration in the Ti-excedent compounds (b) and (f), which shows the begining of occurence of a  $\text{M}_7\text{X}_8$ -type superstructure, corresponding to an assembling of Ti pairs around some iron atoms.
- We have identified the strong-field Fe site (not well understood in our previous work), as the Fe-site having one Fe neighbour along the c-axis. This configuration is similar, as far as the configuration along the c-axis is concerned, to both sites of  $\text{Fe}_3\text{Se}_4$  (of ideal  $\text{Cr}_3\text{S}_4$ -order) having strong-field Fe-sites /10/,
- We have found, also, that although the strong-field Fe-site results from the existence of excedent iron, its intensity does not depend on the amount of this iron but on the total amount of vacancies the intensity increasing when the number of vacancies decreases. This means that the condition for having a high-intensity strong-field site is not to have, simply, a large amount

of Fe but to have large amount of Fe in both layers so that the probability to have Fe atoms with one Fe neighbour along the c-axis become large,

- We have, finally, observed, that there exist, in all the compounds of the present study, a very small dispersion of  $\delta$ -values for all the iron-sites. This property of closeness of isomer shifts for all the iron-sites of a multisite compound was already reported /11/ as a common property of a large number of intermetallic iron compounds having a metallic-type conductivity, and was observed, also in NiAs-type compounds /12/.

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- /5/ Spectra were also obtained at 77K and 300K. The same, as for 4.2K, results were obtained at 77K (number of sites and intensities), apart a mean  $\approx 10\%$  decrease of H, and a decrease of  $\delta$  ( $\delta \approx 0.92 \pm 0.02$ ). At 300K, the spectra are superposition of two doublets, similarly to the results obtained in reference /1/.
- /6/ By application of the known binomial formula (see, for ex., reference /7/).
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